Environmental Health Studies on Peconic River Headwaters: Water and Sediment Chemistry

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ABSTRACT

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The purpose of this research was to collect scientific environmental health data on water and sediments from remediated and natural sites of the Peconic River (PR) headwaters at the Brookhaven National Laboratory (BNL) and to compare results with available earlier findings. The specific objectives were to: (a) analyze samples for physico-chemical factors; (b) compile and analyze data statistically; and (c) to identify the interrelationships between abiotic factors. We hypothesized that waters of the PR would be acidic with excessive turbidity, nutrient poor, low dissolved oxygen (DO) levels, and free of contaminants. We have collected 54 surface samples (<15cm deep at 150m intervals) randomly from 7 experimental sites (LH1-7). Experimental sites were plotted using eXplorist 200 Global Positioning System (GPS) and ArcInfo Geographic Information Systems (GIS). Field data were obtained on DO, temperature, pH, turbidity, and conductivity using Yellow Spring Instruments, Inc. (YSI) probe. Water samples were analyzed using Hach DR890 colorimeter. Filtered and acidified water samples (pH<2) were used to estimate metal content using Inductively Coupled Plasma Spectrometer (ICP). Sediment samples were air dried, sieved, and saved in Ziploc bags. Macro and micronutrients were measured using LaMotte Soil Test Kits. Sediments were acidic (6.00±0.00 to 6.25±0.94 at LH3 and LH5, respectively) and nutrient poor. Water was acidic (4.61±0.10 to 5.87±0.04 at LH2 and LH5, respectively) and low in DO (1.49±0.17 to 5.67±0.70mg/L at LH3 and LH1, respectively). Samples had traces to zero chlorides, nitrates, and sulfates. Alkalinity ranged from 10.5±5.65 to 83.13±3.26mg/L. Sediment ANOVA results showed significant mean differences ($P<0.05$ and $P<0.01$) between elements, aluminum (Al), iron (Fe), lead (Pb), and chromium (Cr). In conclusion, experimental results were in partial agreement with our hypothesis (nutrient poor sediments and water; and low DO and high turbidity in water). However, we reject the null hypothesis, since the mean differences between groups were significant. Also, water and sediments of the PR natural sites have greater metal content (Al, Fe, Pb) than in the remediated sites. In some instances, however, current elemental contents of Al, Cd, Fe, Pb, Mg, and K in sediments of remediated sites exceeded the earlier findings.

INTRODUCTION

Brookhaven National Laboratory (BNL), owned by the U.S. Department of Energy (DOE) and operated by associated Universities, Inc., is located on Long Island, NY, and encompasses about 5,265 acres of the native Long Island Pine Barrens ecosystem (Figure 1). Historical data of DOE at BNL indicated the presence of organic and approximately 14 inorganic contaminants (methyl mercury, copper-Cu, mercury-Hg, lead-Pb, silver-Ag, and iron-Fe) in the sediments of the PR, due to the laboratory practices during the 1940's through the 1980's [1&2].

Sediment in running waters is an important ecological factor and plays a critical role on biotic organisms and the water quality. Pollution loads in wastewater are established independently of the river flow of the river Arno and concluded that low flow periods or when the capacity of the river is reduced, the level of DO can fall which eventually prevents survival of aquatic species [3]. Problems such as low DO, fish extinction, and algal blooms in flowing waters were discussed [4]. Data on the total concentrations of phosphorus (P), calcium (Ca), and Fe in surface sediments were investigated on several locations of Thames catchments, River Swale in Yorkshire, and the headwaters of the Great Ouse [5]. Phosphorus plays a critical role in water quality and plant growth in fresh water bodies [6, 7,8, & 9].

No peer-reviewed literature, published in scientific journals is available on the environmental health issues, such as water and sediment chemistry and its impact on biota, of the PR headwaters (flowing waters). Hence, the purpose of this research was to collect scientific environmental health data on water and sediments from the remediated and natural sites of the PR headwater complex at BNL and to compare results with available earlier findings. The specific objectives were to: (a) analyze samples for physico-chemical factors; (b) compile and analyze data statistically; (c) identify the interrelationships between abiotic factors; and (d) provide a knowledge base on natural sites of BNL (LH3 and LH4 – never tested) for future research.

Our hypothesis was that the Peconic River headwaters would be acidic with excessive turbidity, nutrient poor, low dissolved oxygen (DO) levels, and sediments would be nutrient poor and free of contaminants. There would be no significant difference in means (<0.05) of physico-chemical factors between groups and within groups.

We have investigated two major sections of the PR headwaters: remediated zone (LH1, LH2, LH5, LH6, and LH7) and natural zone (LH3 and LH4) as shown in Figure 1. The experimental sites are located between 18.679241 – 18.682044 E and 45.25797 – 45.28239 N (eXplorist 200 GPS coordinates). Average depth of waters was about 30-45cm in most of our experimental sites. The PR is a 25-mile coastal plain stream that begins in the Manorville drainage basin and about 12 mile of this runs through the BNL, where the upper drainage basin is located. The PR drains in an easterly direction and flows into Flanders Bay, an arm of the Peconic Bay (North Eastern Atlantic Study).

MATERIALS AND METHODS

Eight surface water and sediment samples (not more than 15 cm deep) at 150 m intervals were collected, from each site of a total of seven experimental sites from the PR headwaters at BNL over a period of 10 weeks, and saved in 500 and 250 mL Nolgen bottles, respectively. The sampling sites were plotted, as shown in figure 1, using eXplorist 200 Global Positioning System (GPS) and ArcInfo Geographic Information Systems (GIS). Water samples were kept in a cooler for chemical analysis. Field data on DO, temperature, conductivity, pH and turbidity in water were obtained using the YSI (Yellow Spring Instrument Inc.) probe. Hach-DR 890 (the colorimeter) was used to test total chlorine, nitrate and ammonia N, tannin, sulfate, phosphorus, and suspended solids. The Digital Titration-16900 was used for testing total hardness and alkalinity. At the completion of water analysis for physico-chemical factors, we added 2-5 mL 1:1 nitric acid:DI water to each sample, filtered 100 mL water using Whatman 40 filter paper, and preserved the samples for trace metal analysis.

Sediment samples were air-dried and sieved through 2mm sieve to remove organic matter such as roots. Air dried samples were used to measure macro and micro nutrients using LaMotte Soil Test Kits (pH, K, P, Ca, Cl, Mn, Fe, sulfate (SO_4^{-2}), Al, NH_3-N, and nitrate-nitrogen). Percentage of moisture was obtained by drying samples in an oven at 65^0 C for 36 to 48 h. Air-dried sediment samples (5g each) were digested using 100mL Kjeldahl flasks, following EPA 3050B method. Samples were digested with concentrated 10mL nitric acid (HNO_3) and 10mL hydrochloric acid (HCl) and were allowed to soak overnight. Samples were then digested on hot plates (not more than 95^0C) for 3-4 h and let the samples to cool overnight and filtered using Whatman 541 filter paper. Digestion extracts were diluted with deionized distilled water and made the final volume to 100 mL using volumetric flasks, labeled, and saved in 125 mL Nolgen bottles for the ICP analysis.

Three replicates per site for water and five replicates per site for sediments were used for ICP (Liberty 100 Emission Spectrometer) analysis to estimate Ag, Al, Pb, Cd, Mo, Cr, Cu, Mg, K, Fe, and Mn (EPA3050B method). Mean, variance, standard deviation, standard error, student paired T-test, Pearson two-tailed and partial correlations, and one-way ANOVA (Tukey and Duncan tests) were applied to measure significance levels between groups (remediated and natural sites) using SPSS 13.0 version.

RESULTS

Water chemistry:

Water was acidic (4.61±0.10 to 5.87±0.04 at LH2 and LH5, respectively) and low in DO as shown in Figure 2 (1.49±0.17 to 5.67±0.70 mg/L at LH3 and LH1, respectively). Samples had traces to zero chlorides, nitrate and ammonia nitrogen, and sulfates. Alkalinity ranged from 10.5±5.65 mg/L at LH2 to 83.13±3.26 mg/L at LH7 (Figure 3). Metal content in water samples is summarized in Table 1. Among various physico-chemical factors analyzed using one-way ANOVA, mean differences between groups (LH1-LH7; df=6) for temperature, conductivity, DO, ammonia nitrogen, tannin, sulfate, phosphorus, suspended solids, alkalinity, and total hardness were highly significant ($P<0.05$). Two-tailed independent sample T-test between two zones (remediated sites and natural sites; df=52) indicated significant mean differences ($P<0.05$) in data for various chemical factors as summarized in Table 2. Two-tailed Pearson correlations indicated significant relationships between various physico-chemical factors at $P<0.05$ and $P<0.01$, as summarized in Table 3.

Sediment Chemistry:

The sediments were acidic [illegible]±0.00 to 6.25±0.94 at LH3 and LH5, respectively) and nutrient poor. Moisture content varied between 33.46±9.67 to 68.11±6.67% at LH1 and LH4, respectively (Figure 5). One-way ANOVA results confirmed positive and negative significant ($P<0.05$ and $P<0.01$) relationships between elements, aluminum (Al), iron (Fe), lead (Pb), and chromium (Cr). Two-tailed independent sample T-test and two-tailed Pearson correlation results on data are summarized in Tables 1&2. Among all the variables studied in sediments, magnesium and potassium had highest positive significant relationship (0.996**; $P<0.001$). Most of the sediments have excessive amounts of Al and Fe in natural vs. remediated sites

11,090±2010 vs. 4469±832 µg/g Dry wt and 3078±607 vs. 2780±578 µg/g Dry wt, respectively. However, these values are still in excess of the earlier data published in BNL's investigative reports, even in the remediated sites. In addition to Al and Fe, we found Pb, Cd, Mg, and K in higher concentrations than in earlier reported values in remediated sites, as shown in Figures 7&8. Our studies indicated Pb concentrations are higher in natural sites (138.5±30.62µg/g Dry wt) compared to the remediated sites (89.22±14.67µg/g Dry wt), yet, these values are much higher than the data of earlier reports (ECO Data 2003&2005).

DISCUSSION AND CONCLUSION

The BNL has a long history of inorganic and organic contaminants in sediments (1940s-1980s) and is listed as one of the US Environmental Protection Agency's (EPA) National Priorities List. It is necessary to quantify the extent of risks of these contaminants to the BNL's environmental health and to its biota (plants, animals, microbes). In the current research project, we attempted to investigate some remediated and unexplored natural areas of PR complex to identify the quality and quantity of various contaminants in water and sediment. According to the New York State Department of Environmental Conservation, Eastern USA background (ppm) for lead varies widely (undeveloped and rural areas may range from 4-61 ppm compared to suburban areas or near highways typically range from 200-500 ppm). Suffolk County Department of Health Services (Article 12 SOP#9-95) has published (i) action levels/cleanup objective levels (ppm) of 400/100 (Pb), 500/25 (Cu), 100/10 (Cr), 100/5 (Ag), and 10/1 (Cd). Based on these standards, we conclude that lead levels in LH4-LH7 sites have exceeded the background values of rural and undeveloped areas (LH4 has 203.63±29.39 µg/g Dry Wt.).

Current research results have indicated high acidic sediments along with slightly acidic waters in the PR complex. Borg (1987) made similar observations that surface water in North America has become acidic due to acid compounds and metals [10]. Warnau and Pagano (1994) stated that the main sources of lead input into the marine environment are rivers and atmosphere. They reported that the Sea Urchins are affected mostly by high levels of lead, mostly in Atlantic coast [11]. Ramachandran *et al* (1997) reported that aquatic life was more susceptible to the toxic effects of copper but not cadmium [12].

Sediments of the PR headwaters have a maximum of 38.89±29.37µgCu/g Dry Wt. at LH1, where we have observed an increased flow of water. Neal *et al* (2000) observed that Cu, Cl, Mg, Mo, K exhibit dilution with increasing flow and increase of Al, Fe, and nitrate (NO_2^-) with increasing flow in Thames River [13]. Stow (2001) reported that symptoms of excessive eutrophication are algal blooms, low DO, fish kills, and outbreaks of toxic microorganisms in the Neuse River, North Carolina [14]. Ramachandran *et al* (1997) reported that carbon dioxide concentrations are higher in the summer, which can lead to the cause of the water being very acidic. They have also observed that the suspended solid concentrations were higher in the summer when compared to autumn. Experimental results indicated that all our study sites have low DO without any visible fish, with a few encounters of frogs, and excessive amounts of tannins and suspended solids in acidic waters and sediments.

In conclusion, experimental results were in partial agreement with our hypothesis (nutrient poor sediments and water; and low DO and high turbidity in water). However, we reject null hypothesis, since our hypothesis was proven wrong regarding contaminants and mean differences among the groups of data sets. We have also observed that water and sediments of PR natural sites have higher concentrations of metals (Al, Fe, and Pb) than in the remediated sites. In some instances, however, current elemental contents of Al, Cd, Fe, Pb, Mg, and K in sediments of remediated sites were greater than the earlier observations (ECO Data 2003 and 2005).

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Tables

	F	Sig.	t	df	Sig
Water					
Nitrate N	7.61	0.008	2.06	39.82	0.046
Magnesium	4.4	0.05	-2.17	19	0.043
Ammonia N	17.15	0	2.3	52	0.026
					0.001*
Sulfate	10.75	0.002	2.32	36	0.026
Hardness	0.001	0.98	-2.84	26.96	0.009
Sediment					
Phosphorus	9.53	0.003	2.07	52	0.043
			3.19	38	0.003*
% Moisture	1.61	0.21	-4.25	52	0
			-4.61	34	0.000*

Table 1. Two-tailed T-Test (P<0.05; *Equal Variances Assumed).

RZ					**NZ**				
μg/gDryWt.	**Mean**	**SE (n=15)**	**Min**	**Max**	**μg/gDryWt.**	**Mean**	**SE (n=6)**	**Min**	**Max**
Mo	-0.07	0.02	0	-0.16	**Mo**	-0.06	0.02	-0.01	-0.16
Ag	-0.38	0.01	-0.3	-0.41	**Ag**	-0.39	0.01	-0.36	-0.395
Al	0.5	0.07	0.03	0.46	**Al**	0.57	0.2	0.23	0.7
Mn	0.07	0.01	0.03	0.14	**Mn**	0.05	0.01	0.02	0.06
Fe	1.85	0.23	1.22	4.08	**Fe**	1.53	0.33	0.92	2.78
Cr	-0.03	0.01	0	0	**Cr**	-0.03	0.01	0	-0.07
Mg	1.44	0.12	0.51	1.92	**Mg**	2.28	0.56	1.05	4.97
Pb	-0.48	0.14	-0.07	-0.86	**Pb**	0	0.23	-0.11	-0.45
Cu	0.05	0.01	0	0.1	**Cu**	0.1	0.02	0.02	0.19
Cd	0.01	0	0	0.01	**Cd**	0.01	0	0	0.03
K	1.46	0.41	0.46	6.9	**K**	1.04	0.14	0.6	1.46

Table 2. Results on various elements (macronutrients and toxic metals) in the Peconic River headwaters (RZ = Remediated Zone; NZ = Natural Zone).

		Sediments	Water
Cr	**Mo**	0.462**	
Fe	**Al**	0.629**	**0.819****
Mn	**Al**	0.340*	**-0.561****
Mn	**Fe**	0.564**	**0.488****
Pb	**Cr**	0.526**	
Cd	**Cr**	-0.435**	
Cd	**Pb**	-0.530**	
K	**Cr**		**-0.477***

Table 3. Pearson Correlations (P<0.05*; P<0.01**) between variables in sediments (n = 35) and water (n = 15).

Figures

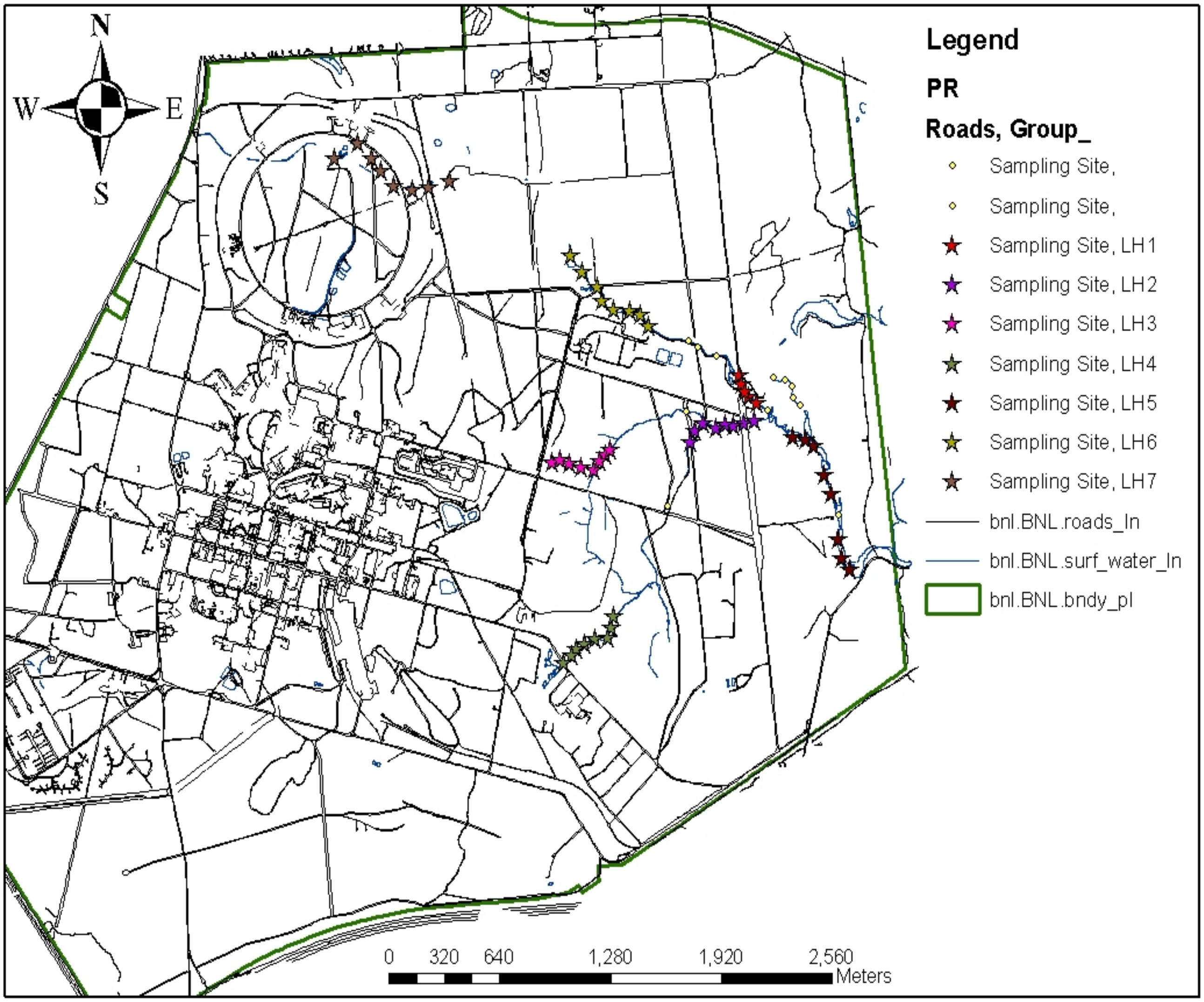

Figure 1. The Peconic River headwaters' experimental sites at Brookhaven National Laboratory.

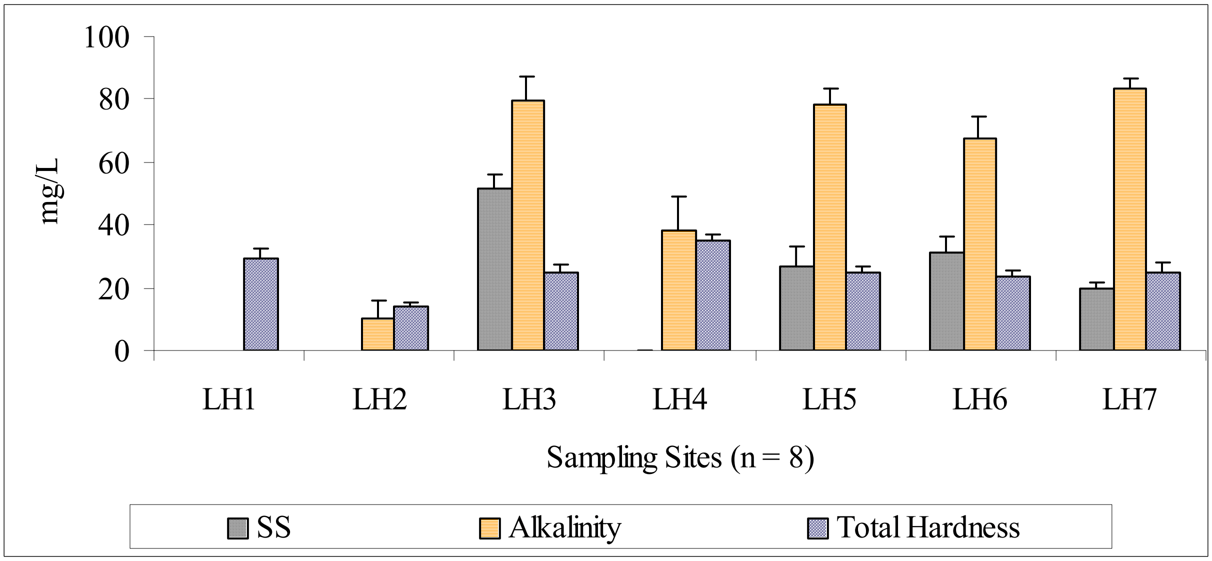

Figure 2. Dissolved oxygen and tannins in the Peconic River headwaters.

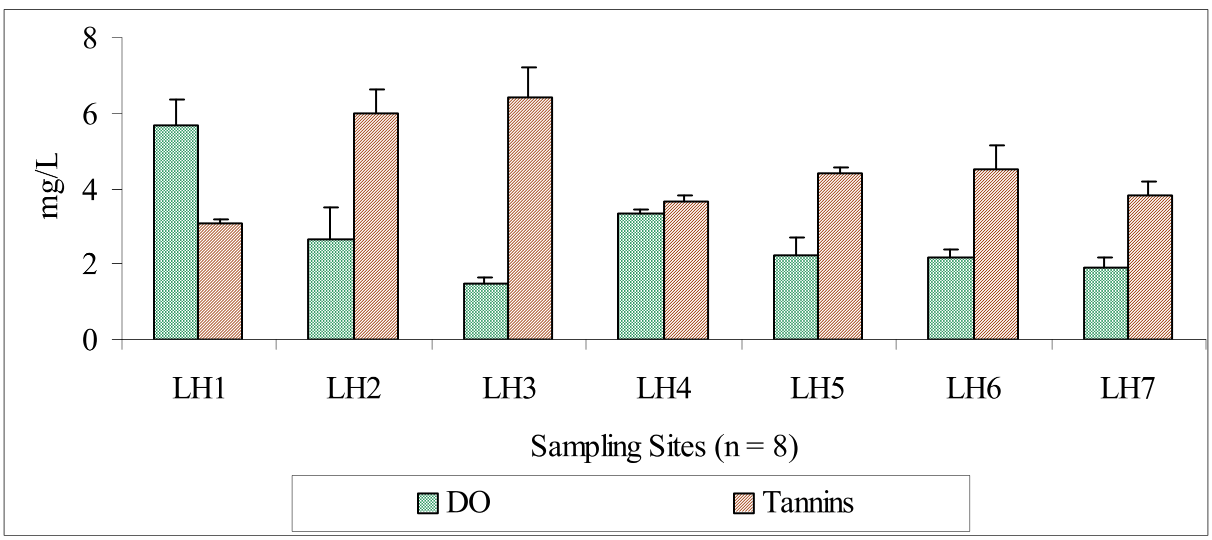

Figure 3. Suspended solids, alkalinity, and total hardness in the Peconic River headwaters.

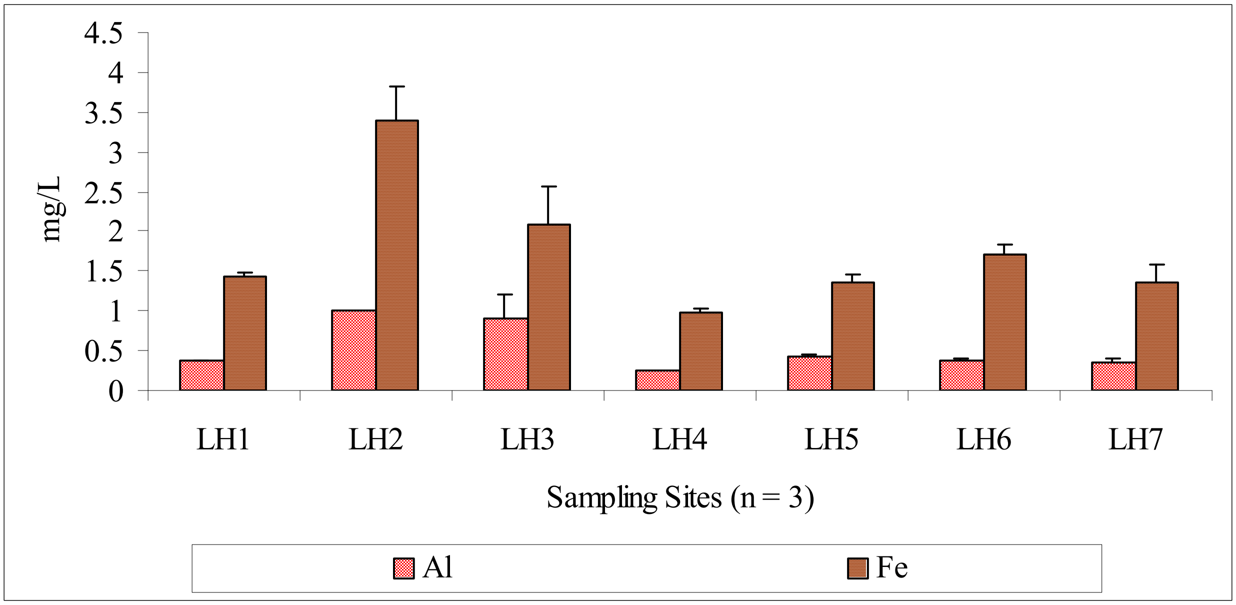

Figure 4. Heavy metals in the Peconic River headwaters (ICP data)

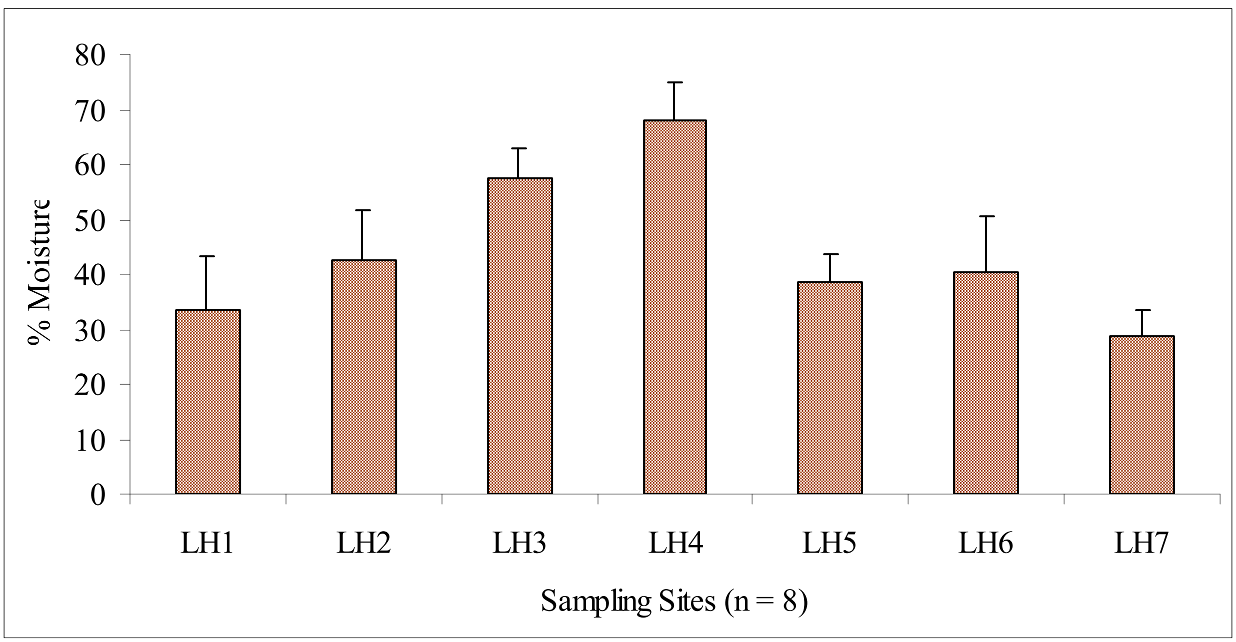

Figure 5. Percentage Moisture in the Peconic River headwater sediments.

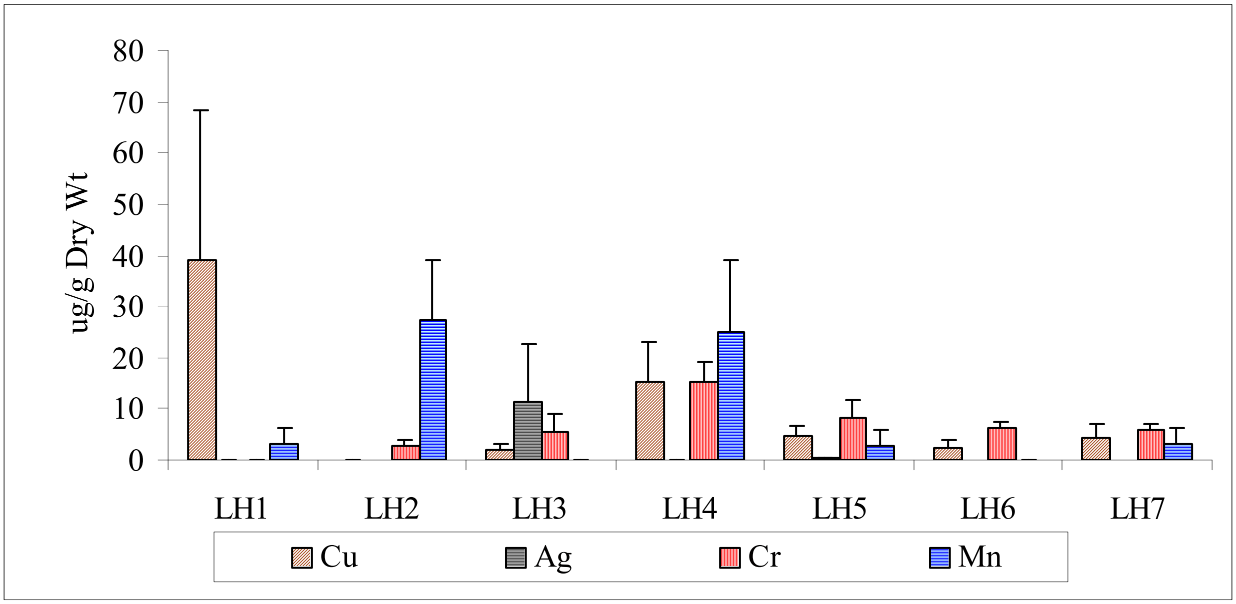

Figure 6. Copper, silver, chromium, and manganese (heavy metals) in the Peconic River headwater sediments.

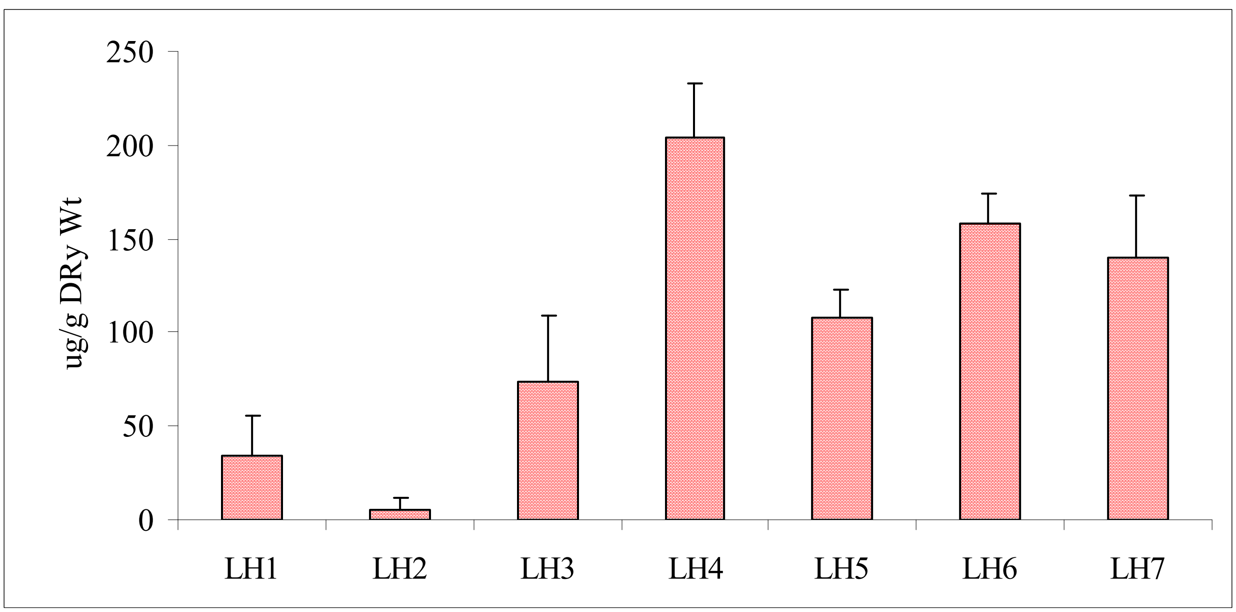

Figure 7. Lead content in the Peconic River headwaters.

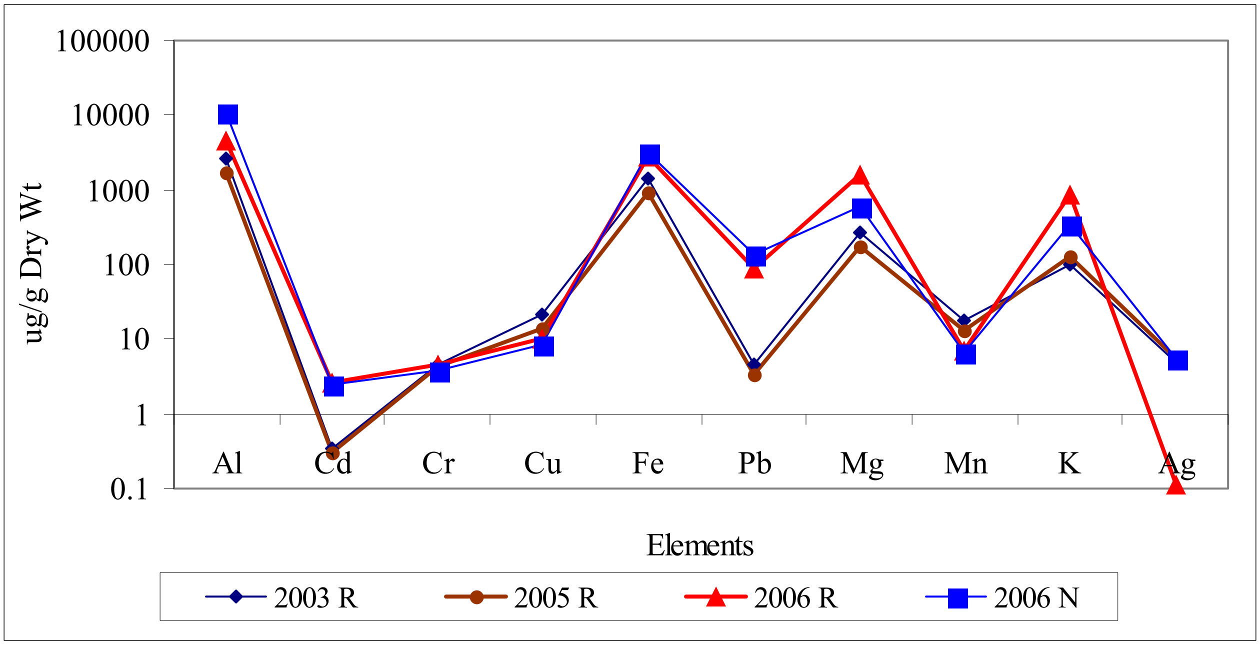

Figure 8. Comparative summary on several elements (macronutrients and heavy metals) between the years 2003 and 2005 with our current research results in remediated and natural sites.