Kearny Marsh Restoration Project
Preliminary Report

November 23, 2005

Rutgers Environmental Research Clinic

Executive Summary

The Kearny Marsh system is contaminated due to current and historical inputs of landfill leachate, combined sewer overflows, and municipal stormwater discharges. The New Jersey Meadowlands Commissions (NJMC) has determined that remediation and restoration of this ecosystem is a high priority. Successful remediation of the site requires an understanding of the current source and transport of toxic contaminants, including both heavy metal and organic pollutants, the location of historical contaminant “hot spots”, and the potential for sequestration and/or biotransformation of priority pollutants.

Representative samples from locations within approximately 25% of the Kearny Marsh have been analyzed for concentrations of heavy metals, PAHs, and PCBs. The samples were obtained from an area that is approximately 1,725 square acres located in the northwestern portion of the marsh adjacent to the Gunnell Oval ball fields (See Map, Appendix I). This area was selected for our initial sampling activities due to historical data indicating high levels of contaminants in this section of the marsh. Our preliminary analyses confirm that planning an effective restoration strategy will require an understanding of the interactions involving contaminants, sediment properties, and biological processes.

Chromium, copper, nickel, lead, and zinc were found to have concentrations exceeding the Ontario sediment quality criteria used by the State of New Jersey. Levels of Hg were above the regulatory level in all Grids sampled except Grid 9, and a Hg “hot spot” was identified in Grid 16. High correlations between Cr, Cu, Fe, and Zn indicate that these metals may come from the same source. The presence of Hg was not correlated with the other metals, and it is quite possible that the source of Hg contamination is different from that of the other heavy metals. We believe that overall our Cr and Hg results are biased on the low side due to analytical procedures, and we recommend re-sampling these metals using different extraction protocols to increase the extraction efficiency. We recommend obtaining representative sediment samples from locations within the remaining 75% of Kearny Marsh to more completely map sediment contaminant levels within the system. We also recommend further Hg analysis within and adjacent to the Quad 16 “hot spot” to determine the extent of the extremely high Hg contaminant levels (14 ppm; Hg SEL 2 ppm). We propose the analysis of PCBs within a sediment depth profile as an inexpensive assay to determine the age of the sediment contaminant inputs. This assay, in conjunction with the hydrological study, will determine whether the contaminant levels observed are the result of historical or ongoing contamination.

Organic material is the dominant particle fraction in the sediments sampled and total sediment organic carbon ranges from 19% to 42%. It appears that Kearny Marsh sediments have relatively high levels of extractable organic carbon material that is water soluble. The bioavailability and toxicity of the heavy metal contaminants will be determined by association with this organic material. We recommend that suspended particulate matter by analyzed after sediment perturbation and that bioavailable fractions be quantified by determining metal speciation for both the sediments and the suspended particulate matter.

The high levels of organic material in Kearny Marsh sediments indicate the strong possibility of high rates of microbially mediated gas production, which potentially could breech any capping materials. We recommend establishing mesocosm and field experiments to monitor sediment gas production below, and water quality above, the AquaBlok™ capping material. We also recommend laboratory microcosm studies to determine the effect of heavy metal contaminants on native sediment microbial processes that result in gas production, and the effect of such gas production on cap stability and functionality. In partnership with the NJMC, Rutgers University has submitted a proposal to obtain funding ($274,384) for these microbial process and engineering studies through the NOAA Cooperative Institute for Coastal and Estuarine Environmental Technology (CICEET) program. A decision on our joint Pre-Proposal application will be available on Dec. 22, 2005.

This report and other relevant scientific papers and reports related to the Kearny Marsh are now accessible through the Rutgers web site www.rerc.rutgers.edu. The data included in this report, as well as data from the previous Kearny Marsh studies, are available in a downloadable database from this web site. Access to the data is password protected, and the password is available to NJMC staff and all Rutgers project scientists.

Background

The Kearny Marsh is located in the Town of Kearny and is part of the New Jersey Meadowlands District. The system is contaminated with current and historical inputs of landfill leachate, combined sewer overflows, and municipal stormwater discharges. The New Jersey Meadowlands Commissions (NJMC) has determined that remediation and restoration of the ecosystem is a high priority. Successful remediation of this site will involve collection and treatment of highly contaminated leachate that continues to enter the marsh system from the uncapped Keegan landfill and remediation of highly contaminated sediments. Documented contaminants include cadmium, chromium, copper, manganese, lead, iron, nickel, zinc, PCBs, DDE, DDD, DDT, dieldrin, endosulfan H, as well as numerous other halogenated organic compounds that are currently being transported into the marsh through groundwater movement. Restoration of the ecosystem may also be impacted by the presence of combined sewer overflows (CSOs) that empty directly into the Kearny Marsh.

The goal of the collaboration between Rutgers University, Cook College and the NJMC is to provide solutions for remediation of the Kearny Marsh through the development of engineered methods to interdict and treat on-going discharges to the marsh ecosystem and to evaluate technological options to remediate the existing contaminated sediments. To successfully accomplish this complex remediation and restoration an interdisciplinary approach is required. A whole systems approach will take into account the source and transport of toxic contaminants and organic nutrient inputs and the potential for sequestration and/or biotransformation of these compounds.

Work supporting the goal of restoration was begun with an initial assessment of the extent of sediment contamination in Kearny Marsh. This preliminary report describes the sampling, analyses and evaluation of sediment characteristics and contaminants in the northwest quarter of Kearny Marsh adjacent to the Gunnell Oval ball fields. The data obtained from these analyses is in this report and is also available on the Rutgers web site (www.rerc.rutgers.edu). The data and the accompanying report are digitally accessible to NJMC staff through use of a password.

Methods

Sample Collection: The initial sediment sampling was conducted adjacent to the Gunnell Oval ball fields in the northwestern quarter of the marsh (Figure 1, Appendix I). This location was selected because historical data shows high contaminant concentrations, particularly heavy metals, in the sediments in this section of the marsh. Using an Eckman dredge samples were collected from up to 5 locations within 11 twelve-acre square sections (N=55 samples to test for priority contaminant levels; N=33 samples to analyze microbial capabilities; N=11-33 samples to determine sediment characteristics). Specific GPS points were noted for all sampling locations within each Grid.

Sediment samples for contaminant analysis were stored at 20 ^{o}C in glass jars with plastic screw lids with minimal headspace. Sub-samples of sediments were thawed and homogenized before extraction for contaminant and water content analysis. Water content was determined by weighing a sediment sample before and after drying to constant weight in a 105°C oven.

Contaminant Analyses

Metal Analysis: Rutgers personnel performed metals analysis at the Meadowlands Environmental Research Institute (MERI). For metals analysis, wet sediment sub-samples (100-500 mg) were digested in Teflon vials using 10 ml of metals grade concentrated nitric acid. Digestion proceeded for one hour at ambient conditions, and then for 25 minutes in a microwave digester, followed by 90 minutes of cooling. Extracts were evaporated to ~1 mL on a hotplate then transferred into 10 mL volumetric flasks and diluted with distilled water. Trace metals were then measured via Flame Atomic Absorption. Mercury (Hg) was measured by Cold Vapor Atomic Absorption (CVAA).

PAH, PCB Analysis: Wet sediment samples (~5 g) were ground with dry sodium sulfate to bind excess water and the mixture was loaded into a Soxhlet extraction apparatus. Samples were then injected with surrogate standards (PCBs 14, 23, 65, and 166, and PAHs d_{10}-anthracene, d_{10}-fluoranthene, d_{10}-benzo[e]pyrene) before extraction. Each sample was extracted in a Soxhlet apparatus for 24 hours in dichloromethane. These extracts were then reduced in volume by rotary evaporation and subsequently concentrated via N_2 evaporation. The samples were then fractionated on a column of 3% water-deactivated alumina. The PCB fraction was eluted with hexane, while the PAH fraction was eluted with 1:1 dichloromethane:hexane. These two fractions were concentrated under a gentle stream of nitrogen gas, and injected with internal standard. For PCBs, the internal standards were PCBs 30 and 204. For PAHs, the internal standards were d_{10}-phenanthrene, d_{10}-pyrene, and d_{12}-benzo[a]pyrene. PCBs were analyzed on an HP 6890 gas chromatograph equipped with a ^{63}Ni electron capture detector using a 60-m 0.32 mm i.d. DB-5 (5% diphenyl-dimethyl polysiloxane) capillary column with a film thickness of 0.25 μm. Sixty peaks representing 93 congeners were quantified. The PAHs were analyzed on a Hewlett Packard 6890 Gas Chromatograph (GC) coupled to a Hewlett Packard 5973 Mass Selective Detector (MSD) operating in Selective Ion Monitoring (SIM) mode using a 30m × 0.25mm i.d., J&W Scientific 122-5062 DB-5 (5% diphenyl-dimethylpolysiloxane) capillary column with a film thickness of 0.25 μm. Thirty-six individual PAH compounds were quantified: fluorene (FL), phenanthrene (PHEN), anthracene (ANT), 1-methylfluorene (1MF), dibenzothiophene (DBT), 4,5-methylenephenanthrene (4,5MP), methylphenanthrene(s), sum of 5 compounds (Σ_5MPs), methyldibenzothiophenes, sum of three compounds, (Σ_3MDBTs), fluoranthene (FLT), pyrene (PYR), 3,6-dimethylphenanthrene (3,6DMP), benzo[a]fluorene (BaF), benzo[b]fluorene (BbF), retene (RET), benzo[b]naphto[2,1-d]thiophene (BNT), cyclopenta[cd]pyrene (CPP), benz[a]anthracene (BaA), chrysene + triphenylene (CHR + TRI), naphthalene (NPT), benzo[b]fluoranthene + benzo[k]fluoranthene (BFLTs), benzo[e]pyrene (BeP), benzo[a]pyrene (BaP), perylene (PER), indeno[1,2,3-cd]pyrene (IP), benzo[g,h,i]perylene (BghiP), dibenzo[a,h]anthracene + dibenzo[a,c]anthracene (DBA), and coronene (COR).

For each PAH, the identity and chromatographic retention time was confirmed by the use of a calibration standard. The calibration standard contained known concentrations of the deuterated surrogate compounds, deuterated internal standard compounds, and all of the compounds of interest in this study. The mass of each PAH was determined by isotopic dilution using the masses of deuterated PAH internal standard added.

Sediment Characteristics

Sediment Preparation: The eleven sediment samples were placed in a 50 °C oven for 7 days to evaporate the majority of the water. A fraction (500 g) of the partially dried sediment sample was then freeze-dried to completely remove any moisture. The dried samples were crushed with a mortar and pestle to break up large clumps. The samples were then stored in glass jars for future analysis.

Particle Size Distribution: Sediment particle size distribution was determined using a standard wet sieving method. Diluted sodium hexametaphosphate solution (200 mL of ~0.5 mM) was added to 15 g of the dried sediment and stirred for one hour to disaggregate sediments. After disaggregation, the slurry was poured through a stack of sieves with a pan at the bottom and rinsed with diluted sodium hexametaphosphate solution several times to assure that all the solids had been transferred. The sieve stack was then shaken for 2 hours. After completion of the sieving, the sediment fractions were placed in a 70 ºC oven for 24 hrs. After drying, the weights of the sieves before and after removal of the sediment fractions were recorded. The weight difference was used to determine the weight of the various sediment particle size ranges.

Sediment Organic Matter (SOM) Fractionation: The organic matter associated with each sediment was fractionated into humic acid (HA) and particulate organic matter (POM) using a wet chemical procedure developed in the Huang laboratory (Song et al. 2002). In brief, 20 g of each freeze-dried sediment sample was ground until no sandy particles could be felt. The sample was divided into two fractions, one (5 g) to be used in TOC analysis described below, and one (15 g) used for SOM fractionation. The sediment was extracted with NaOH solution and the supernatants obtained were acidified with 6M HCl solution to pH 1. The HAs were allowed to precipitate over 24 hours. The HA precipitates were rinsed with Milli-Q water freeze-dried, and their weights recorded. The residual solid left after the base-extraction was further treated to remove the inorganic matrix [24 hours with HF/HCl mixture solutions (22M HF and 6M HCl at a volumetric ratio of 2:1) in a 60 °C water bath]. During the reaction the samples were stirred manually. After demineralization, the residual solids were rinsed with dilute HCl solution (0.1 M) followed by a Milli-Q water rinse. Solids were then freeze-dried and weighed. This fraction of organic matter is defined as POM. The mass percentages of HA and POM in the bulk sediments were calculated based on their weights. HA and POM fractions were used directly for TOC and TN measurements.

Analysis of Total Organic Carbon (TOC) and Total Organic Nitrogen (TN): The sediment samples were pretreated to remove inorganic carbon before analysis of TOC. In brief, 5 g of the ground sample was reacted overnight with 0.1M HCl solution at 60 °C.

After they were decarbonated, the residual solids were rinsed with Milli Q water several times until the pH of the supernatants became neutral. The solids were then freeze-dried. The decarbonated sediments and the HA and POM fraction of SOM were analyzed in the Institute of Marine and Coastal Sciences for TOC and TN using a CHNS analyzer (NA1500 Series, Carlo Erba).

Microbial Processes

Anaerobic enrichments were established using Kearny Marsh sediment from grids 1, 7, 9, 10, 16, and a sample taken from the Keegan landfill. Microcosms consisted of 25 g of sediment, 25 ml of Kearny Marsh site water and 50 ml of reduced anaerobic media with or without sulfate (20 mM). Pentachlorobenzene was used as a “model” chlorinated contaminant, and was added to the sediments to achieve a final concentration of 100 μM. The enrichments have been sampled through day 109, and the extractant analyzed on a GC-MS to determine loss of the parent compound and formation of lesser chlorinated metabolites (tetra-, tri-, and di-chlorobenzenes). Dechlorination activity has been detected in these sediments after 100 days of incubation. We will continue to monitor dechlorination activity and the production of microbial metabolites in these cultures, as well as determine the rate of methane gas production.

Preliminary Findings

Contaminant Analysis

Metals: Currently 49 samples have been analyzed for metals. These comprise samples from Grid cells 1, 2, 3, 7, 8, 9, 10, 16, 17, 18, and 19. Standard reference material (SRM) 1944 was also analyzed six times. The SRM metals results yielded concentrations that were within the range of uncertainty given by NIST for this SRM for all metals except Cr and Hg, which were both lower than the certified SRM concentration. The average Cr measured in the SRM was 80% of the certified value. The average Hg measured in the SRM was 55% of the certified value. Results for these two metals should therefore be viewed with caution, remembering that they are biased on the low side. Future sediment samples should be analyzed for Hg using aqua regia (a mixture of nitric and hydrochloric acids) instead of nitric acid to ensure complete digestion of the mineral substrate and therefore better recovery of Hg from the sediment samples.

Detection limits were determined from the reagent blanks. Detection limits were calculated as the average plus three standard deviations of the metals concentration in the blanks. Detection limits for Cd were particularly high, with the results that Cd was below detection limit in all but a few samples. This is likely due to the use of insufficiently pure solvents. We propose to re-analyze Hg and Cd at our labs at Rutgers using aqua regia and cleaner solvents to achieve better detection limits and higher accuracy.

The preliminary metals results are presented as mg/kg dry weight in Table 1 and Figures 1a-g, Appendix II). The first number in each location code in Table 1 refers to the grid cell in which the sample was collected. The Low Effects Level (LEL) and Severe Effects

Table 1. Metals concentrations in Kearny Marsh sediment samples. Values bolded exceed the LEL. Values in red bold exceed the SEL. BDL = below detection limit.

	Concentration		**(mg/kg**	**dry wt.)**				
Location	**Cd**	**Cr**	**Cu**	**Fe**	**Ni**	**Pb**	**Zn**	**Hg**
2-4	BDL	**146**	**131**	10901	**88**	**2054**	**379**	
3-1	**16**	**166**	**292**	32224	**143**	BDL	**653**	
3-2	BDL	**52**	**84**	3863	BDL	**3890**	BDL	
3-3	BDL	**94**	**109**	10166	BDL	BDL	BDL	
7-1	**23**	**311**	**388**	86687	**165**	**451**	**1590**	
8-1	BDL	**203**	**451**	46533	**216**	**2874**	**876**	
8-2	BDL	**53**	**80**	4785	BDL	BDL	BDL	
8-3	BDL	**327**	**423**	46464	**197**	BDL	**1082**	
9-1	BDL	**116**	**436**	22315	**109**	BDL	**440**	
10-3	**42**	**115**	**142**	14353	**121**	**1113**	**328**	
10-5	BDL	**75**	**278**	43770	**133**	**825**	**553**	
16-3	BDL	**34**	**96**	5376	BDL	**9784**	BDL	
17-5	BDL	**85**	**121**	12486	**114**	BDL	BDL	
18-1	BDL	**84**	**341**	31089	**176**	BDL	**516**	
18-2	BDL	**27**	**113**	3549	**238**	BDL	BDL	
19-2	BDL	17	**50**	1504	BDL	**968**	BDL	
19-4	BDL	**66**	**131**	10523	**124**	BDL	BDL	
1-1	BDL	**606**	**211**	20337	**73**	**537**	**691**	**0.67**
1-2	BDL	**239**	**148**	21479	**48**	BDL	**509**	0.088
1-3	BDL	**1130**	**400**	38595	**139**	**1034**	**1457**	0.093
1-4	BDL	**133**	**60**	8060	BDL	BDL	**284**	BDL
2-1	BDL	**824**	**233**	23105	**80**	**533**	**705**	**0.69**
2-2	BDL	**49**	**21**	1542	BDL	BDL	**329**	BDL
2-5	BDL	**54**	**45**	1734	BDL	BDL	**181**	0.19
3-4	BDL	**149**	**195**	16673	BDL	BDL	**665**	BDL
3-5	BDL	**175**	**180**	18592	**101**	**634**	**576**	**0.40**
7-2	BDL	**108**	**100**	9845	**53**	BDL	**389**	**0.29**
7-4	BDL	**290**	**328**	32693	**76**	**671**	**833**	**0.36**
7-5	**9.3**	**234**	**362**	40781	**99**	**763**	**1017**	**1.20**
8-4	BDL	**136**	**204**	13063	**135**	BDL	**564**	**0.87**
8-5	BDL	**95**	**169**	11325	BDL	BDL	**557**	BDL
9-3	BDL	**39**	**52**	5182	**28**	BDL	118	0.13
9-4	BDL	**53**	**68**	4852	BDL	BDL	**263**	BDL
9-5	BDL	23	**42**	1570	BDL	BDL	BDL	BDL
10-1	BDL	**76**	**95**	9335	**41**	**348**	**240**	BDL
10-2	BDL	**41**	**52**	3485	**84**	BDL	BDL	**0.35**
16-1	**14**	**175**	**333**	30227	**104**	**799**	**926**	**1.10**
16-2	BDL	**141**	**217**	20429	**80**	BDL	**672**	**0.24**
16-4	BDL	**180**	**351**	44386	**120**	**829**	**1036**	**14**
17-1	BDL	**143**	**329**	20000	**120**	**984**	**677**	**1.4**
17-3	BDL	21	**24**	1864	BDL	BDL	BDL	BDL
17-4	BDL	**158**	**222**	16569	**93**	**594**	**434**	**0.57**
18-3	BDL	**36**	**50**	3494	BDL	BDL	BDL	BDL
18-5	BDL	**282**	**585**	26399	**217**	**1944**	**848**	**0.22**
19-3	BDL	**566**	**229**	21619	**132**	**794**	**841**	**0.71**
19-5	BDL	17	**48**	1058	BDL	BDL	BDL	BDL

	Cd	**Cr**	**Cu**	**Fe**	**Ni**	**Pb**	**Zn**	**Hg**
LEL	0.6	26	16	None	16	31	120	0.2
SEL	10	110	110	None	75	250	820	2

Levels (SEL) shown in Table 1 are the Ontario sediment quality criteria used by the State of New Jersey. Table 1 also indicates the number of samples in which the metal was above the detection limit (BDL), the LEL and the SEL. Because our Hg results may be biased on the low side, it is likely that Hg exceeds the LEL in more than the 15 samples shown in Table 1. Because all of the metals tested exceed the LEL in the majority of samples, metals are clearly a priority class of contaminants in Kearny Marsh.

Table 2 is a comparison of this data set versus the data collected by Langan Associates (1999). Differences between the two data sets do not imply that either set of data is flawed. Sample collection was separated by 6 years, and although in some cases we tried to revisit the same sampling locations, spatial variability in the sediment metals concentrations is large. Thus spatial and temporal variability in metals concentrations could account for any differences between our data and Langan's.

Table 2. Average metals concentrations (mg/kg dry weight) and Relative Standard Deviations (RSD) for the 32 samples described herein and the data set of Langan Associates (1999).

	Cd	Cr	Cu	Ni	Pb	Zn
This report						
average	21	187	196	120	1597	656
RSD	62%	128%	73%	49%	127%	56%
Langan 1999						
average	1.8	199	76	19	188	280
RSD	280%	471%	167%	128%	194%	156%

Table 3 displays correlation coefficients (R^2) between the various metal concentrations. Hg showed no significant correlation with any of the other metals, suggesting that the dominant source of Hg in Kearny Marsh is probably different than the sources of the other metals. The highest concentration of Hg (14 mg/kg) was measured in Grid cell #16. Even if this data point is removed, Hg concentrations still display little or no correlation with the other metals.

Cr, Cu, Fe, and Zn are strongly correlated with each other, suggesting that their presence in the Marsh is primarily due to a single source. We speculate that these heavy metals may be related to the chromium ore processing residue (COPR) deposited extensively in the Meadowlands as "clean fill"(Geelhoed et al. 2003).

Table 3. Correlation coefficients for various metals in Kearny Marsh

	Cr	Cu	Fe	Ni	Pb	Zn
Cu	**0.6663**					
Fe	**0.6496**	**0.6841**				
Ni	0.2063	0.4515	0.2538			
Pb	0.1085	0.0430	0.0850	0.2385		
Zn	**0.7353**	**0.6443**	**0.8195**	0.4539	0.0153	
Hg	0.0133	0.0774	0.3135	0.0401	0.0084	0.2168

PAHs, PCBs: PAH concentrations in Kearny Marsh sediments (Fig. 2a, Appendix II) are presented in Table 4, and Table 5 gives a comparison of the average values in Kearny Marsh sediment and sediments in the NY/NJ Harbor Estuary (Adams et al. 1998). PAH concentrations in Kearny Marsh sediment (Fig. 2b, Appendix II) are relatively high, similar to sediments of the upper New York Harbor. PCB concentrations for Kearny Marsh and the NY/NJ Harbor Estuary(Adams et al. 1998) are compared in Table 6. These are presented as the sum of all PCB congeners, or "ΣPCBs". ΣPCBs concentrations are relatively high in many of the Kearny Marsh samples. PCBs pose a problem in disposal of the dredge material should it eventually be determined that Kearny Marsh needs to be dredged to remove contamination.

Table 4. Polycyclic Aromatic Hydrocarbons (PAHs) in Kearny Marsh sediment (mg/kg dry weight).

Location	**1-001**	**2-001A**	**2-001**	**3-001**	**7-001**	**8-001**	**10-001**	**16-004**	**16-001**	**17-004**	**18-001**	**19-003**	**Detection Limit**
Fluorene	0.43	0.16	0.23	0.14	0.18	0.095	0.10	0.18	0.47	0.10	0.097	0.12	0.0040
Phenanthrene	5.1	0.88	1.2	0.91	0.97	0.48	0.75	0.79	2.6	0.52	0.36	0.37	0.013
Anthracene	0.98	0.31	0.40	0.24	0.31	0.098	0.15	0.26	0.92	0.11	0.067	0.12	0.44
1Methylfluorene	0.23	0.088	0.11	0.078	0.15	0.055	0.055	0.25	1.1	0.053	0.070	0.12	0.034
Dibenzothiophene	0.27	0.10	0.15	0.044	0.12	0.049	0.063	0.15	0.41	0.049	0.030	0.055	0.000018
4,5 Methylenephenanthrene	1.5	0.38	0.48	0.33	0.57	0.15	0.20	0.48	1.2	0.17	0.11	0.18	0.0024
Methylphenanthrenes	2.6	0.15	0.20	0.15	0.13	0.058	0.10	0.092	0.86	0.0014	0.053	0.089	0.0099
Methyldibenzothiophenes	28	10	13	6.8	25	6.7	5.0	6.9	90	7.9	4.1	12	297
Fluoranthene	11	2.0	2.6	1.6	2.3	0.76	1.1	1.6	4.9	0.81	0.43	0.52	0.011
Pyrene	8.9	1.8	2.4	1.4	2.2	0.68	0.93	1.6	1.3	0.70	0.35	0.54	0.0021
3,6-Dimethylphenanthrene	40	14	21	11	20	9.6	8.9	23	68	9.0	13	5.4	2.5
Benzo[a]fluorene	7.4	1.3	96	1.5	3.8	0.64	0.53	3.5	8.2	0.57	1.1	2.1	0.0061
Benzo[b]fluorene	1.9	0.45	0.45	0.31	0.60	0.15	0.20	0.47	1.3	0.15	0.085	0.16	0.00022
Retene	18	6.0	7.7	19	9.0	2.7	2.3	14	47	0.0059	1.8	4.5	6.7
Benzo[b]naptho[2,1-d]thiophene	1.2	0.29	0.40	0.21	0.33	0.11	0.14	0.13	0.59	0.11	0.062	0.072	0.000020
Cyclopenta[cd]pyrene	2.0	0.55	0.71	0.40	2.0	0.17	0.26	0.23	1.1	0.18	0.086	0.11	0.082
Benz[a]anthracene	4.5	1.2	0.16	0.86	1.2	0.38	0.57	0.50	2.3	0.40	0.19	0.24	0.00013
Chrysene/Triphenylene	5.8	1.5	0.20	1.1	1.6	0.52	0.68	0.65	2.8	0.51	0.27	0.34	0.00056
Naphthacene	5.2	1.4	1.9	0.96	1.5	0.45	0.53	0.82	2.3	0.43	0.17	0.22	0.00032
Benzo[b+k]fluoranthene	11	3.5	4.6	2.3	3.4	1.1	1.3	1.3	5.4	1.0	0.50	0.69	0.38
Benzo[e]pyrene	38	10	14	6.6	12	3.4	3.7	6.2	24	3.0	1.6	2.3	0.030
Benzo[a]pyrene	7.0	2.0	2.7	1.3	2.1	0.61	0.76	1.0	4.1	0.56	0.27	0.36	0.00058
Perylene	2.6	0.76	1.1	0.57	1.1	0.81	0.45	1.2	1.8	0.31	0.67	1.1	0.00074
Indeno[1,2,3-cd]pyrene	1.0	0.83	1.2	1.0	1.7	0.48	0.53	0.46	2.3	0.35	0.18	0.22	0.0034
Benzo[g,h,i]perylene	1.3	0.099	0.38	0.12	0.092	0.54	0.026	0.12	1.8	0.080	0.0077	0.044	0.00022
Dibenzo[a,h+a,c]anthracene	2.0	0.40	0.85	0.37	0.60	0.18	0.19	0.17	0.83	0.13	0.0061	0.076	0.0015
Coronene	3.3	1.2	1.2	0.71	0.82	0.49	0.34	0.25	0.67	0.39	0.43	0.28	0.0083
SumPAHs	**211**	**61**	**176**	**60**	**93**	**31**	**30**	**66**	**278**	**28**	**26**	**32**	

Table 5. Comparison of PAH concentrations (μg/kg dry weight, or ppb) in Kearny Marsh sediments and sediments in the NY/NJ Harbor estuary (Adams et al. 1998).

	Jamaica Bay	Newark Bay	Lower Harbor	Upper Harbor	Long Island Sound	Kearny Marsh
Benzo[a]anthracene	231	905	142	1526	395	1037
Benzo[a]pyrene	139	517	113	890	194	1883
Benzo[g,h,i]perylene	186	579	113	849	173	384
Chrysene	313	1077	162	1653	311	1323
Fluoranthene	569	1280	201	2308	325	2435
Fluorene	78	108	28	693	37	192
Ideno[1,2,3-c,d]pyrene	132	576	118	807	195	853
Perylene	114	608	128	975	170	1033
Phenanthrene	364	417	117	2369	198	1249
Pyrene	509	1145	202	2491	364	1900

Table 6. ΣPCB concentrations in sediments of Kearny Marsh and the NY/NJ Harbor Estuary (Adams et al. 1998).

Sample ID	Σ PCB conc (ppb)
1-001	6050
1-001A	726
2-001A	865
2-001	7476
3-004	2775
7-001	2578
8-001	614
10-001	395
10-003	12280
16-001	6125
16-004	3426
16-001	5390
17-004	691
18-001	14770
19-003	2775
Lower Harbor	120
Upper Harbor	429
Jamaica Bay	112
Newark Bay	756

Sediment Characteristics

Particle Size Distribution. The particle size distribution analyses are summarized in Table 7. The results indicate that the sediments collected from the eleven cells were highly heterogeneous and that they consisted mainly of organic matter and plant debris. Each of the 11 sediment samples was separated into 9 different particle size fractions: > 2mm, >1.41mm, >0.841mm, >0.354mm, >0.297mm, >0.210, > 0.125, >0.062mm, and <0.062mm (Table 4). One characteristic is that no clear common pattern in particle size distribution could be found among the eleven sediment samples. During sieving, a large amount of plant debris was observed, and this organic material is the dominant particle in fractions with sizes greater than 0.210 mm. Very little sand was found in the bulk sediment samples. Silt and clay materials appear to be the main inorganic constituents of the sediments minerals.

Organic Carbon Content and the Contents of HA and POM. The total organic carbon contents and total organic nitrogen contents are summarized in Table 8 and Figures 2a,b. All sediment samples had very high organic matter, with total organic carbon ranging from 19.3% to 42.3% (Table 8). These sediments contained high plant residues, high HA and POM contents, and can be classified as peat/bog materials. The TOC/TN ratio (Fig. 2c) ranged from 20 to 34, also indicating that the plant debris is the major SOM. However, there was not a good correlation between TOC and TN ($r^2 < 0.5$), suggesting that the organic matter of the Kearny marsh sediment samples was highly diverse. Another feature of the sediment organic matter is that the contents of HA and POM among the eleven sediments varied dramatically, indicating high levels of heterogeneity within the marsh.

The HA contents ranged from 4.3 to 24.6% and the contents of POM ranged from16.3 to 37.3% of the total mass of the sediment. The sums of these two SOM fractions (HA + POM) constituted about 46-78% of the TOC of the bulk sediments. This suggests two possibilities. One is that some tiny organic particles such as soot carbon particles were lost during the fractionation procedure in which repeated centrifugation and decanting of supernatants occurred. The other is that the sediments contained high concentrations of water soluble organic matter such as fulvic acids. We believe that the second possibility is more likely because the atomic ratio of the lost carbon content and the nitrogen content ranged from about 12 to 38, which is far different from the composition of regular soot particles. Therefore, we believe that the sediments contain high levels of low molecular weight extractable organic carbon material, which may be highly water soluble. Typically low molecular weight increases the ease of biotic uptake.

Implications. The high organic matter content of these sediments is expected to have significant impacts on the speciation and bioavailability of the organic and inorganic pollutants and any subsequent remediation plan. First of all, the organic pollutants are most likely associated with the sediment organic matter due to their preferential sorption on SOM. The large fraction of plant debris and extractable organic matter can constrain biodegradation of the organic pollutants because this natural source of readily available labile organic carbon is available to organisms for growth. Secondly, inorganic pollutants such as Pb, Hg, Cr and Ni are typically associated with the organic matter as salt forms. If this is the case, the bioavailability and toxicity of the metals will be largely determined by complexion with sites on the plant organic matter. Thirdly, the large fraction of water soluble organic matter in the sediments is potentially highly mobile and could be easily resuspended or leached to the overlying water column. If the soluble organic matter carries the major organic and inorganic pollutants as expected, continuous contamination of the water body from the sediments is very likely.

It is believed that not all fractions of organic and inorganic pollutants bound on sediments are equally toxic to living organisms due to their various resistances to desorption as a result of varied binding strength with different sediment components. The resistant and sequestered fractions are environmentally less harmful than the more readily desorbing, labile, or available fractions and could be subject to alternative sediment remediation end points and risk standards. Tessier et al. (1979) has distinguished five different metal fractions. Fraction 1 is termed exchangeable due to its presence at exchangeable sites on clay minerals, and it is regarded as the readily bioavailable fraction. Fraction 2 is bound to carbonates as precipitates that are susceptible to changes of pH. Fraction 3 is chemically bound to iron and manganese oxides. Fraction 4 is the metal fraction bound to various forms of organic matter: living organisms, detritus, coatings on mineral particles, etc. The complexation and peptization properties of natural organic matter (notably humic and fulvic acids) are well recognized. Under oxidizing conditions in natural waters, organic matter can be degraded, leading to a release of soluble trace metals. Fraction 5 is the residual metal. Once the first four fractions have been removed, the residual solid should contain mainly primary and secondary minerals, which may hold trace metals within their crystal structure. These metals are not expected to be released in solution over a reasonable time span under the conditions normally encountered in natural systems.

Table 4. Percentage of the Particle Size Distribution in Kearny Marsh Sediment Samples

Sample	Location	Size Distribution (mm)								
		> 2	> 1.41	> 0.841	> 0.354	> 0.297	> 0.210	> 0.125	> 0.062	< 0.062
KM1	**1-001**	15.04	5.23	10.37	16.55	3.01	9.42	21.38	7.52	11.48
KM2	**2-002**	35.89	2.29	14.18	10.34	1.48	3.69	13.29	5.54	13.29
KM3	**3-002**	34.11	2.78	5.13	19.94	9.05	2.28	1.01	1.96	23.73
KM4	**7-001**	0.69	0.89	7.63	3.96	0.50	2.28	13.68	9.61	60.75
KM5	**8-001**	4.09	3.87	35.62	4.09	1.99	3.10	6.75	7.30	33.19
KM6	**9-001**	7.79	5.63	6.19	54.50	1.50	1.69	2.63	6.75	13.32
KM7	**10-002**	7.16	1.84	4.26	16.25	1.45	32.40	1.74	5.32	29.59
KM8	**16-001**	0.43	0.17	1.11	27.89	5.65	37.04	15.06	4.28	8.38
KM9	**17-001**	2.19	1.53	4.58	16.78	48.24	0.19	1.24	15.35	9.91
KM10	**18-001**	5.47	1.79	8.63	7.79	1.68	64.74	0.53	4.42	4.95
KM11	**19-001**	3.40	2.33	3.20	37.09	0.29	1.65	28.06	16.12	7.86

Table 5. Kearny Marsh Sediment Organic Carbon Content by Fraction.

Sample	Location	HA%	POM%	TOC %	TN %	HA-OC%	HA-N%	POM-OC%	POM-N%	C:N	C:N HA	C:N POM
KM1	**1-001**	7.13	19.79	19.39	0.92	53.18	4.08	48.01	1.23	25	15	46
KM2	**2-002**	19.73	25.77	31.42	1.88	46.11	3.40	52.17	1.41	20	16	43
KM3	**3-002**	18.58	29.75	38.28	1.86	51.15	3.00	58.98	1.51	24	20	46
KM4	**7-001**	11.92	26.30	31.14	1.52	43.64	2.89	49.32	1.45	24	18	40
KM5	**8-001**	24.13	32.04	41.90	1.75	48.52	2.34	58.21	1.79	28	24	38
KM6	**9-001**	24.62	33.62	37.97	1.54	47.26	2.23	52.94	1.32	29	25	47
KM7	**10-002**	18.16	37.33	42.06	1.53	51.26	2.48	58.31	1.95	32	24	35
KM8	**16-001**	4.33	16.34	20.98	0.96	50.12	4.14	46.28	2.06	25	14	26
KM9	**17-001**	22.95	25.95	38.82	1.44	50.65	2.18	51.42	1.42	31	27	42
KM10	**18-001**	17.96	33.33	38.71	1.36	51.45	2.35	59.43	1.55	33	26	45
KM11	**19-001**	21.50	31.36	42.26	1.45	50.12	2.18	58.09	1.83	34	27	37

Recommendations

I. Sediment Contaminants

A. Heavy Metals

Given the concentrations of heavy metals in the samples, the presence of a mercury "hot spot" in Grid 16, and the correlation between certain metal location patterns we recommend a number of steps to determine the extent and source of heavy metal contamination in Kearny Marsh:

1. A whole marsh analysis for the suite of heavy metals (sampling in the 29 additional grids, which includes the 75% of the marsh sediments not sampled)
2. Additional Hg sampling adjacent to Grid 16 to determine the extent of the high Hg concentrations observed. Hg analytic techniques will have been changed to obtain a more efficient extraction (as described above)
3. Water column samples should be analyzed after sediment samples are extracted to determine the effect of resuspension after sediment disturbance on water column metal concentrations
4. Analysis of sediment cores to determine the age of contaminant inputs. Sediments can be dated using the presence of a PCB maximum as a 1975 marker. This approach was chosen because it is much more cost effective than isotopic analysis.

B. Organic Contaminants

Given the elevated concentrations of organic contaminants in the sediments sampled we recommend that the PAH and PCB analyses be completed for the remaining 75% of Kearny Marsh. A comparison of current levels of sediment organic contaminants with the storm and ground water PAH and PCB loadings will help to determine if the sediment contaminants are historical or ongoing inputs.

II. Sediment Characteristics

Based on the TOC analysis and particle size distribution for the sediments sampled, we recommend the following studies that relate the sediment characterization to bioavailability and risk assessment of both metals and organic pollutants:

1. In conjunction with the additional sediment sampling, collect water samples within the same grid cell and analyze water concentrations of dissolved organic carbon (DOC), heavy metals and organic pollutants.
2. To determine the impact of sediment re-suspension after disturbance analyze suspended particulate matter (SPM) before and after a mechanical perturbation at contaminant "hot spots" within the marsh, and characterize these SPM samples for heavy metals, organic concentrations, TOC and POM contents.
3. Quantify bioavailable vs. sequestered fractions of the heavy metals by performing systematic analysis on metal speciation for both SPM and sediment samples.

III. Microbial Processes

Enrichment cultures established with sediment from Grids 1,7,9,10,16 and from the Keegan Landfill have now exhibited the potential to dechlorinate a model PCB contaminant within 100 days without the addition of a new carbon source. Microbial biotransformation of sediment organic contaminants is well documented (for review see Bedard 2003, Gruden et al., 2003, Widdel & Rabus 2001). The presence of elevated levels of organic contaminants in Kearny Marsh sediments suggests the probability of microbial biotransformations, which may result in the production of more or less toxic metabolites. Our labs at Rutgers have previously enriched Kearny Marsh sediments and observed a number of different microbial transformation processes such as debromination (Ravit unpublished data), selenium reduction (Narasingarao unpublished data), and organophosphate breakdown (Häggblom personal communication). It is quite probable that native microorganisms in this system have evolved specific metabolic pathways in response to the elevated levels and types of sediment contaminants. Utilization of these *in situ* organisms may provide a natural means to both (bio)transform the organic contaminants.

Based on the high amount of organic matter (up to 80% in certain locations) present in the Kearny Marsh sediments there exists a high potential for microbial gas production as a result of anaerobic breakdown of organic material. Microbial production of insoluble gaseous products such as hydrogen, hydrogen sulfide, methane and carbon dioxide results in the coalescence of gas bubbles in the sediments, and these bubbles are eventually released into the water column. Gas production by natural processes can potentially affect the stability of engineered sediment caps. When a capping material covers sediments, the release of gas bubbles is impeded until enough pressure builds up to overcome the resistance of the cap. The pressure generated can potentially cause a breech, releasing gas as a "burp" into the overlying water column. This "burping" has the potential to carry contaminated sediment and pore water up through the cap. The natural gas production may be significant in Kearny Marsh sediments because of their high organic matter content. We propose the following studies to determine the effect of microbial processes in Kearny Marsh that may affect cap performance:

1. Field monitoring of gas production from sediments and assessment of water quality in the water column overlying the current field test plots of AquaBlok capping material
2. Analysis of sediment cores to determine dimensions and properties of the highly organic peat layer
3. Microcosm studies to determine whether the heavy metal concentrations in Kearny Marsh sediments have the potential to inhibit microbial processes including beneficial biotransformation as well as methane production

Combining these natural bioprocesses with sediment capping technology to contain pollutants may provide a unique technology for dealing with Kearny Marsh sediment contaminants. To fund the extensive bench top and mesocosm studies required to develop such a technology Rutgers University, the NJMC, Hull & Associates, and AquaBlok, Ltd.

have jointly applied for funding ($274,384) from the NOAA sponsored Cooperative Coastal Estuarine Environmental Technology (CICEET) program. This funding will support two Ph.D. graduate researchers (an engineer and a microbiologist) who will study the feasibility of combining AquaBlok capping technology with stimulation of desirable microbial processes for their thesis research. A decision regarding this pre-proposal funding application will be available on December 22, 2005.

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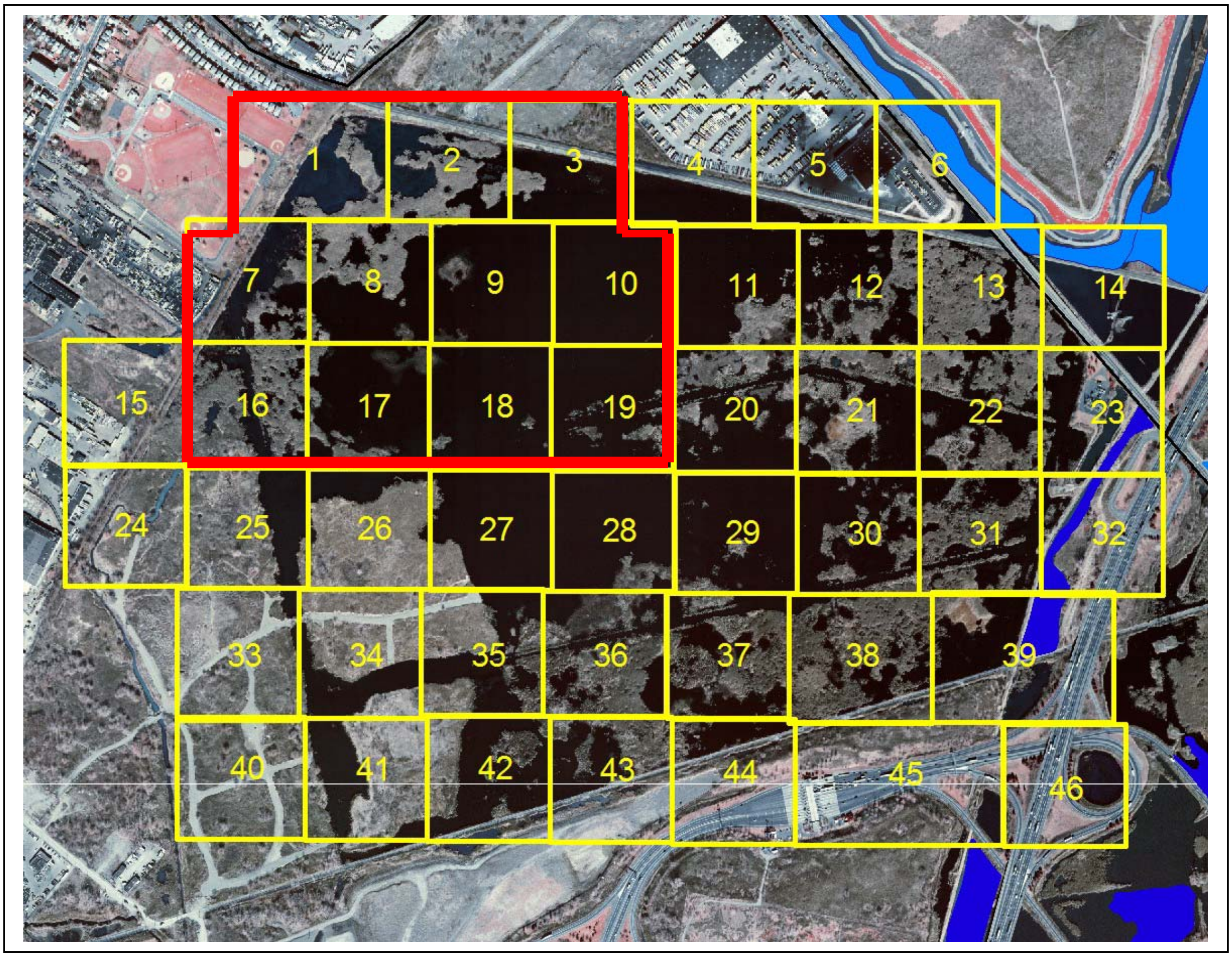
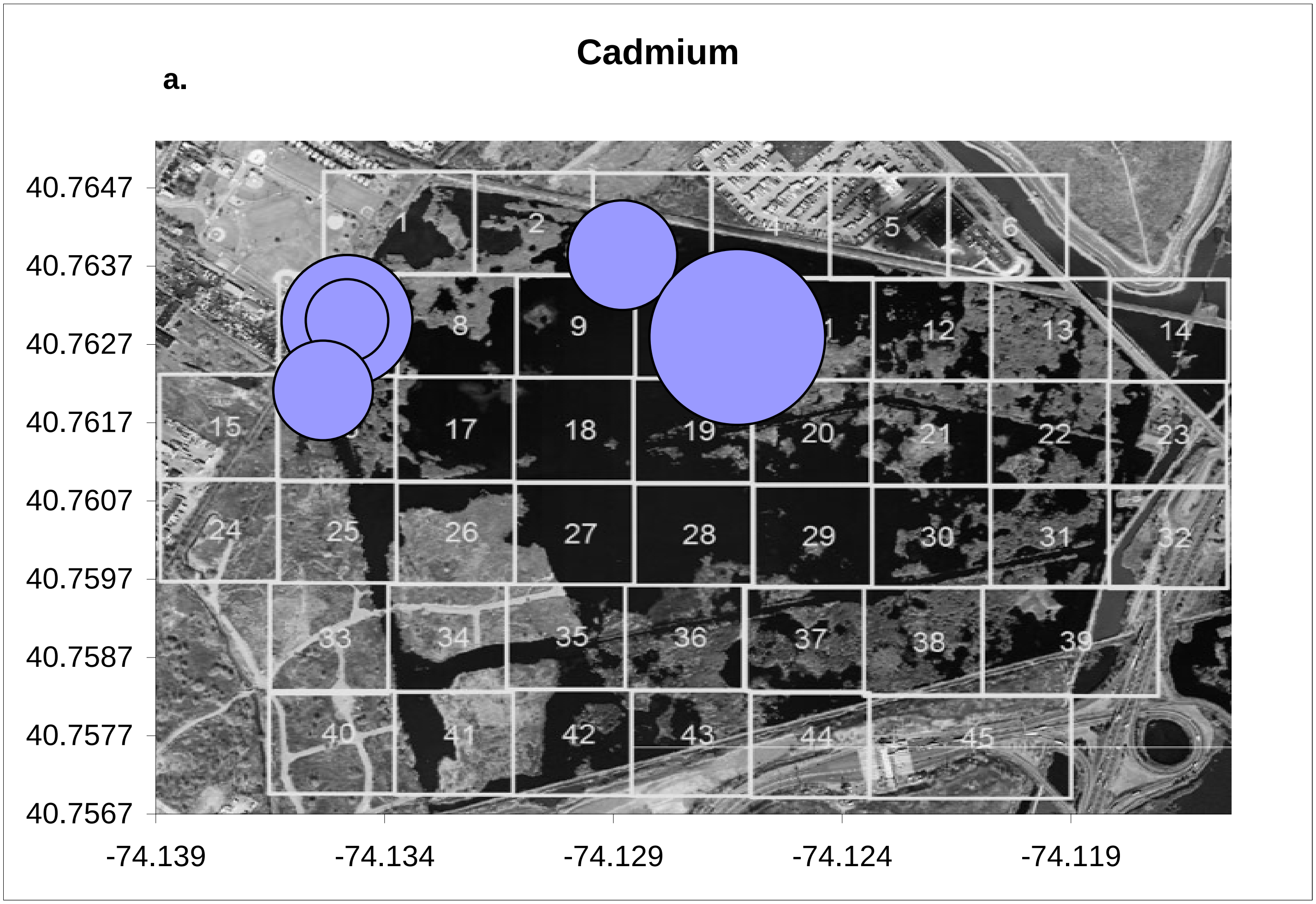
Appendix I – Maps

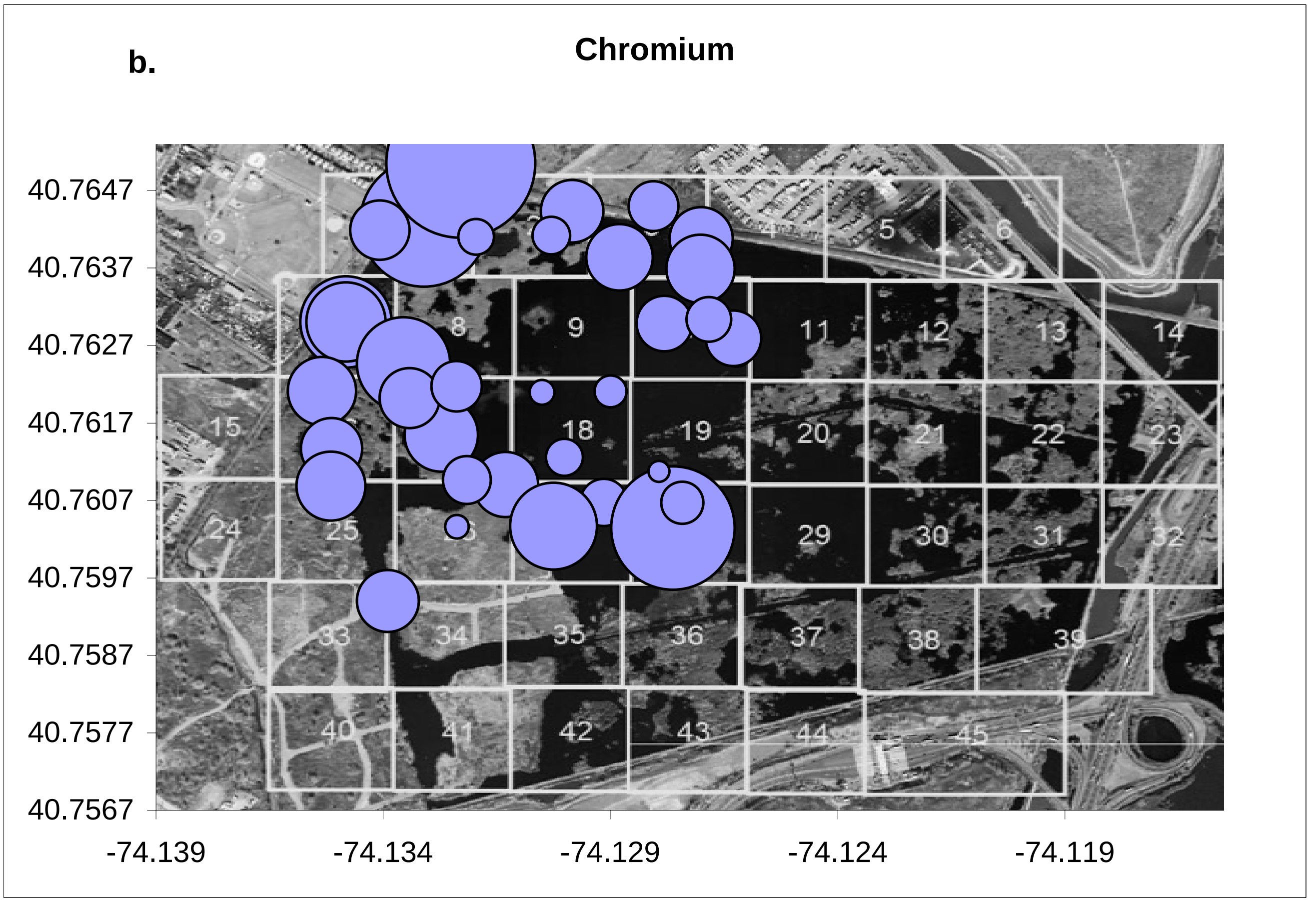
Kearny Marsh grid system map. Section outlined in red was sampled in May 2005. Five samples were taken within each quadrant and GPS points noted for each sampling location.



Appendix II – Figures

Figure 1. Heavy metal concentrations in sediments obtained from the northwestern section of Kearny Marsh (Grid cells 1-3, 7-10, 16-19. See Map, Appendix I). The size of the bubble represents concentration in PPM (mg/kg). Circle within a circle represents multiple samples in a given quadrant.

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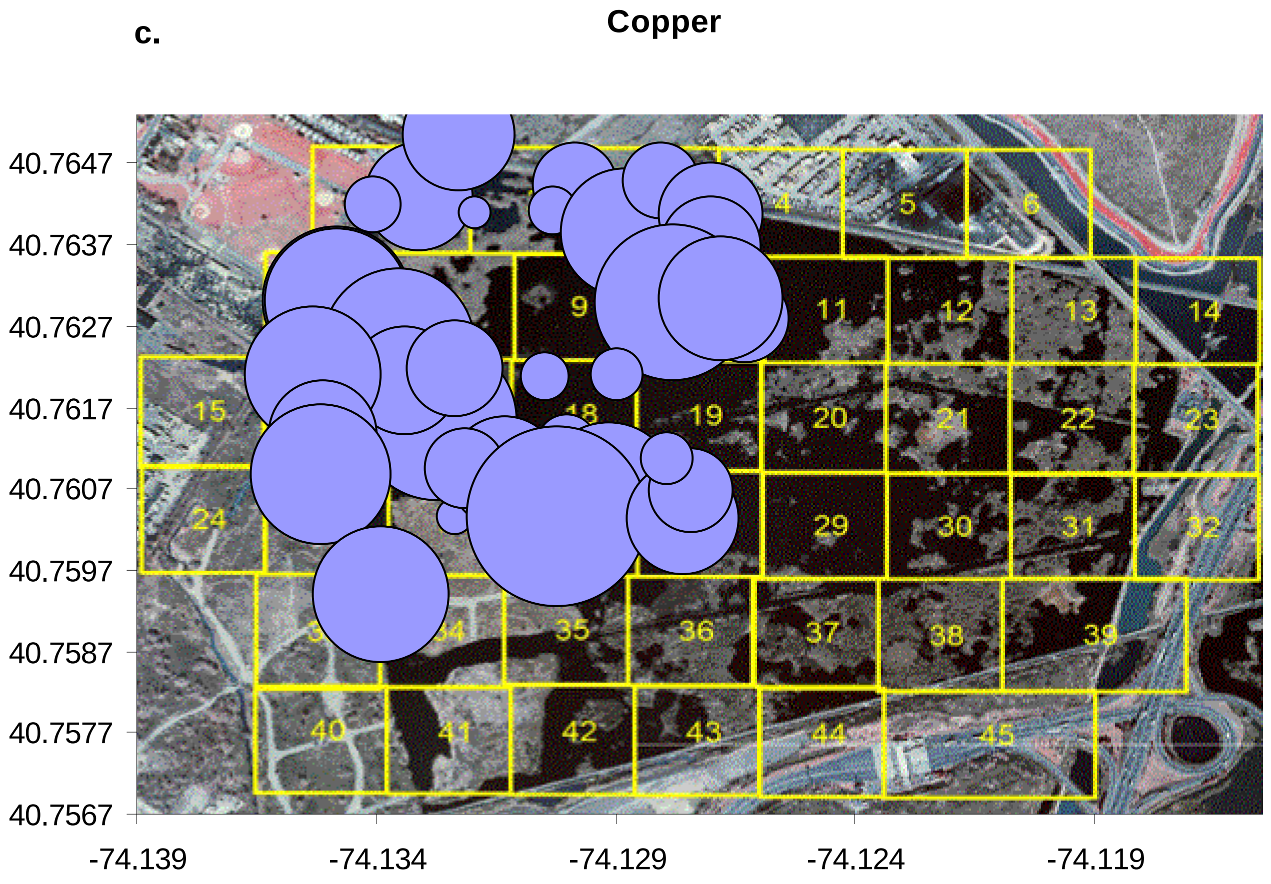
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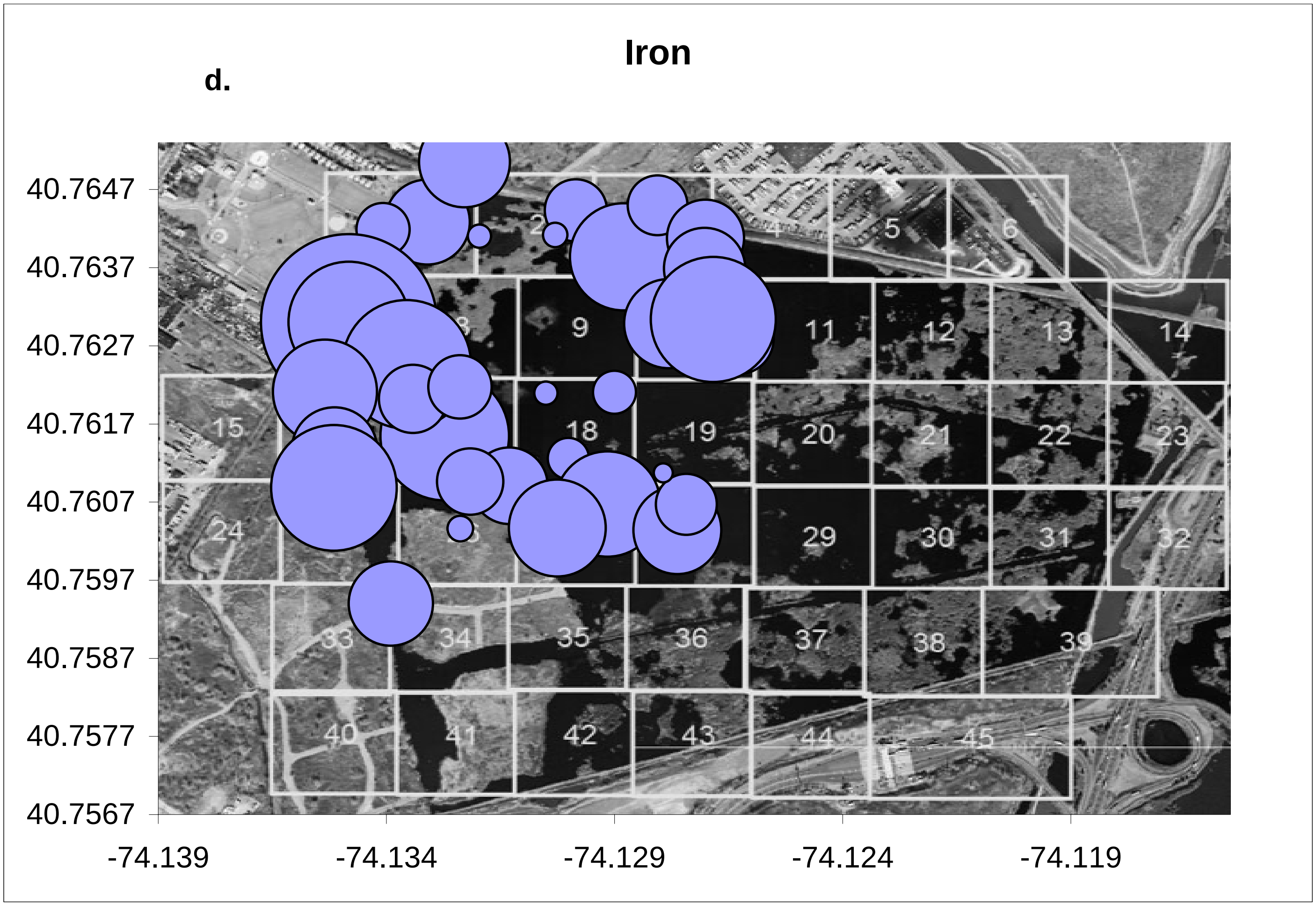
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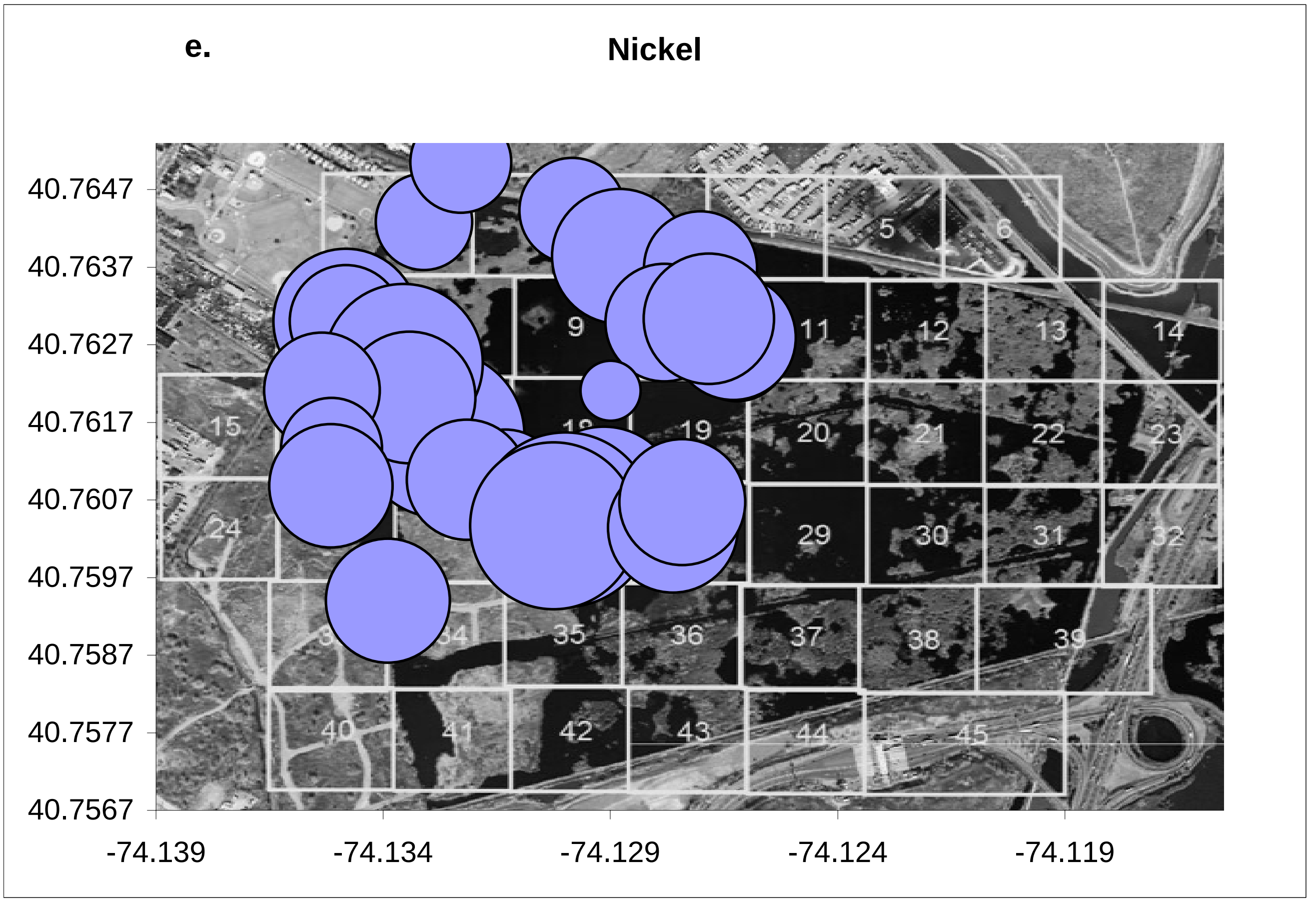
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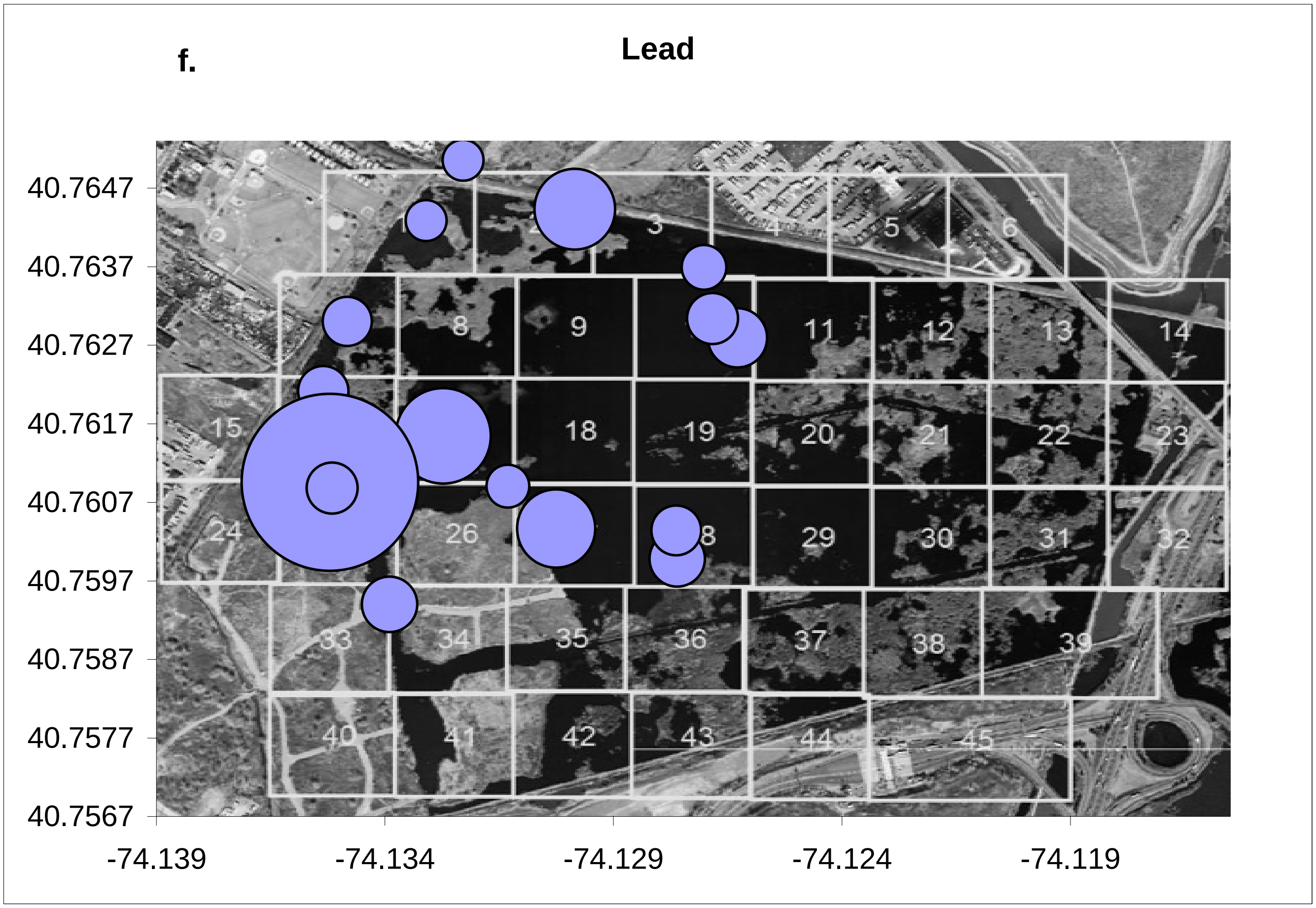
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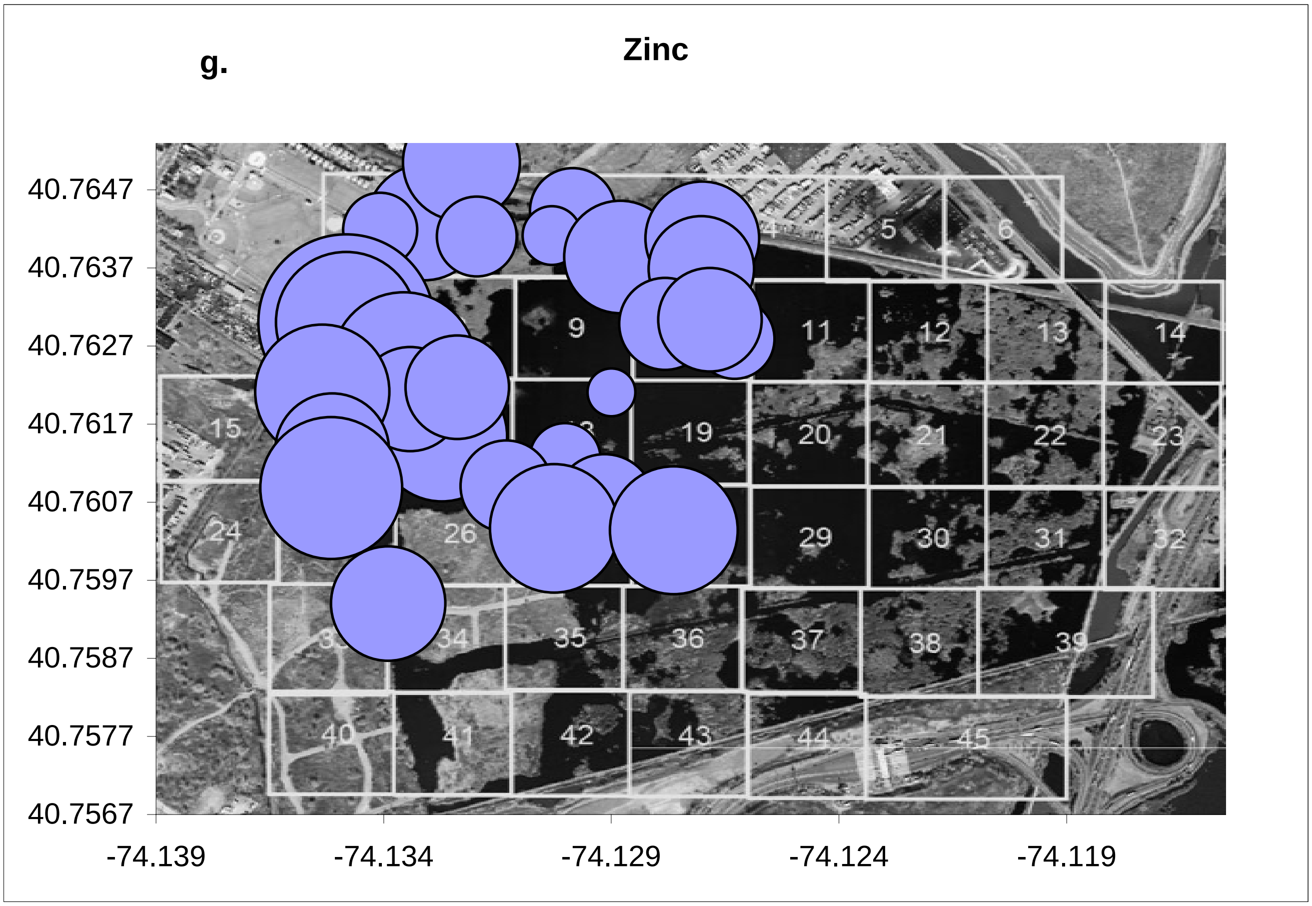
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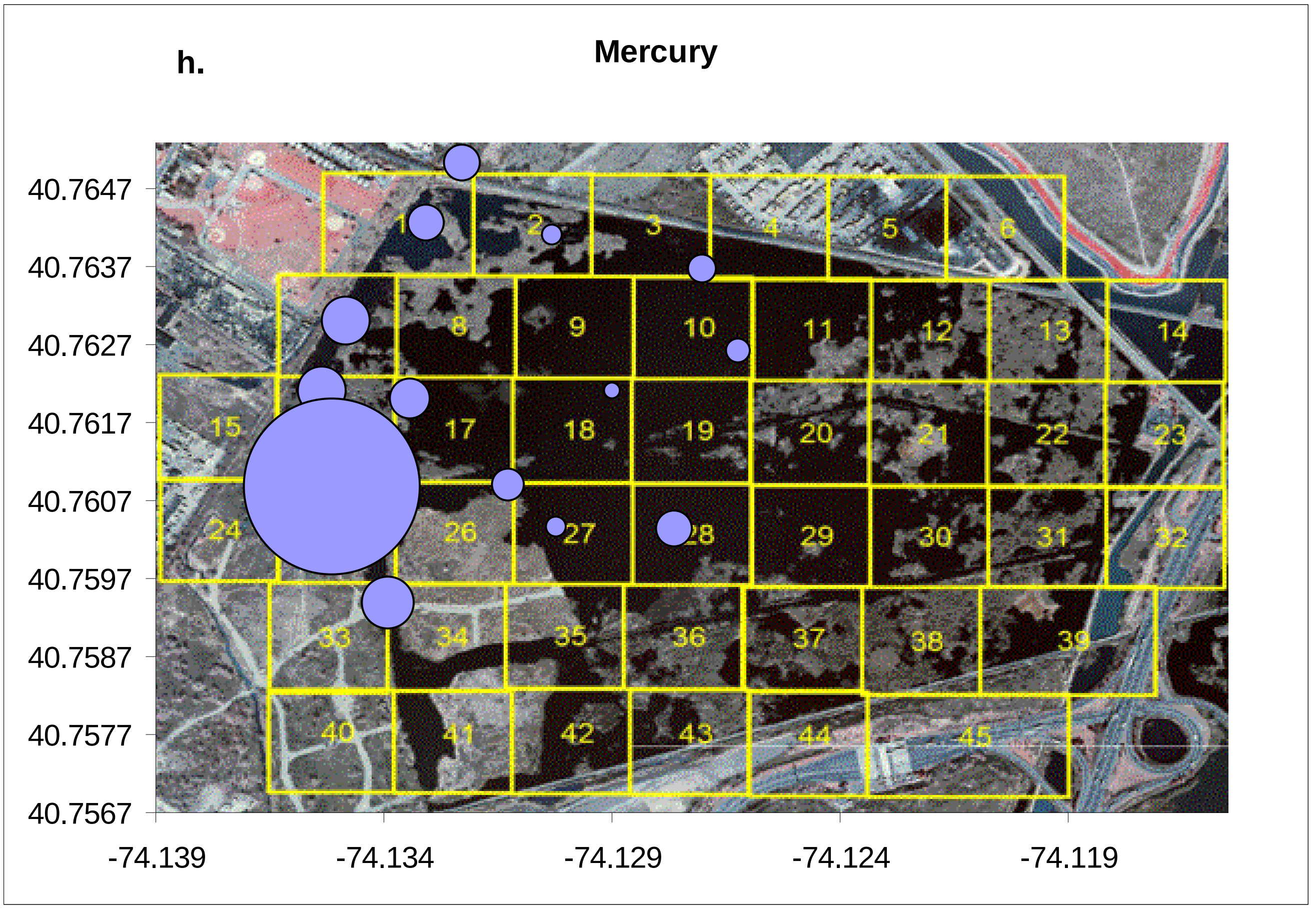
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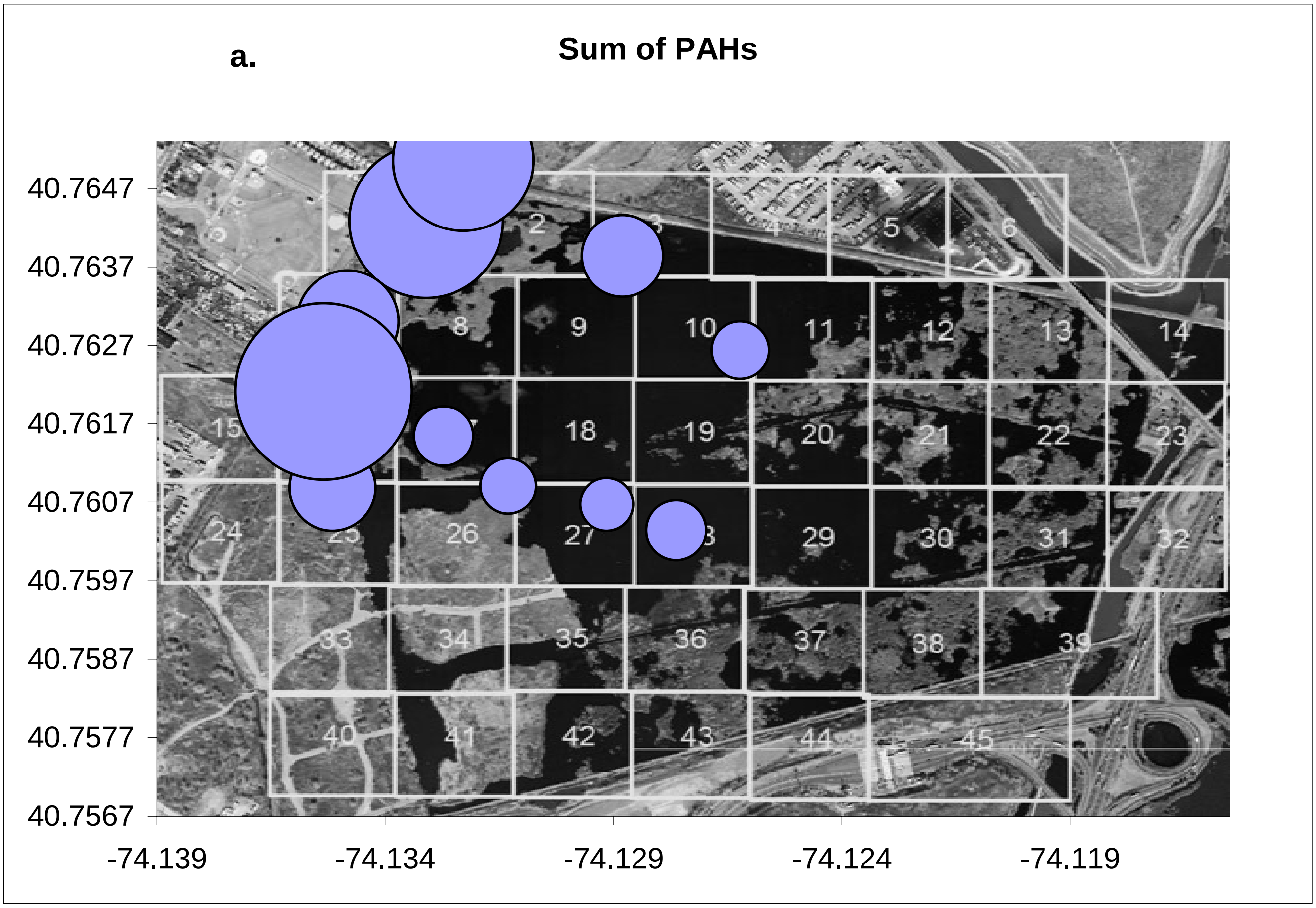
Figure 2. Sum of PAHs and PCBs present in sediments sampled from Kearny Marsh (Grid Cells 1-3, 7-10, 16-19. See Map, Appendix I). The size of the bubble represents concentrations in PPB (μg/kg).



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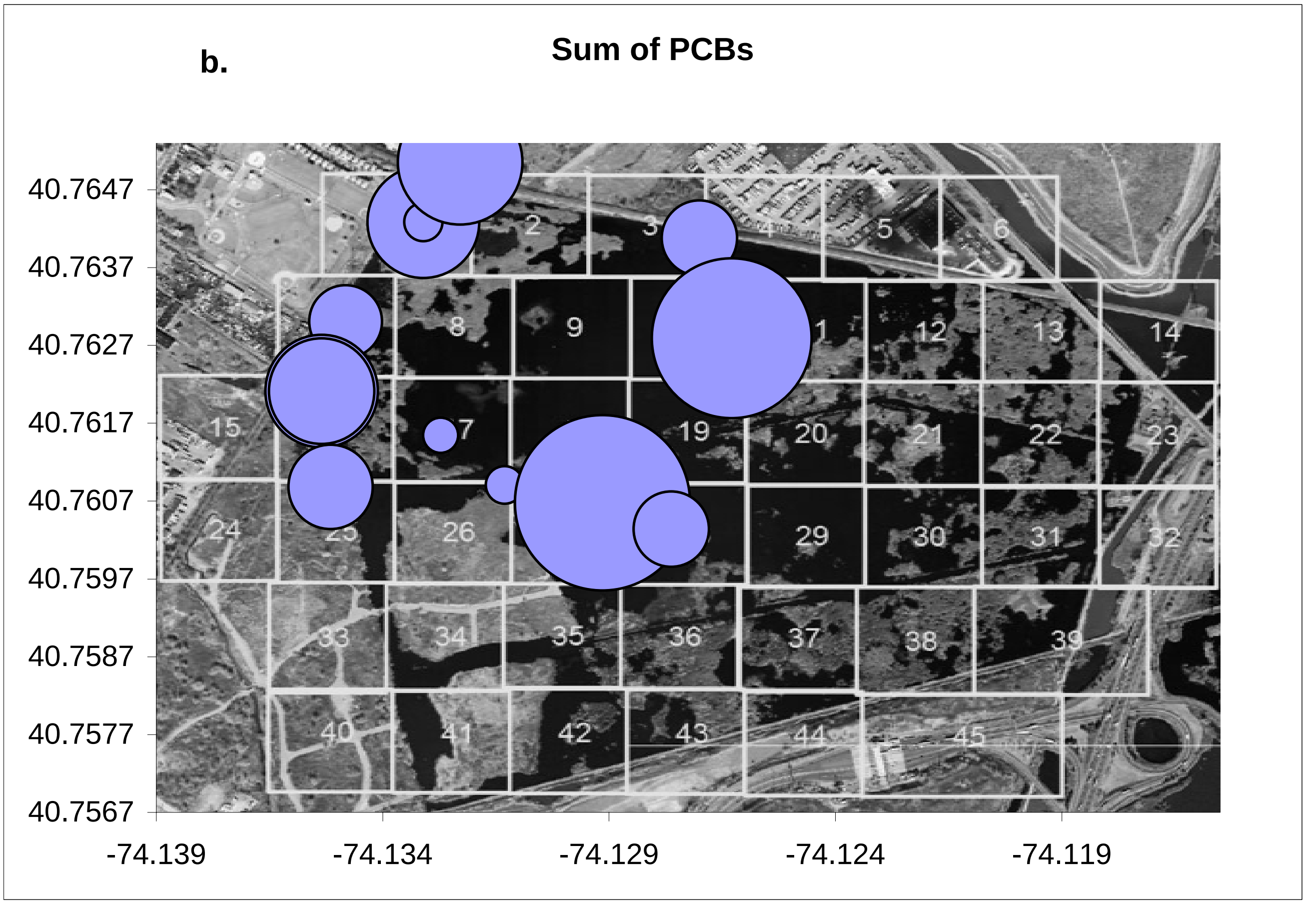
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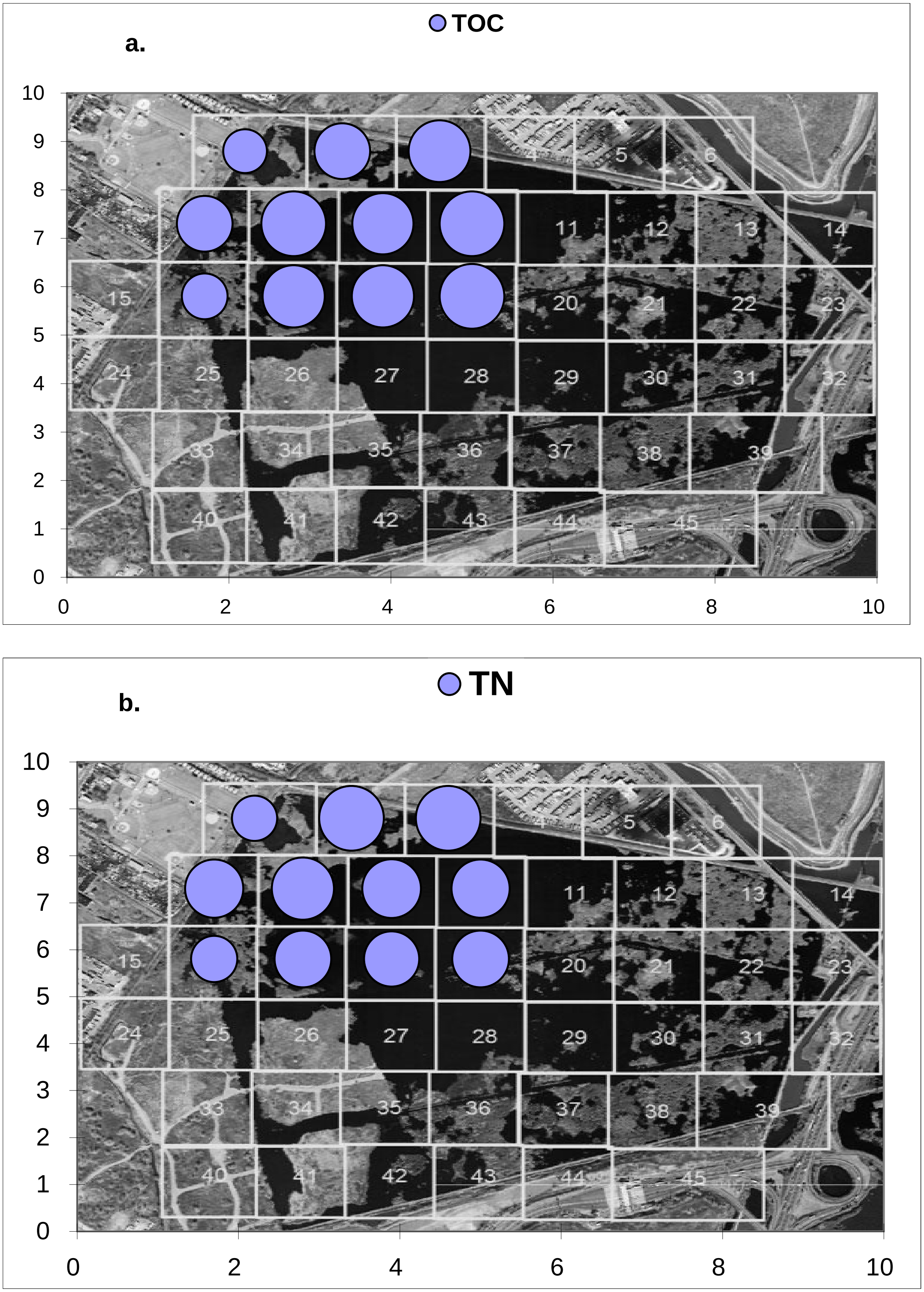
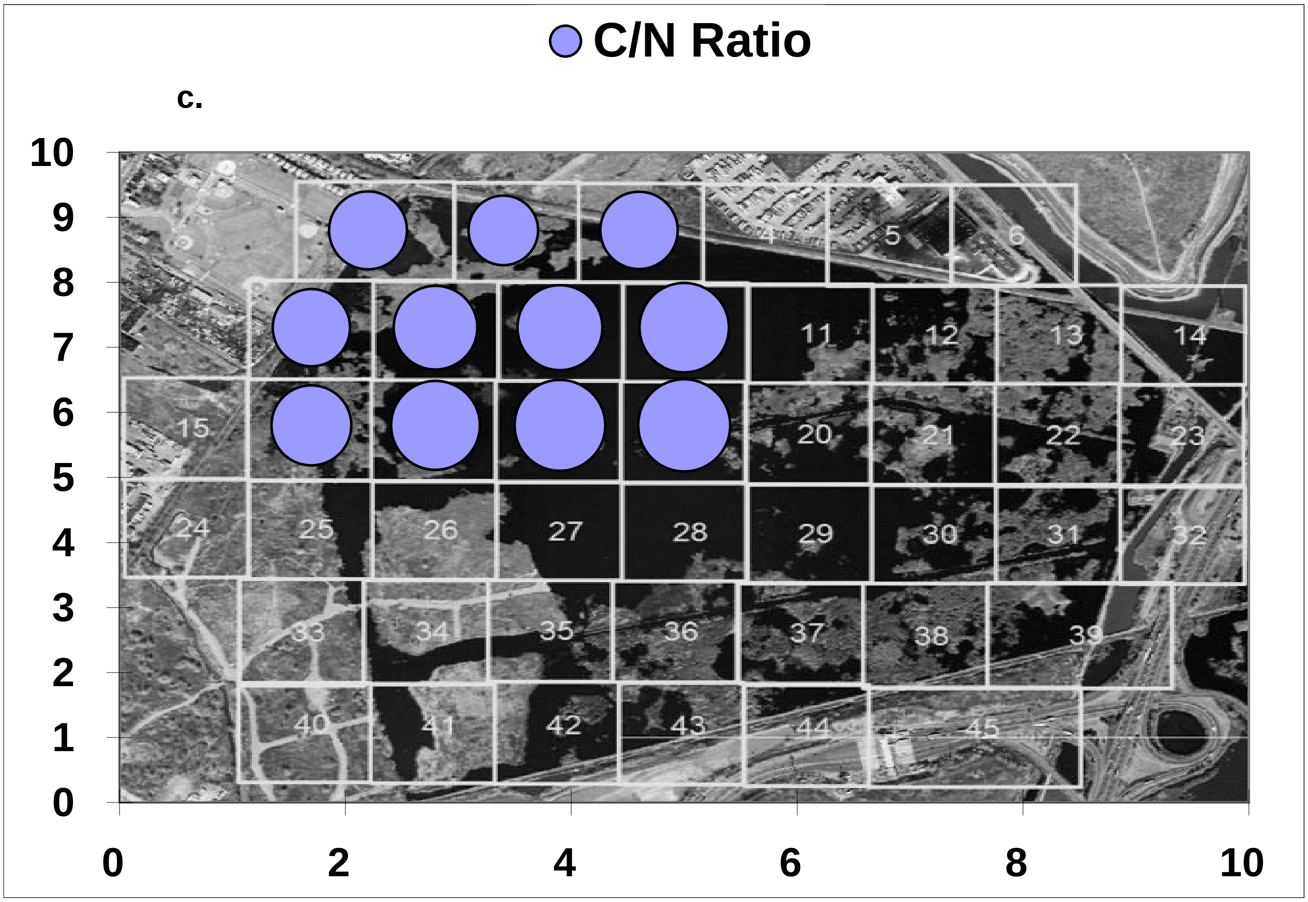
Figure 3. The proportion of A) sediment total organic carbon (TOC), B) total nitrogen (TN), and C) the carbon to nitrogen ratio in Kearny Marsh sediments (Grid Cells 1-3, 7-10, 16-19. See Map, Appendix I).





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