Final Report

for:

Assess the Potential for Accumulation of Toxic Trace Elements in Biota near Burton Island Ash Disposal Site Indian River Bay, Delaware

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Executive Summary

This study was initiated by the Center for the Inland Bays (CIB) to document whether material eroding or transported from the ash disposal site at Burton Island, into the adjacent waterways, was potentially exposing the aquatic biota of Island Creek to toxic trace elements that could cause ecologically detrimental effects. Sediments and organisms (Mummichogs {*Fundulus heteroclitus}* and Ribbed Mussels {*Geukensia demissa}*) were collected at five marsh sites adjacent to the ash disposal site on Island Creek and five sites were selected on Pepper Creek, as geographically distinct reference sites. The sediment and organism composite samples were then analyzed for a suite of potentially toxic trace elements, which included As, Cd, Cu, Cr, Hg, Ni, Pb, Se, Tl and Zn. The results of the analyses, for most of the elements, suggested no difference in concentration between the two sites. For *Fundulus*, only one element, Se, had a highly significant difference between the two sites at the 1% or $p \leq 0.01$ level. For *Geukensia*, As had a significant difference between the two sites at the 5% or $p \leq 0.05$ level; while Ni, and Cu are nominally different at the 5% level, and there was highly significantly different between the two sites at the 1% or $p \leq 0.01$ level for Se. These results suggest that the Island Creek organism samples are somewhat enriched in elements of concern, (i.e. As and Se) as compared to the nearby control site, Pepper Creek. The concentrations of the trace elements in the sediment samples from Island and Pepper Creeks are similar to other collected throughout Delaware. The Island Creek sediment samples contain a higher mean concentration of Al, As, Cr, Cu, Fe, Ni, and Se, but as in most cases, the standard deviations of the distributions overlapped. This suggests that the concentrations of trace metals in these creeks could be elevated relative to Pepper Creek, but still be representative of concentrations around the region.

A key question or concern associated with these analytical results were what effects the concentration levels of particular elements have upon the aquatic biota of the Burton Island region. Further review and assessment was done by Delaware Department of Natural Resource and Environmental Control (DNREC) to aid in addressing these concerns. In short, this assessment suggested that concentrations of Se in *Geukensia* and *Fundulus* are well below the ecological risk thresholds for Se exposure. The DNREC review stated, "It is concluded that the selenium concentrations in the mummichogs from Burton Island are within the expected range of background levels. More importantly, the concentrations in the mummichogs and ribbed mussels are well below a concentration expected to cause reproductive effects in these species (Appendix A)."

These existing conditions and concentration levels of trace elements found in the *Geukensia*, *Fundulus,* and sediment samples currently do not warrant an expansion of sampling to evaluate the potential ecological impacts of bioaccumulation. The future conditions of the island could change due to rising water levels and/or changes in the rate of pore water movement, because of this, it is recommended that tissue and sediment samples be periodically sampled and analyzed (in methods consistent with this study) to evaluate any changes in the prevalence and concentration of trace elements and metals through bioaccumulation in the surrounding biota.

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A1 - INTRODUCTION/BACKGROUND

The purpose of this project was to document whether material (either sediment, ash, and/or trace toxins) eroding off and/or transported from the ash disposal site at Burton Island into the Indian River and Island Creek, are contributing to significant accumulation of toxic trace elements in nearby marshes and biota. Sediments and organisms (Mummichogs {*Fundulus heteroclitus}* and Ribbed Mussels {*Geukensia demissa}*) were collected at five marsh sites adjacent to the ash disposal site on Island Creek to the South, where previous sampling has illustrated that ash or its constituent contaminates have been transported (in surficial and /or groundwater) or have been deposited due to erosion into the Indian River (Shaw, 2008) Five reference sites were selected on Pepper Creek, geographically distinct but similar to the ash disposal sites to serve as controls.

Delmarva Power & Light purchased Burton Island in 1949 for the construction of the Indian River Generating Station. Burton Island encompasses approximately 214.86 acres, of which approximately 144.23 acres represent then former ash management area, while the remaining 70.63 acres represent the active power generation station. In the early 1950's, the eastern end of Burton Island was utilized by the Army Corps of Engineers for disposal of spoils dredged from the Indian River between the Millsboro Dam and the Indian River Inlet. Delmarva Power & Light began using the area for ash disposal when the first coal fired power generating unit was placed in operation in 1957 (Shaw, 2008).

Fly ash and bottom ash were sluiced to the portion of the island just beyond the power plant. Bottom ash was later removed and used to build roadways on the island. Fly ash was used to construct a perimeter berm system. Berms were constructed at a height of approximately 20 feet, consisting of approximately a 4 foot base of soil, 14 feet of fly ash, and a 2 foot cap of bottom ash. By the mid 1960's the system of berms and access roadways was completed on the eastern end of the island. Fly ash was sluiced to the island through a 12" pipe. The pipe was moved between the north side of the center access road and the south side approximately every two years to distribute the fly ash to the various cells. Water decanted from the fly ash flowed into a settling pond near the tip of the island and eventually discharged to Island Creek (to the south). Fly ash generated during power generation activities was deposited / landfilled in this manner on Burton Island for a time period from approximately 1957 to 1979 (Shaw, 2008).The disposal resulted in the elevation of the ground surface by about 15± feet over most of the island, and the wholesale conversion of tidal marshes and flats to upland (Decowsky, 2010).

With the start-up of Unit 4 in 1980, a new ash landfill was constructed and permitted to the south and across Island Creek from the old ash landfill. Since that time, all ash generated at the facility has been deposited in the new ash landfill (Shaw, 2008).

In 2005, a Delaware Department of Natural Resources and Environmental Control (DNREC) scientist observed erosion of the ash berms (at the upland/intertidal interface) into the surrounding waterways (Island Creek and Indian River). The site was then referred to DNREC's Site Investigation and Restoration Branch (SIRB), which started an investigation. Initial soil and shoreline sampling revealed levels of metals exceeding DNREC standards. NRG and DNREC negotiated a Voluntary Cleanup Program agreement for the investigation of the site, which is still underway (Decowsky, 2010).

This study was undertaken to assess any potential effect of bioaccumulation of trace metals and elements from ash that had previously eroded into Island Creek and Indian River or by elements transported from off the landfill through groundwater. Concerns about the impact of the landfill on the biota of the Indian River and Indian River Bay bays were voiced by residents of the Inland Bays Watershed through editorials in several newspapers and the CIB's Citizens Advisory Committee (CAC) and the Scientific and Technical and Advisory Council (STAC) meetings. These concerns fostered the CIB to initiate this study, in conjunction with the Smithsonian, to collect and analysis data that could be used to inform the Voluntary Clean-up Process (VCP) and the Natural Resources Damage Assessment (NRDA) for the Burton Island remediation.

A2 - PROJECT DESCRIPTION

Four specific objectives were developed for this project, which included:

1. Obtaining 5 surface sediment samples, and composites samples of *Fundulus heteroclitus* and *Geukensia demissa* from marsh adjacent to Burton Island ash disposal site, along Island Creek.
2. Obtaining 5 surface sediment samples, and composite samples of *Fundulus heteroclitus* and *Geukensia demissa* from marshes along Pepper Creek, which is also on Indian River Bay, but remote from Burton Island ash disposal site, thus limiting exposure to any potential toxins at Burton Island. These sites will serve as the project control.
3. Analysis of the sediment, and organism composite samples for a suite of potentially toxic trace elements, including As, Cd, Cu, Cr, Hg, Ni, Pb, Se, Tl and Zn.
4. Documenting differences between the contaminants in sediment samples and organisms samples taken from ash disposal sites and the control sites.

B1 - SAMPLING PLAN AND LOCATIONS

Surface sediments grab samples and the organism composite samples were collected on the surface of the marsh fringing the Burton Island ash disposal site, in areas where samples were previously collected in the development of the facilities evaluation report (Figure 1) and also in areas where higher erosion rates have resulted in ash deposits from the uplands having been observed eroding into Indian River and Inland Creek (Figure 2). The surface sediment grab samples and organism's composite samples were co-located for their collection. The actual locations of the sites were determined by the presence of and ability to collect the target organisms (Figure 3, 4 and 5). Five sites remote from Burton Island, along Pepper Creek were also chosen to be the project reference locations. Pepper Creek was chosen for the reference locations because Island Creek and Pepper Creek have similar salinities and overall environmental regimes (Figure 6). Any prospective exposure of pollutants along Pepper Creek likely resulted from contaminant sources other than Burton Island ash disposal site and will be representative of the background conditions of the Western Indian River Bay system.

Sediment samples were collected in the field; with all means necessary to not cross contaminate samples during the process of collection. Approximately 200 grams of sediment, from a homogenized surface sample (0-5 cm) was collected in a whirl pack bag, with the air excluded, and frozen on dry ice for storage and shipping. The sediment samples were collected using a petite ponar, and then the samples were placed in a plastic sample bin where it was homogenized

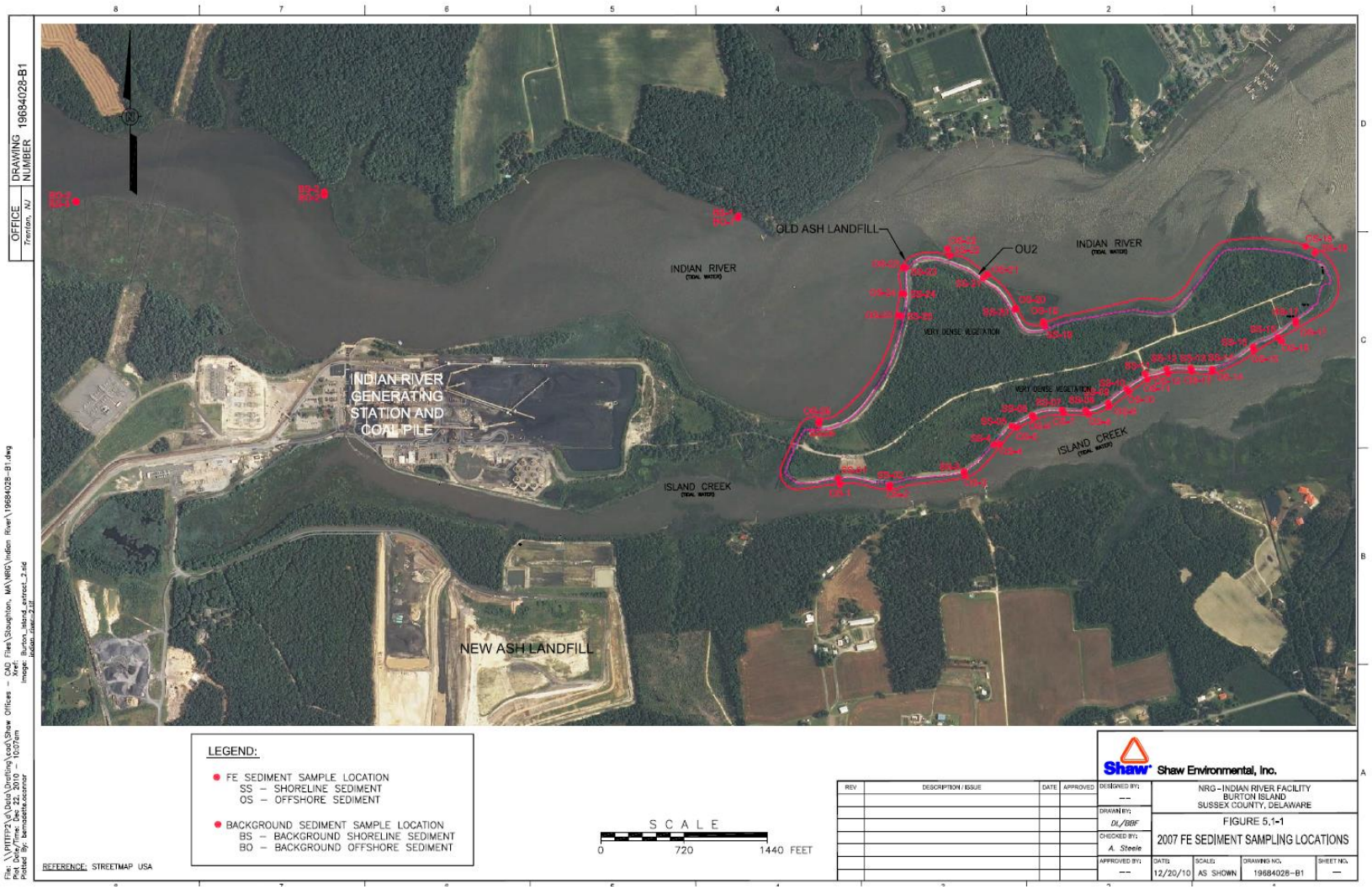

Figure 1. Map showing the intertidal and subtidal sampling locations collected during the VCP site investigation (Shaw 2011).

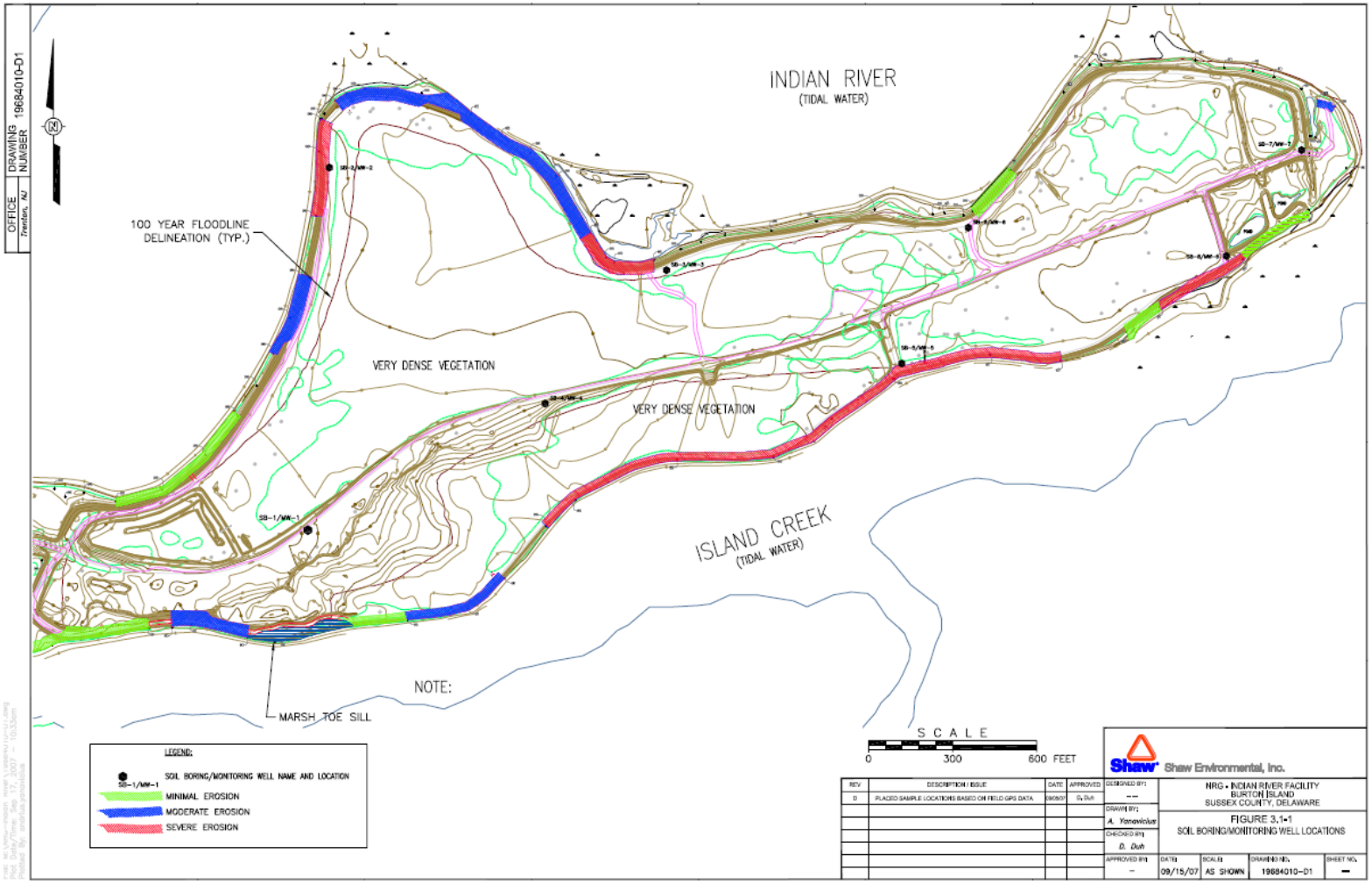

Figure 2. Map showing the qualitative extent of shoreline erosion around Burton Island(Shaw 2011).

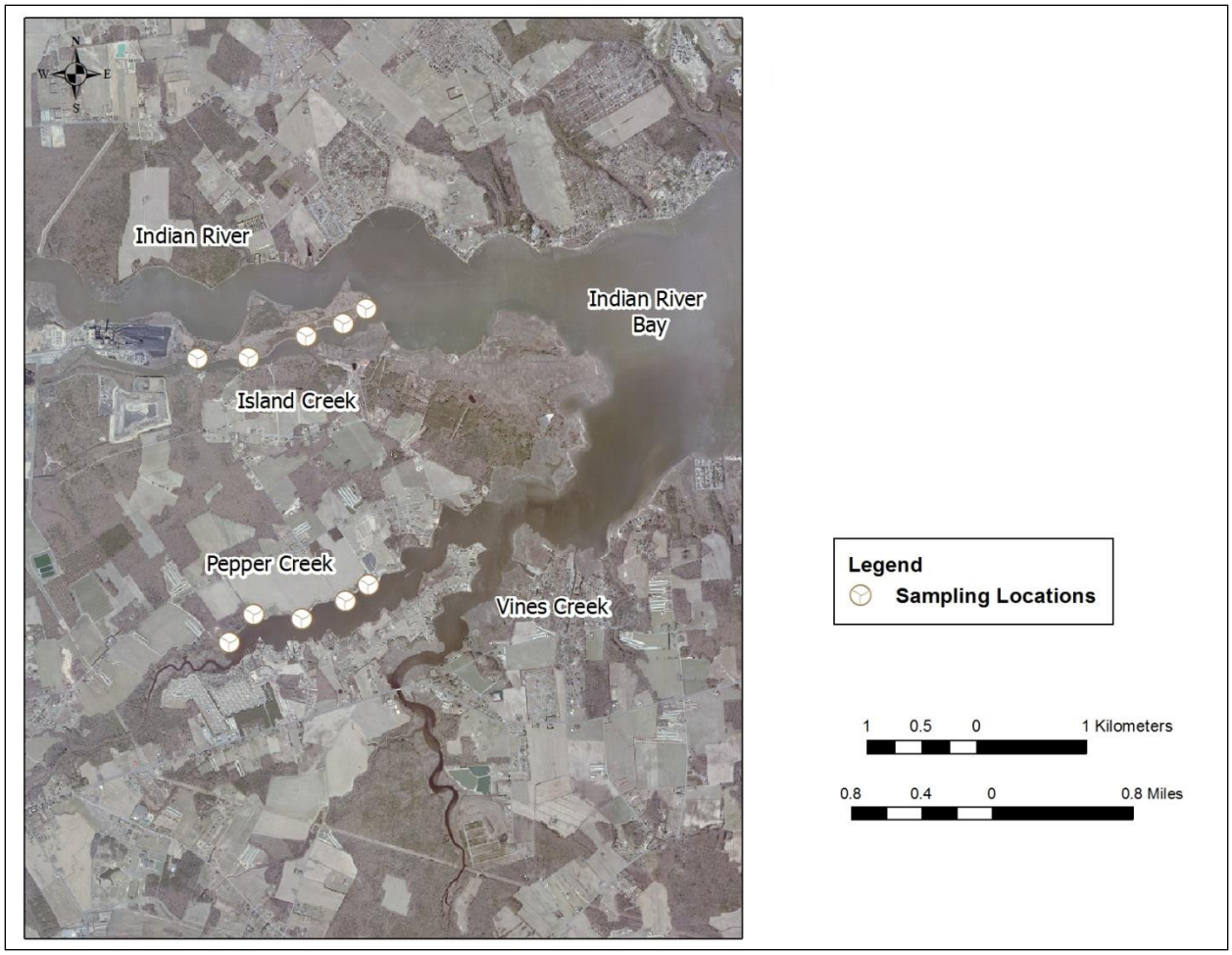

Figure 3. The five sampling locations along Island Creek, adjacent to Burton Island and the five sampling locations on Pepper Creek, remote from Burton Island.

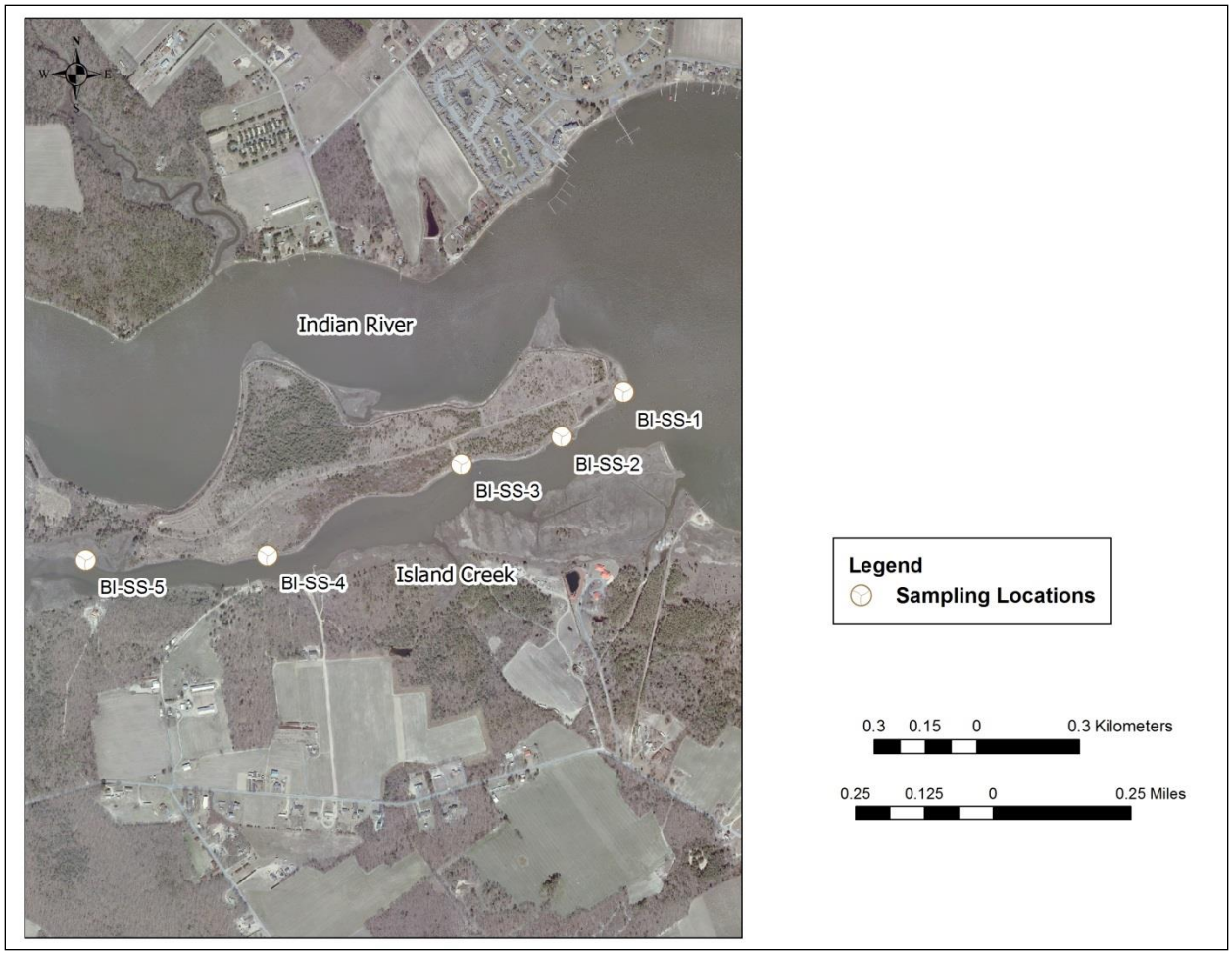

Figure 4. The five sampling locations along Island Creek, adjacent to Burton Island.

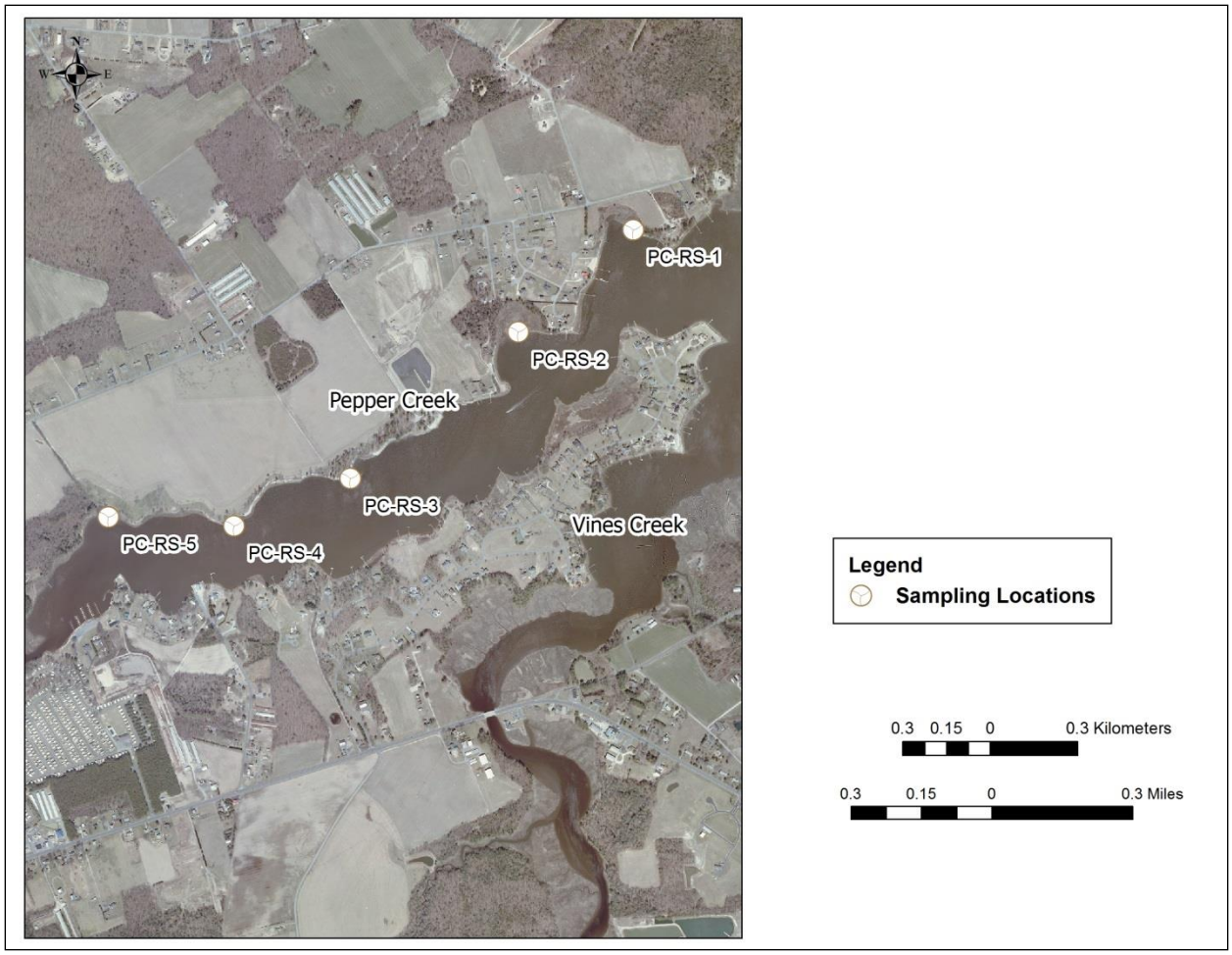

Figure 5. The five sampling locations along Pepper Creek, the control sites for the project which are remote from Burton Island.

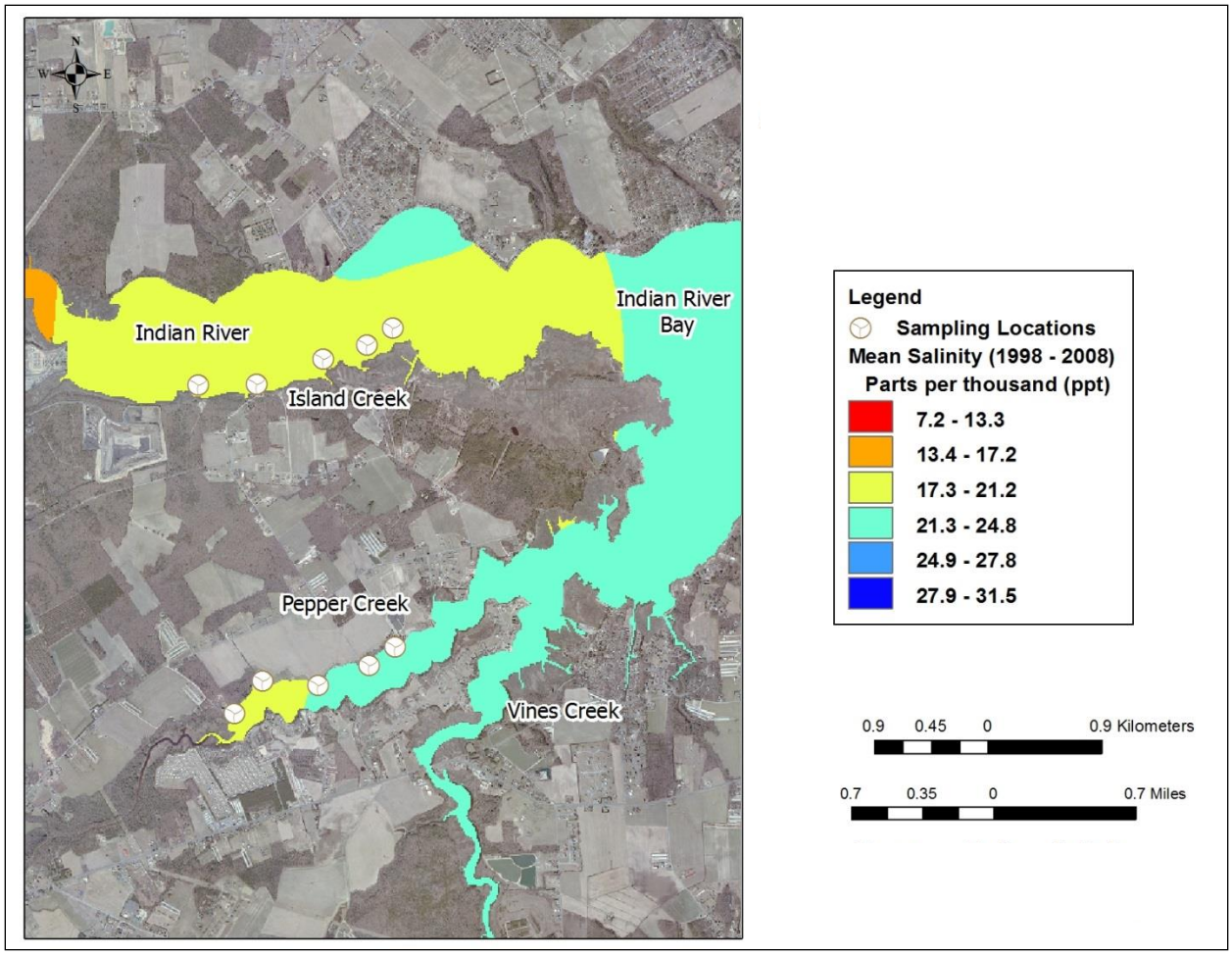

Figure 6. Distribution of sampling locations along Island Creek and Pepper Creek, in relation to the long-term mean salinity (1998 to 2008) of the Western Indian River Bay.

and sub-sampled using a sterile plastic scoopula. The plastic scoopula was discarded after each sample, and a new sterile sampler used for each site. The petite ponar and sampling bins were washed using deionized water and phosphorus free detergent, after each sample collection, and then dried with sterile KimWipes®. All personnel wore latex gloves during all stages of sample collection and processing. Gloves were changed before all sampling equipment was cleaned, and then before the subsequent sample was collected.

For all *Fundulus heteroclitus and Geukensia demissa* samples, 5 organisms were collected at each site to create composite samples for each organism, to reduce variance in the analysis between sites. The length of the *Fundulus* individuals for each sample were kept to a range of 70 mm to 100 mm (total length).The length of the *Geukensia* collected for the composite samples were kept to a range in lengths of 80 mm to 120 mm. *Fundulus* were collected by a cast and/or dip net, rinsed with deionized water, placed in a whirl-pak bag, and frozen using dry ice for storage and shipping. *Geukensia* were collected by hand, scrubbed with a plastic brush to remove loose detritus, rinsed with deionized water, placed in a whirl pak bag, and frozen using dry ice for storage and shipping. Sediment and composite organism samples were hand delivered to the Smithsonian Environmental Research Center (SERC) lab, frozen with dry ice, by Delaware Center for the Inland Bays Science Coordinator. Plastic gloves were worn during the sediment and organism sampling to prevent cross contamination. The sediment and composite organism samples were collected on October 12th and 15th, 2012 and kept frozen with dry ice until they were transported to the SERC lab, on October 16th, 2012.

B2 - SAMPLE PREPARATION IN THE LABORATORY

Sediment samples for contaminant analysis were thawed, thoroughly stirred to homogenize the sample and sub-sampled for analyses. One sample, approximately 10 g, was weighed into an aluminum weigh boat, dried to constant weight at 60 C, reweighed, ashed at 450 C in a muffle furnace, cooled and reweighed. From these weights we determined the Wet to Dry Weight Ratio, the Wet Bulk Density, the Dry Bulk Density, and the Loss on Ignition (LOI, a measurement of organic carbon content) (See SOPs). A second aliquot, approximately 1 g wet weight, was wet digested in a Perkin Elmer Multiwave microwave digester, using HCl, HNO_3 and HF, for a total digestion of the sediment. Samples were diluted to 50 ml with deionized water, and analyzed for all the trace elements except Hg. The third sample, approximately 5 g, was wet digested with HNO_3/H_2SO_4 on an open flask digest for Hg analysis.

The composite samples for tissue were thawed. *Geukensia* were shucked using a stainless steel oyster knife. Organisms were rinsed with deionized water and blotted dry with paper towels. Composite samples were homogenized with a tissue grinder, and samples collected for wet weight/dry weight, trace metal digestion by microwave digest using HCL, HNO_3 and H_2O_2 for all elements but Hg, using approximately 0.2 g dry weight of sample. Separate samples for Hg, approximately 5 g wet weight, were digested using the HNO_3/H_2SO_4 open flask digest above.

B3 - SAMPLE ANALYSIS

Sediment and tissue samples were analyzed for Al, Ba, Ca, Fe, K, Mg, Mn, Na, S, Si, Sr, at SERC, by Inductively Coupled Plasma-Optical Emission Spectrophotometry (ICP-OES) using the SERC's Perkin Elmer Optima 8300 ICP-OES (Martin et al, 1991).

Cd, Cr, Cu, As, Ni, Pb, Tl, and Zn were analyzed at SERC by Inductively Coupled Plasma-Mass Spectrometry using SERC's Perkin Elmer SCIEX - ELAN 6100 ICP-MS. Cd, Cu, Ni, Pb, Tl, and Zn analysis by ICP-MS were all carried out in standard mode (no Dynamic Reaction Cell, DRC, cell gas, while Cr and Se were analyzed using DRC mode with methane as a reaction cell gas, and As was analyzed by DRC mode, using oxygen as a reaction cell gas. DRC mode is used to reduce polyatomic ions in the plasma which can give positive interferences with certain analytes by ICP-MS (Creed et al, 1994)

Hg was analyzed by cold vapor flow injection ICP-MS using the fast FIAS system with the PE ICP-MS above (Telliard 2005).

C1 - RESULTS

Complete results of the analysis of the organism and sediment samples for trace elements and associated parameters are detailed in Appendix I. Summary results of the analysis of tissues for the lower level (rarer) trace elements, measured by ICP-MS are presented in Table 1.

Table 1. Concentrations (µg/g dry), standard deviations of concentrations, and % relative standard deviation (RSD) for minor trace elements in samples of *Fundulus heteroclitus* and *Geukensia demissa* collected at the Island Creek (IC) and Pepper Creek (PC), and the p-value of the two site comparison using a two-sample t-test.

Fundulus heteroclitus		As	Cd	Cr	Cu	Hg	Ni	Pb	Se	Tl	Zn
IC (n=5)	Mean	3.55	0.013	9.95	22.72	0.10	3.97	2.36	2.38	0.005	184.77
	Std. Dev.	0.79	0.006	9.93	13.80	0.05	2.70	2.02	0.35	0.002	31.82
	% RSD	22	51	1	61	48	68	86	15	34	17
PC (n=5)	Mean	3.14	0.020	9.78	41.36	0.12	3.75	4.42	1.54	0.008	163.92
	Std. Dev.	0.87	0.006	5.29	27.11	0.06	1.48	1.77	0.05	0.004	18.45
	% RSD	28	28	54	0.66	66	39	40	3	49	11
	p (two tailed)	0.46	0.08	0.97	0.21	0.56	0.88	0.12	0.0007**	0.21	0.24
Geukensia demissa											
IC (n=5)	Mean	10.71	0.44	0.84	14.04	0.105	0.75	1.27	2.63	0.005	58.71
	Std. Dev.	1.30	0.15	0.31	5.18	0.026	0.25	0.46	0.29	0.001	6.61
	% RSD	12	34	37	37	25	33	36	11	24	11
PC (n=5)	Mean	8.95	0.40	0.59	9.41	0.070	0.49	1.00	1.99	0.004	58.90
	Std. Dev.	0.53	0.06	0.17	0.56	0.037	0.08	0.27	0.13	0.001	4.75
	% RSD	6	14	29	6	53	16	27	6	28	8
	p (two tailed)	0.02*	0.58	0.15	0.08	0.12	0.06	0.29	0.002**	0.15	0.96

* Denotes significance at the 5% or $p \leq 0.05$ level
** Denotes significance at the 1% or $p \leq 0.01$ level

From these results we can see that the objective of using composite samples to reduce the variability of the samples between subsites was moderately successful; most of the site element combination have % relative standard deviation (RSD) of 50% or less. The relative standard deviation is also known as the coefficient of variance. The RSD measures the precision of the average of your results, with a lower percentage indicates a lower variability in the data set. Equally, a higher percentage indicates the data set is more varied.

For most elements there is no suggestion of a difference in concentration between the two sites. For *Fundulus*, only one element, Se, has a highly significant difference between the two sites at

the 1% or p≤ 0.01 level (Table 1). For *Geukensia,* As has a high level of significant difference between the two sites at the 5% or p≤ 0.05 level, while Ni, and Cu are nominally different at the 5% level (not corrected for multiple comparisons) and again, only Se was highly significantly different between the two sites at the 1% or p≤ 0.01 level (Table 1). In both cases, Se was higher in the Burton Island sites than in the control site, Pepper Creek.

Summary results for trace elements usually found naturally in higher concentrations in organisms, which are mostly essential trace elements, and measured by inductively coupled plasma optical emission spectrometry (ICP-OES), are given in Table 2.

Table 2. Concentrations (mg/g/dry), standard deviations, and % RSD for minor trace elements in samples of *Fundulus heteroclitus* and *Geukensia demissa* collected at the Island Creek (IC) and Pepper Creek (PC), and the p-value of the two site comparison using a two-sample t-test.

Fundulus Heteroclitus		Al	Ba	Ca	Fe	K	Mg	Mn	Na	S	Sr
Site											
IC	Mean	0.38	0.011	76.35	0.75	13.31	2.77	0.086	6.21	10.53	0.49
	Std. Dev.	0.18	0.003	8.95	0.35	0.72	0.23	0.017	0.71	0.44	0.06
	% RSD	48	30	12	46	5	8	20	11	4	11
PC	Mean	0.67	0.011	65.96	1.11	12.29	2.49	0.057	5.44	10.30	0.43
	Std. Dev.	0.34	0.004	12.53	0.46	0.94	0.48	0.014	0.91	0.44	0.11
	% RSD	50	34	19	41	8	19	24	17	4	25
	p-value	0.13	0.98	0.17	0.20	0.09	0.27	0.02*	0.18	0.44	0.28
Geukensia demissa											
IC	Mean	0.13	0.0019	3.75	0.30	10.04	5.47	0.015	38.9	13.43	0.06
	Std. Dev.	0.02	0.0007	2.17	0.04	0.43	1.54	0.005	11.4	1.20	0.03
	% RSD	17	37	58	14	4	28	32	29	9	46
PC	Mean	0.14	0.0017	2.50	0.29	9.94	6.20	0.009	43.19	13.98	0.05
	Std. Dev.	0.06	0.0004	0.42	0.07	0.80	1.43	0.002	10.79	1.84	0.01
	% RSD	44	21	17	24	8	23	18	25	13	18
	p-value	0.81	0.67	0.24	0.93	0.82	0.46	0.05*	0.56	0.59	0.52

* Denotes significance at the 5% or p≤ 0.05 level

As with the rarer trace elements, there is little evidence of consistent differences between the two sites for these elements. Only Mn is significantly different between the two sites at the 95% confidence level, for both organisms, with higher concentrations at Burton Island, compared to Pepper Creek (Table 2).

A comparison of sediment concentrations of the minor trace elements (ICP-MS) is presented in Table 3.

The two sampling areas show considerable within area variation, nevertheless, several of the elements show distinctive difference in concentrations of the minor trace elements, As, Cr, Cu,

Ni, and Tl all show significantly greater concentrations at the Burton Island site at the 95% confidence level, compared to the control Pepper Creek site.

Table 3. Concentrations (µg/g dry), standard deviations of the concentrations, and % RSD for minor trace elements in sediment samples collected at the Island Creek (IC) and Pepper Creek (PC), and the probability that the two sites are the same using a two-sample t-test.

Sediment		As	Cd	Cr	Cu	Hg	Ni	Pb	Se	Tl	Zn
IC	Mean	19.7	0.23	86.5	47.6	0.085	61.0	23.5	1.21	0.71	121.4
	Std. Dev.	10.6	0.19	36.6	30.6	0.051	42.7	9.0	0.89	0.28	48.3
	% RSD	54	81	42	64	60	70	39	73	40	40
PC	Mean	7.6	0.31	43.8	22.2	0.103	18.7	29.6	0.46	0.47	138.7
	Std. Dev.	4.5	0.25	25.0	10.9	0.078	11.7	10.6	0.44	0.15	54.1
	% RSD	59	79	57	49	75	62	36	95	32	39
	p-value	0.05	0.56	0.06	0.12	0.68	0.07	0.35	0.13	0.13	0.61

A comparison of the sediments for the two sites for the higher concentration "structural" trace elements, or elements whose concentration are less than 1000 ppm or 0.1% of a sediments composition, measured by ICP-OES is presented in Table 4:

Table 4. Concentrations, standard deviations of the concentrations, and % RSD for major trace elements in samples collected at the Burton Island (BI) and Pepper Creek (PC), and the probability that the two sites are the same using a two-sample t-test. All concentrations are in mg/g dry weight.

Sediment		Al	Ba	Ca	Fe	K	Mg	Mn	Na	S	Si	Sr
BI	Mean	71.1	0.66	7.01	78.3	18.1	7.41	0.25	14.8	13.8	205	0.28
	Std. Dev.	28.4	0.29	2.14	59.6	3.4	3.54	0.06	9.7	11.8	3	0.17
	% RSD	40	44	31	76	19	48	25	66	85	1	60
PC	Mean	44.5	0.60	5.61	31.7	19.3	6.66	0.3	15.1	14.7	212	0.2
	Std. Dev.	15.5	0.13	2.62	17.9	2.9	4.43	0.1	10.2	12.6	9.7	0.0
	% RSD	35	22	47	56	15	67	28	67	86	5	18
	p-value	0.10	0.69	0.38	0.13	0.56	0.77	0.52	0.96	0.92	0.15	0.13

It is clear from the results that the sediment is fairly heterogeneous from site to site. One factor influencing this is likely sediment grain size and composition. Estuarine sediments are commonly mixtures of sand, slit and clay in various proportions, and the proportions can substantially over small distances depending on currents, wave energy, etc. One way to control for this variation is to normalize the sediment to an element that is predominant in one fraction or another. We chose to normalize the sediment to Al, since Al is an important component of alumino-silicates in silts and clay, and not of sand, which is almost entirely SiO_2.

Table 4 shows considerable variation in Al content within the two areas. Table 5 shows the results when the minor trace elements (i.e. the ICP-MS elements) are normalized to Al, which will help to eliminate variations caused by difference in sand content.

Table 5. Aluminum normalized concentrations (mg/g) of minor trace elements, standard deviations of the concentrations, and % RSD in sediment samples collected at the Island Creek (IC) and Pepper Creek (PC), and the probability that the two sites are the same using a two-sample t-test.

Site		As/Al	Cd/Al	Cr/Al	Cu/Al	Hg/Al	Ni/Al	Pb/Al	Se/Al	Tl/Al	Zn/Al
IC	Mean	0.30	0.0035	1.20	0.64	0.0013	0.79	0.35	0.017	0.0103	1.75
	Std. Dev.	0.17	0.0029	0.08	0.26	0.0007	0.25	0.11	0.012	0.0031	0.55
	% RSD	58	84	7	41	57	32	32	73	30	31
PC	Mean	0.16	0.0062	0.92	0.48	0.0024	0.38	0.68	0.0085	0.0107	3.07
	Std. Dev.	0.05	0.0036	0.25	0.13	0.0022	0.13	0.21	0.0069	0.0008	0.48
	% RSD	29	58	27	27	94	35	31	81	7	16
	p value	0.12	0.23	0.046	0.26	0.32	0.013	0.014	0.23	0.80	0.004

Comparing the results in Table 3 with table 5, we see that in most, but not all cases, the % RSD of the samples within each region are reduced, and in a few cases, Cr, Ni, Pb and Zn, the differences between Burton Island and Pepper Creek become significant at the 95% level. However, it made the difference of As between the two regions, which was borderline 95% significant without normalization, less significant.

Table 6. Aluminum normalized concentrations (mg/g) of major trace elements, standard deviations of the concentrations, and % RSD in sediment samples collected at the Island Creek (IC) and Pepper Creek (PC), and the probability that the two sites are the same using a two-sample t-test.

Site		Ba/Al	Ca/Al	Fe/Al	K/Al	Mg/Al	Mn/Al	Na/Al	S/Al	Si/Al	Sr/Al
BI	Mean	0.0099	0.102	1.014	0.282	0.113	0.0038	0.236	0.214	3.39	0.0039
	Std. Dev.	0.0039	0.018	0.400	0.090	0.057	0.0009	0.156	0.188	1.72	0.0012
	% RSD	39	18	40	32	50	24	66	88	51	32
PC	Mean	0.0158	0.122	0.669	0.468	0.135	0.0067	0.314	0.283	5.45	0.0036
	Std. Dev.	0.0080	0.031	0.185	0.123	0.055	0.0021	0.144	0.184	2.57	0.0009
	% RSD	51	25	28	26	41	31	46	65	47	25
	p value	0.18	0.27	0.12	0.026	0.56	0.021	0.44	0.57	0.17	0.67

For the higher concentration "structural" (ICP-OES) elements, normalization to Al had less dramatic effects; while % RSD were reduced more often than not, only K and Mn were improved to the point of significant differences between Burton Island and Pepper Creek (Table 6). This shows that over all, the sediment of the two regions has similar gross composition and texture after correction for grain size.

D1 - DISCUSSION

Clearly, the most interesting results of the comparison of trace elements in organisms between Island Creek and Pepper Creek is the difference between Se, which is higher in Island Creek than Pepper Creek, and the difference is highly significant in both organisms ($p < 0.01$ for *Fundulus* and $p < 0.05$ for *Geukensia*). Of interests as well, was the difference in Arsenic for *Geukensia* only, which was higher in Island Creek than Pepper Creek, at the $p<0.05$ level. Since Se and As are elements widely associated with the fly ash from power plants (Besser et al., 1996; Swaine et al., 1997), it is tempting to think of this as a likely result of the leachate from the ash piles near Island Creek into the creek waters, either via surface run off, subsurface transport, or the slumping of ash material into the creek. While entirely possible, the data do not provide direct evidence of this, and further work would be necessary to prove that the higher than normal levels of Se in organisms found in Island Creek originates from the Burton Island ash disposal area.

The concentrations of trace elements found in the organisms from both sites are generally in line with the concentrations of the same elements in similar organisms in the mid-Atlantic region. To illustrate this, the data for a similar mussel, *Mytilus edulis* from the Delaware coastline was obtained from the NOAA "Mussel Watch" data base (COAST, 2013).

Mussel Watch sites are chosen to avoid point sources of pollution and to reasonably represent the broad areas of Coastline, and compare it to our data for Island Creek and Pepper Creek for the elements they have in common (Table 7).

Table 7. A comparison of the results of trace elements in *Mytilus edulis* from Delaware "Mussel Watch" sites to the results for *Geukensia demissa* from Island Creek and Pepper Creek in this study.

	Mussel Watch *Mytilus*	Island Creek *Geukensia*	Pepper Creek *Geukensia*
	Mean ± Std. Dev.	Mean ± Std. Dev.	Mean ± Std. Dev.
Al	0.58 ± 0.46	0.13 ± 0.02	0.14 ± 0.06
As	10.18 ± 1.52	10.71 ± 1.30	8.95 ± 0.53
Cd	0.95 ± 0.69	0.44 ± 0.15	0.40 ± 0.06
Cr	2.35 ± 1.64	0.84 ± 0.31	0.59 ± 0.17
Cu	25.66 ± 51.76	14.04 ± 5.18	9.41 ± 0.56
Fe	0.79 ± 0.52	0.30 ± 0.04	0.29 ± 0.07
Pb	1.57 ± 0.68	1.27 ± 0.46	1.00 ± 0.27
Mn	0.024 ± 0.008	0.015 ± 0.005	0.009 ± 0.002
Hg	0.157 ± 0.077	0.105 ± 0.026	0.070 ± 0.037
Ni	2.37 ± 1.01	0.75 ± 0.25	0.49 ± 0.08
Se	4.48 ± 1.15	2.63 ± 0.29	1.99 ± 0.13
Zn	394 ± 1090	58.7 ± 6.61	58.9 ± 4.75

From these comparisons, that in virtually every case, our findings in *Geukensia* from Island and Pepper Creeks are within the standard deviation of the mean values found for *Mytilus* in Delaware, and in the lower end of the distribution in the Mussel Watch data. For Se, our

samples are below the 1σ range of the Mussel Watch data. This may be a result of using different organisms, or an environmental effect. For example, Se concentrations in marine organisms are generally higher than in freshwater and brackish water organisms, for reasons which are not yet clear, but may relate to the production and use of organo-sulfur compounds by marine phytoplankton as osmoregulators, and the production of Se analogues of those compounds.

To compare the sediment from this study with other nearby sediment values, we also obtained sediment data from the "Mussel Watch" data set from samples from Delaware, and compared it to the samples from this study (Table 8).

Table 8. Concentrations of trace elements in Island Creek and Pepper Creek sediments with sediments from other sites in Delaware from the "Mussel Watch" data set.

	Mussel Watch Sediment	Island Creek Sediment	Pepper Creek Sediment
	Mean ± Std. Dev.	Mean ± Std. Dev.	Mean ± Std. Dev.
Al (mg/g)	49.2 ± 12.5	71.1 ± 28.4	44.5 ± 15.5
As (µg/g)	7.9 ± 3.1	19.7 ± 10.6	7.6 ± 4.5
Cd (µg/g)	0.34 ± 0.13	0.23 ± 0.19	0.31 ± 0.25
Cr (µg/g)	62.8 ± 41.9	86.5 ± 36.6	43.8 ± 25.0
Cu (µg/g)	14.1 ± 6.3	47.6 ± 30.6	22.2 ± 10.9
Fe (mg/g)	24.5 ± 6.9	78.3 ± 59.6	31.7 ± 17.9
Pb (µg/g)	24.9 ± 7.7	23.5 ± 9.0	29.6 ± 10.6
Mn (µg/g)	525 ± 336	251 ± 64	282 ± 78
Hg (µg/g)	0.104 ± 0.054	0.085 ± 0.051	0.103 ± 0.078
Ni (µg/g)	21.2 ± 8.5	61.0 ± 42.7	18.7 ± 11.7
Se (µg/g)	0.40 ± 0.41	1.21 ± 0.89	0.46 ± 0.44
Zn (µg/g)	114 ± 39	121 ± 48	139 ± 54

The concentrations of trace elements in sediments from Island and Pepper Creeks are similar to other sediments collected in Delaware. The Island Creek sediment samples contain a higher mean concentration of Al, As, Cr, Cu, Fe, Ni, and Se, but as in most cases, the standard deviations of the distributions overlap, suggesting that the concentrations of trace metals in these creeks could be elevated, but still representative of concentrations around the region.

The results of this study suggest that the Island Creek organism samples are somewhat enriched in elements of concern, such as As and Se compared to the nearby control site, Pepper Creek. This was considered to be a possibility in the design of the study, as As and Se are known to be enriched, and relatively soluble in fly ash. These results suggest, but do not prove, that higher As and Se in the organisms from Island Creek sites were exposed to As and Se from the ash disposal deposits.

The differences between organisms in Island and Pepper Creeks could result in some difference between the sites not due to the ash disposal at Burton Island, either a difference in the source

water, or the source of the sediment for the two areas. This seems unlikely given the proximity of the two sites, and the similar regions for their watershed. However, the analysis of the sediment does show a difference, in this case not statistically significant in the Se content, 1.21 ± 0.89 µg/g in Island Creek compared to 0.46 ± 0.44 µg/g. This could be the result from either natural sources or from the ash disposal site. Another possibility is that the difference arises from a salinity effect. According to Figure 6, the average salinity regimes of the Island Creek and Pepper Creek sampling sites overlap, but the Pepper Creek sites probably encompass a wider range of salinity, and higher salinity on average. It is possible that the higher average salinity of Pepper Creek suppressed the uptake of Se in the organisms or in the available organism's food (Riedel and Sanders, 1996; Riedel et al, 1996).

If the difference in Se is the result of the Burton Island landfill, there remains the question of how the exposure of the organisms to Se from the ash occurred. There are several possible routes, including water borne Se washing off the surface of the ash disposal area in to Island Creek, subsurface movement of dissolved Se in ground water into the Island Creek, or as a result of solids enriched in Se washed off the ash disposal site. The Remedial Investigation Report (2011), showed that the infiltration of tidal waters into the underlying sediments of Burton Island drive the flow of water below and through the island. The input of freshwater to Burton Island is solely due to meteoric (i.e. rain) input of freshwater, with an outward flow of fresh groundwater from Burton Island occurring less than 10 percent of the time, resulting in a net inward flow. The main driving forces in the flow pathways and groundwater elevation contours (mounding of the groundwater on the island) is the differences in hydraulic head that are created due to the rising and falling of the daily high and low tides (Figure 7, 8, and 9). It is unknown how the groundwater dynamics below Burton Island will respond to rising tidal levels, as local relative sea-level (LRSL) rise and the scouring of the Indian River Inlet have elevated the water levels and changed the tidal prism for the Inland Bays. This study was not designed to answer the question of what effect will rising water levels play on changing pore water concentrations, although the results of the sediment analysis provide supportive evidence to the hypothesis that previous erosion of the Island was a source of input of elements into the waters surrounding Burton Island (as compared to the sediments sample concentrations from the reference sites along Pepper Creek).

A key question or concern associated with results of this study analysis were what effect the current concentration levels of particular elements have upon the aquatic biota of the Burton Island region. These concerns could not adequately be address by the authors, but rather a separate assessment of the analytical data collected during this project was conducted by DNREC, and in this review the concerns associated with Se were addressed (Appendix A). The full assessment of the analytical data review and overview of the potential ecological risks associated with the exposure of Se, in particular, can be found in full within Appendix A. A key component of this DNREC review, as it states, is "A key question is whether the concentrations of selenium in the mummichogs and ribbed mussels reported by the CIB represent an ecological

risk to those species. This question is relevant because bioaccumulated metal is not necessarily toxic (Rainbow, 2002)." In short though, his assessment suggested that concentrations of Se in *Geukensia* and *Fundulus* are well below the ecological risk thresholds for Se exposure. DNREC states in their review, "It is concluded that the selenium concentrations in the mummichogs from Burton Island are within the expected range of background. More importantly, the concentrations in the mummichogs and ribbed mussels are well below a concentration expected to cause reproductive effects in these species (Appendix A)."

The concentration of arsenic in the sediment and biota (*Geukensia* and *Fundulus),* between Pepper Creek and Island Creek, have a very similar separation in concentration, as was documented in the Se concentrations. There was a clear difference in mean concentration of As in the sediment samples, with a mean consecration of 19.7 $\pm$ 10.6 µg/g for Inland Creek as compared to 7.6 $\pm$ 4.5 µg/g for Pepper Creek (Table 3). This difference was statistically significance at the 5% level ($p \leq 0.05$ level). Arsenic is a naturally occurring element in the earth's soil, with a DNREC default background standard for soils being 11 µg/g. The Island Creek sediment samples are in exceedance of that level, but this is not surprising as elevated levels of As were document in the 2008 Facility Evaluation Report, with concentrations ranging from 1.6 µg/g to 160 µg/g for the offshore and shoreline sediment samples (Shaw, 2008). There was no statistical difference in As concentrations within *Fundulus* sampled at Island Creek and Pepper Creek, 3.55 $\pm$ 0.79 µg/g and 3.14 $\pm$ 0.87 µg/g respectively (Table 1). The As concentrations in *Fundulus* do not seem to be affected by elevated levels within the sediments, but rather the concentrations are the result of the level of As in the tidal water and sorbed detrital food particles throughout the bay. Arsenic concentration, in *Fundulus,* are more likely characteristic of the overall arsenic loading within the watershed (both through natural and man-made pathways), not hot spot elevated concentrations resulting from one particular site within the watershed. The statistically higher levels of As in the *Geukensia* samples of Island Creek, at the 1% level ($p \leq 0.01$ level) than that of Pepper Creek, are results that should be carefully monitored in the future, but as for the current conditions of not a huge ecological concern (Table 1). The Island Creek total arsenic concentrations, in *Geukensia,* are well below the FDA action levels for total arsenic in clams, oysters, and mussels of 86 µg/g ww. The Island Creek mean total arsenic concentrations of 10.71 $\pm$ 1.30 µg/g in the *Geukensia* samples are at levels that are corollary to mean total As concentrations found in the "Mussel Watch" *Mytilus edulis* samples for Delaware (10.18 $\pm$ 1.52 µg/g), so the concentrations found at Island Creek are not unrepresentative to values through the State of Delaware (Table 7).

These existing conditions and concentrations levels of trace elements found in the *Geukensia*, *Fundulus,* and sediment samples currently do not warrant a spatial expansion of sampling to evaluate the potential ecological impacts of bioaccumulation. It should be noted that an ongoing sampling program is in place by NRG and DNREC SIRB to evaluate and monitor the concentration of elements around, and that are potentially transported off of, Burton Island through groundwater and surface water. The future conditions of the island could change due to

rising water levels and/or changes in the rate of pore water movement, and because of this, it is recommended that tissue and sediment samples are periodically sampled and analyzed (in methods consistent with this study) to evaluate any changes in the prevalence and concentration of trace elements and metals through bioaccumulation in the surrounding biota.

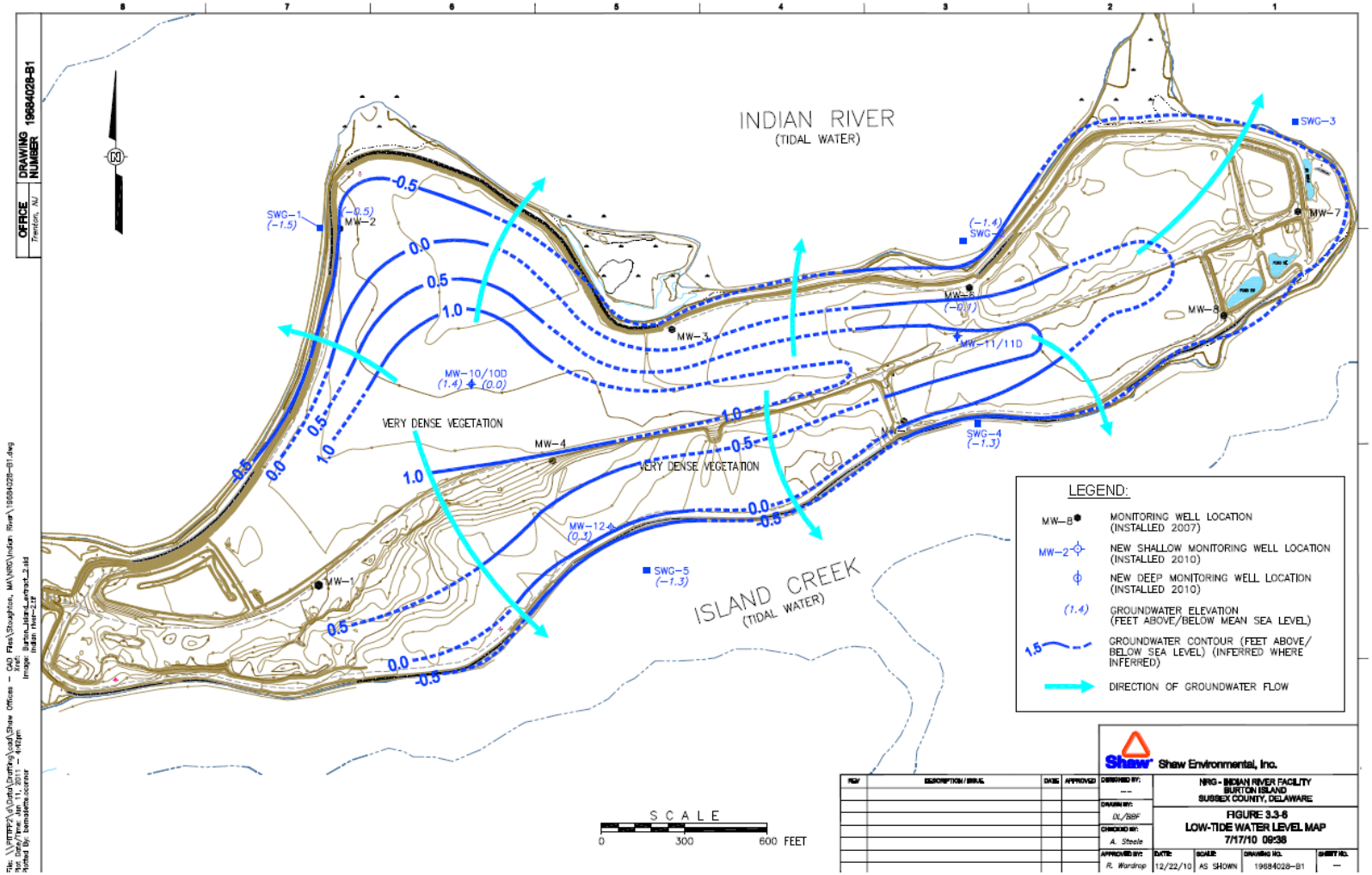

Figure 7. The sub-surface groundwater flow paths and groundwater elevations for Burton Island, at low-tide (Shaw, 2008).

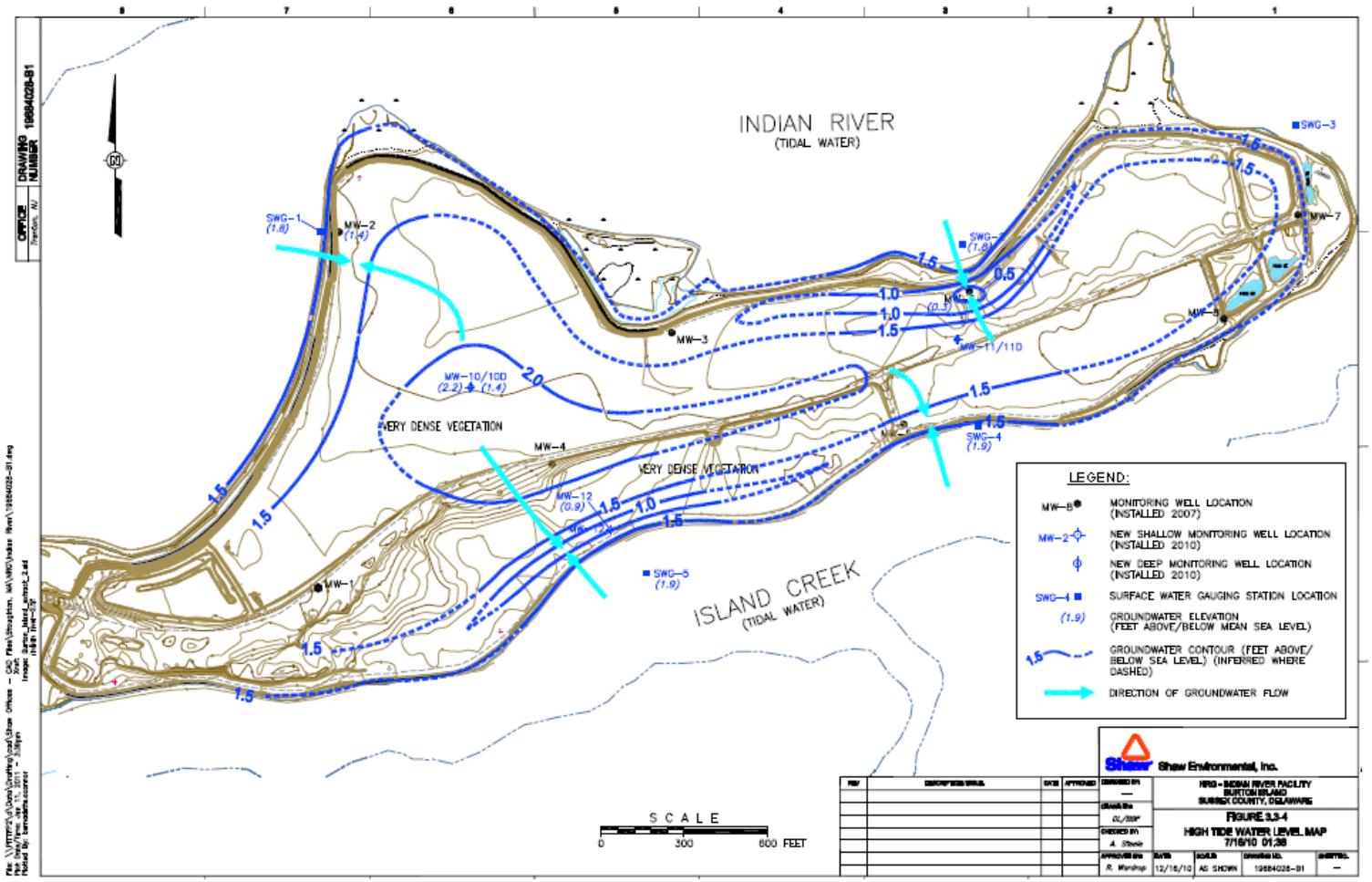

Figure 8. The sub-surface groundwater flow paths and groundwater elevations for Burton Island, at high-tide (Shaw, 2008).

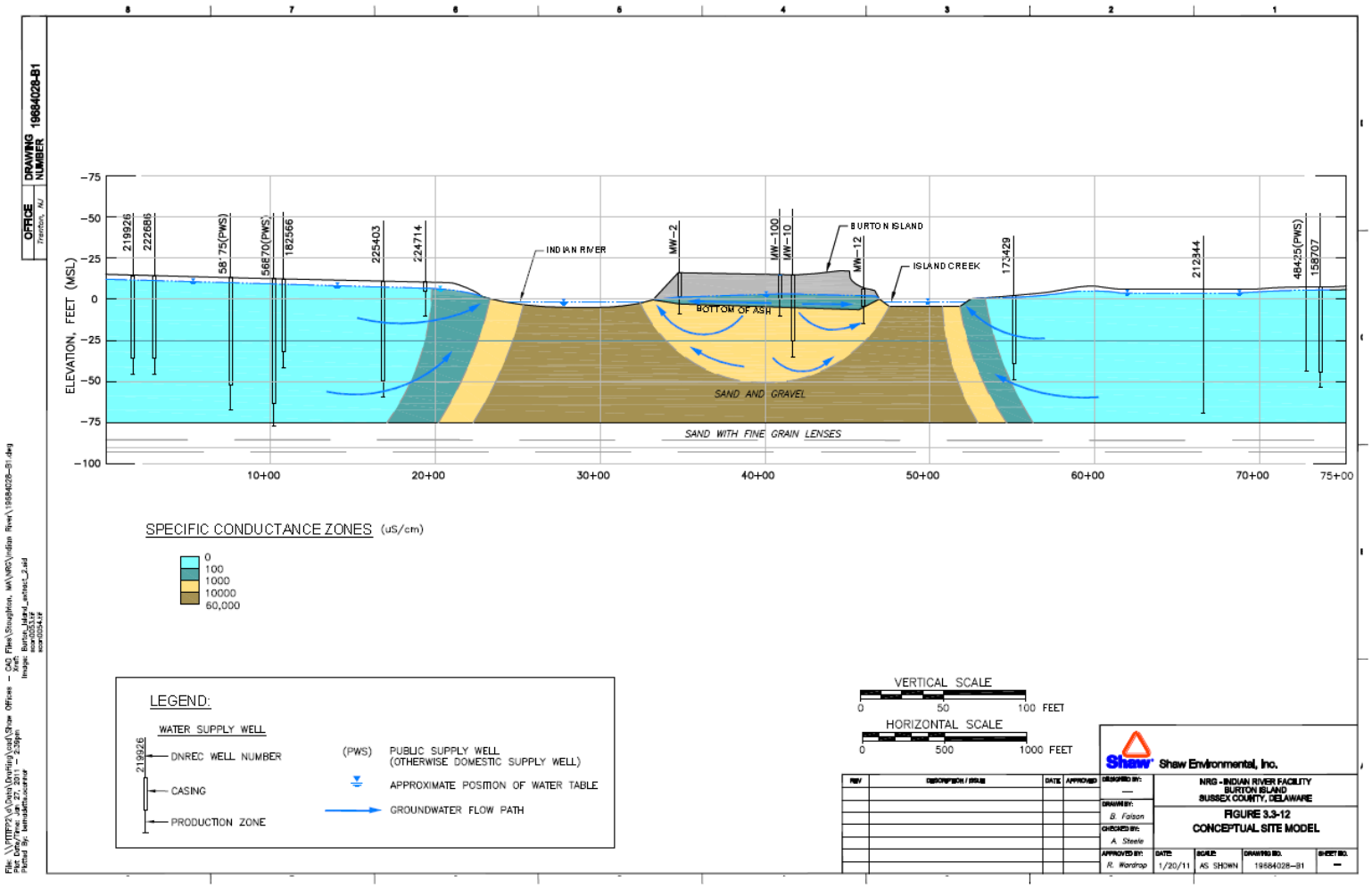

Figure 9. A conceptual site model of the groundwater flow paths and groundwater elevations below Burton Island (Shaw, 2008).

E1. QUALITY OBJECTIVES AND CRITERIA FOR MEASUREMENT DATA

The terms used to define data quality are accuracy, precision, completeness, comparability, representativeness and method sensitivity. The definition and application of these terms to this project are described below. Data quality objectives for accuracy, precision, and comparability are shown in Table 8 for measurements made during the project. Table 8 also contains QC information on measurements and frequency of QC samples needed during the chemical analysis of tissue and sediments. As described in the following discussion, precision and accuracy objectives are based on standard method performance information and past laboratory performance.

Table 9. Data Quality Objectives for Sample Collection and Chemistry

QC Measurement	Frequency	Acceptable Limits
At least 4 external cal. Std.	Daily prior to use or failure of cont. cal.	r^2 >0.99
1 int. cal. Std. (IPR/OPR)	Every 10 samples	Concentration within ±10% of correct value
QCS standard	1 per analytical run	Concentration within ±10% of nominal concentration
Method Blank	Every 10 samples	< 2 X MDL
Digestion blank	Every 10 samples	
Spiked sample	Every 10 samples	Addition to be with 15% of known addition
Duplicate sample analysis	Every 10 samples	15% RPD or ± 5 × MDL
Duplicate digest analysis	Every 10 samples	To check homogeneity
Duplicate Sample analysis	1 per site	
Standard Reference Material (SRM)	Every 10 samples	Within ± 2 × SRM confidence interval or ± 15%

Accuracy - The measure of confidence in a measurement; the closeness of agreement between the observed value and an accepted value.

The accuracy of chemical analysis is determined through the analysis of method and process blanks, Initial and Ongoing Precision and Accuracy samples (IPR/OPR), QCS standards standard reference material (SRM) and matrix-spiked samples. Method (reagent) blanks were used to measure contamination associated with reagents and laboratory handling. Digestion blanks were used to measure contamination associated with the full process of laboratory digestion and analyses. QCS standards are standards derived from a different source than the standards for the standard curve, to provide independent verification of the concentrations. Matrix spikes were performed by adding a known quantity of target analyses into digested samples and preparing and analyzing the sample in the same manner as other samples. SRMs are materials that have been certified by a recognized authority (e.g., National Institute of Standards and Technology) which are treated and analyzed as an actual sample. SRMs are materials that have been certified by a recognized authority (e.g., National Institute of Standards and Technology) which are treated and analyzed as an actual sample. For matrix spikes, percent recovery will be calculated as follows:

$$\% \text{ Recovery} = S - U / C_{sa} \times 100$$

where:

S = measured concentration in spiked aliquot
U = measured concentration in unspiked aliquot
C_{sa} = actual concentration of spike added

For IPR/OPR, QCS and SRMs is used, percent recovery was calculated as follows:

% Recovery = (C_1/C_2) x 100

where:
C_1=measured value
C_2=nominal or certified value

QC parameters from the organism samples (low concentration element) measure by ICP-MS are given in Table 10 (tissues) and Table 12 (sediments), and for high concentration (ICP-OES) in Table 11 (tissues) and Table 13 (sediments). The MDL is calculated as 3 time the standard deviation of the digestion blanks, rounded up to the nearest single digit, and corresponds to approximately a 99% certainty that the concentration measured was not due to random variation above zero. IPR/OPR (Initial/Ongoing Precision and Recovery) is an ongoing standard run initially and once in 10 samples, QCS (Quality Control Standard) is a standard from a independent origin than the standard used to make the standard curve. Mean Spike Recovery gives the mean of the measured recovery (%) of spiked samples in the run. DORM 3 and NIST 1566b are Certified Reference Materials, and mean RPD is the average of the Replicate Percent Deviation for samples analyzed in duplicate.

From these tables, we can see that the linearity of the standard curves were all satisfactory, the IPR/OPR values show that the sample calibration held over the whole sample run, and that the QCS reinforces the correctness of the calibration. Mean Spike Recovery was within the desired envelope (±15%) except for As which was slightly above. Recovery of DORM-3 was within the desired envelope except for Pb, which was low, and Tl which was high. Recovery of NIST 1566b was low for As and high for Se. For both Cr and Se, the initial run using, NH_3 as the DRC gas was rejected for a number of reasons including bad spikes, and the samples were re-run using CH_4 as the DRC gas, which resulted in more satisfactory QA/QC on the second run.

For the ICP-OES elements, the recovery of some elements in the SRMs was less than ideal. DORM-3 (Dogfish muscle tissue) only has values for Al and Fe, which had 60% and 84% recovery respectively. For NIST 1566b (mussel tissue), most of the recoveries were low (around 80%), although Al was very low (but its value was barely above the detection level in those samples). The digest employed for tissue is not as well suited for geologic samples, since it lack HF, and it's likely that some fraction of these elements in the mussel tissue is from residual sediment.

Precision - The degree of agreement among repeated measurements of the same characteristic on the same sample or on separate samples collected as close as possible in time and place.

Measures of analytical precision for sediment chemistry analyses were determined by the analysis of laboratory duplicates. Duplicates will be prepared by homogenizing and splitting a

sample in the laboratory and carrying the subsamples through the entire analytical procedure. Precision will be expressed in terms of relative percent difference (RPD) as follows:
% RPD = $ABS[C_1 – C_2/((C_1+C_2)/2)] \times 100$

where:
ABS = absolute value
C_1= first measured value
C_2 = second measured value

Table 10. QC parameters from the organism samples (low concentration element) measured by ICP-MS.

QA/QC Parameters	As	Cd	Cr	Cu	Hg	Ni	Pb	Se	Tl	Zn
Standard Curve r^2	0.9997	0.9993	0.9978	0.9997	0.9999	0.9984	0.9985	0.9994	0.9987	0.9989
Low Standard (µg/L)	0.01	0.01	0.01	0.1	0.005	0.01	0.03	0.1	0.01	0.1
High Standard (µg/L)	30	100	100	300	2.5	100	100	100	100	300
Avg. Digestion Blank (µg/L)	0.187	0.018	0.365	0.376	0.0012	0.173	0.022	0.253	0.007	9.375
Std. Dev. Digestion Blank (µg/L)	0.047	0.001	0.101	0.737	0.0010	0.065	0.005	0.302	0.003	0.919
MDL rounded up (µg/L)	0.20	0.004	0.40	3.00	0.004	0.20	0.02	1.0	0.008	3.00
IPR/OPR Mean Recovery (%)	106.9	103.1	102.1	102.1	101.9	103.7	103.5	99.1	103.7	102.1
QCS Recovery (%)	107	104	103	100	102	101	85.6	102	87.3	102
Mean Spike Recovery (%)	118	95.2	104	98.7	95.7	98.9	106	104	107	112
DORM 3 Recovery (%)	105	102	80.1	96.2	101.0	91.0	54.8	114	240	98.5
NIST 1566b Recovery (%)	43.3	96.2	N.C.	93.6	85.8	89.3	93.7	142	N.C.	95.3
Analytical Dup. Mean RPD (%)	1.2	8.3	3.2	1.9	0.7	2.7	5.3	2.8	9.0	2.0
Digest Dup. Mean RPD (%)	4.0	25.7	4.5	14.1	4.9	5.4	7.8	22.5	97.8	7.9
Sample Dup. Mean RPD (%)	9.1	25.5	50.4	55.6	18.6	44.5	38.4	6.6	36.0	11.4

We have multiple levels of precision measurements in this study. The first is the analytical replications in Tables 10-13. For the analysis of low level elements in the both tissues and sediments (Table 10 and 12) the % RPD of the duplicates is well within the target of ± 15%. For the high concentration elements measured by ICP-OES in tissues there are a few exceptions (Table 11). Al, Ba and Ca all exceed the 15% mean RPD, but these are largely due to low values in the samples, which causes high relative variation. For sediment, where the concentrations of these elements are much higher, all of the % RPDs were below the ±15% criterion.

Table 11. QC parameters from the organism samples (high concentration element) measure by ICP-OES.

QA/QC Parameters	Al	Ba	Ca	Fe	K	Mg	Mn	Na	S	Sr
Standard Curve r^2	0.9991	0.9999	1.0000	1.0000	0.9822	0.9996	0.9999	0.9996	1.0000	0.9995
Low Standard (mg/L)	0.03	0.03	0.3	0.03	0.3	0.1	0.03	0.3	0.1	0.003
High Standard (mg/L)	30	10	100	30	10	30	10	100	30	1.0
Avg Digestion Blank (mg/L)	-0.06	-0.003	0.070	0.01	-0.9	0.02	-0.001	-1.9	-0.2	0.0002
Std. Dev. Digestion Blank (mg/L)	0.044	0.001	0.034	0.002	4.7	0.003	0.001	1.2	0.1	0.0001
MDL rounded up (mg/L)	0.20	0.003	0.20	0.005	15.0	0.01	0.002	4.0	0.40	0.001
IPR/OPR mean recovery (%)	97.6	105.7	98.9	106.3	94.8	99.4	104.7	99.1	104.2	107.3
QCS mean recovery (%)	95.3	100.4	98.6	99.7	101.9	100.2	100.7	95.3	103.5	106.3
Mean % Spike Recovery (%)	98.6	102.2	122.3	107.9	110.3	99.8	101.6	103.5	99.5	105.2
NIST 1566b Recovery (%)	26.8	80.1	82.8	81.5	111.8	79.9	92.1	59.4	86.3	88.1
DORM 3 Recovery (%)	60.3	N.C.	N.C.	84.4	N.C.	N.C.	N.C.	N.C.	N.C.	N.C.
Analytic Dup. Mean % RPD	20.1	30.7	21.2	14.6	4.7	12.4	8.4	4.6	9.6	11.5
Digest Dup. Mean % RPD	6.7	12.1	8.8	6.9	5.1	7.4	6.7	2.0	6.9	8.6
Sample Dup. Mean %RPD	23.9	19.1	26.9	18.1	4.1	17.7	17.2	16.4	12.4	21.5

Representativeness - Extent to which data actually depict the true environmental condition, characteristic of a population, parameter variations at a sampling point or process condition.

The use of accepted sampling procedures and analytical methods procedures will assure representativeness of the data compared to local, regional (Chesapeake Bay) and international studies and monitoring. In each site, one tissue sample and one sediment sample will be digested in duplicate so that the sample homogeneity can be assessed.

The results of the analysis of a duplicate digest for one sample from each site for both tissue and sediment as Digest Duplicate Mean RPD % in Tables 10 through 13. In general, the mean % RPDs for the duplicate digest is greater than for the analytical replicate, as we would expect, but not greater than the ±15% variation we hope to achieve. There are some exceptions, and these mostly relate to low concentrations.

Finally, at each area, one site was sampled in duplicate, the sample homogenized, digested and analyzed separately, and compared to the original sample, to get an estimate of how well a single sample represents a particular site. These results are labeled Mean Sample Duplicate RPD%. Comparison of these results to the analytical and digest RPDs shows that overall, as one would expect, the Sample RPDs tend to be larger than the Analytical and Digest RPDs.

Table 12. QC parameters from the sediment samples for low concentration elements measured by ICP-MS.

Sediments	As	Cd	Cr	Cu	Hg	Ni	Pb	Se	Tl	Zn
r2	0.9997	0.9995	0.9999	0.9998	0.9999	0.9996	0.9998	0.9994	0.9999	0.9992
Low Standard (µg/L)	0.01	0.01	0.01	0.1	0.005	0.03	0.03	0.1	0.01	0.1
High Standard (µg/L)	100	100	100	300	2.5	100	100	100	100	300
Mean Digestion Blank (µg/L)	0.6	0.07	-0.4	0.1	0.001	0.3	-0.1	1.0	0.02	9.5
Std. Dev. Digest Blank (µg/L)	0.079	0.010	0.081	0.072	0.0010	0.031	0.012	0.372	0.007	0.408
MDL rounded up (µg/L)	0.30	0.04	0.30	0.30	0.004	0.10	0.04	2.00	0.03	2.00
IPR/OPR mean recovery (%)	102.0	98.7	96.4	101.2	101.9	101.0	100.6	97.4	100.6	102.4
QCS Recovery (%)	100	94.1	96.2	96.7	102.0	99.4	83.4	100	85.6	90.0
Mean % Spike Recovery (%)	55.4	87.9	94.3	94.5	95.7	108.5	93.0	93.8	95.3	14.8
MESS 3 % Recovery	98.5	80.9	92.3	98.7	92.3	97.4	98.2	94.0	97.1	101.1
Analyt. Dup. Mean % RPD	0.5	6.3	0.5	1.1	1.9	1.0	1.4	11.4	1.6	2.2
Digest Dup. Mean % RPD	23.7	21.0	6.0	11.7	14.1	13.6	14.1	68.3	16.4	15.9
Sample Dup. Mean RPD (%)	35.2	53.6	16.6	32.4	18.8	25.9	27.4	43.4	13.7	20.3

Comparability - The extent to which data from one study can be compared directly to either past data from the current project or data from another study. In this case, we compared the data to similar data from the same regions collected by the NOAA 'Mussel Watch" program. In general, the results were similar across a wide range of elements which were measured in

Method Sensitivity - The capability of methodology or instrumentation to discriminate among measurement responses for quantitative differences of a parameter.

Sensitivity for the chemical analyses are defined as method detection limits, or the minimum concentration of a substance that can be measured and reported. Detection limits for the parameters of interest in this project are given in Tables 10-14 are based on the applicable acceptable methods. In Tables 10-13, Method detection limits (MDL) are presented as those for the digested samples, based on the variation of digest blanks (MDL = 3 X Std. Dev. of the Digest Blanks). Since the sediments and the tissues had slightly different digestions, MDLs are calculated separately from the digest blanks for each type of digest for each element analyzed. In practice, however, each sample has its own sample weight, its own sample volume, which leads to slightly different MDL as applied to each sample. However, since sample sizes were not limiting, the sample weights and sample volumes were similar for a given matrix, and an average MDL for sediments and tissue on a per sample weight basis is given in Table 14.

Ideally, the values measured in the field should be approximately ten fold above the MDL, the so called "quantitation limit". For the most part, our measurements are comfortable above this level. However, Tl in tissue is only approximately 5 times greater than that limit and Se in tissue approximately ten times the limit (compare Means in Tables 1-4 with MDLs in Table 14. We also analyzed for Tin (Sn) in tissue and sediments, and those results were consistently less than the MDL, and have not been reported.

Table 13. QC parameters from the sediment samples for high concentration elements measured by ICP-OES.

Sediments	Al	Ba	Ca	Fe	K	Mg	Mn	Na	S	Si	Sr
r2	0.9996	0.9998	1.0000	0.9999	0.9995	0.9997	0.9999	0.9998	0.9999	0.9999	0.9999
Low Standard (mg/L)	0.03	0.03	0.3	0.03	0.3	0.1	0.03	0.3	0.1	0.1	0.003
High Standard (mg/L)	30	10	100	30	10	30	10	100	30	30	10
Mean Digestion Blank (mg/L)	0.310	-0.001	0.064	0.031	-0.999	0.049	0.003	-2.421	1.248	6.52	0.003
Std. Dev. Digest Blank (mg/L)	0.733	0.003	0.012	0.037	0.496	0.010	0.000	5.058	0.502	1.87	0.002
MDL rounded up (mg/L)	3.0	0.009	0.04	0.20	2.0	0.03	0.001	16.0	2.00	12.0	0.006
Mean IPR/OPR recovery (%)	98.8	104.3	100.7	106.2	107.9	102.3	106.7	99.3	105.3	104.8	102.3
QCS mean recovery (%)	98.2	102.5	103	102	108	103	102	92.5	106	96.3	101
Mean Spike Recovery (%)	114.4	105.2	102.4	107.1	119.7	100.4	110.7	97.5	107.6	110.7	105.3
MESS-3 Recovery (%)	86.5	N.C.	91.7	91.7	89.7	96.1	96.6	99.2	57.4	75.0	99.6
Analyt. Dup. Mean RPD (%)	0.4	1.1	2.6	1.2	6.7	2.1	2.1	10.0	6.3	0.9	1.9
Digest Dup. Mean RPD (%	8.2	6.0	15.6	14.5	8.5	12.9	12.6	7.1	30.0	6.0	10.0
Sample Dup. Mean RPD (%)	17.2	6.4	21.2	23.0	10.0	34.6	21.9	30.8	68.2	15.2	14.9

Table 14. Measurements, Methods and Target Detection Limits for Sediment and Tissue Analyses (dry weight).

Measurement	Reference Method	Target Detection Limit and units	Mean Sediment Detection Limit	Mean Tissue Detection Limit
Aluminum	Modified NOAA (1993)	1.0 mg/g	0.5	0.04
Arsenic	“	0.5 µg/g	0.07	0.04
Cadmium	“	0.01 µg/g	0.009	0.001
Calcium	“	1.0 mg/g	0.1	0.04
Chromium	“	0.5 µg/g	0.07	0.08
Copper	“	1.0 µg/g	0.07	0.6
Iron	“	0.1 mg/g	0.04	0.001
Lead	“	0.01 µg/g	0.008	0.004
Mercury	“	0.5 ng/g	0.1	0.006
Manganese	“	1.0 µg/g	0.2	0.4
Nickel	“	1.0 µg/g	0.02	0.04
Potassium		0.02 mg/g	0.5	3.0
Selenium		0.1 µg/g	0.5	0.2
Sodium		0.05 mg/g	4.0	0.8
Thallium		0.01 µg/g	0.01	0.002
Zinc	“	10.0 µg/g	0.5	0.6

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APPENDICES

Appendix A: Comments and Review of Study by Rick Greene (DNREC)

Assessment of Biota and Sediment Data Collected by the Center for the Inland Bays in Conjunction with the Burton Island Bioaccumulation Study

May 10, 2013

Rick Greene
Delaware DNREC
Division of Watershed Stewardship
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Introduction: The Center for the Inland Bays (CIB) collected biota and sediment samples from the Delaware Inland Bays in 2012 to assess whether material eroding off and/or transported from the Burton Island former coal ash disposal site in upper Indian River is contributing to significant accumulation of toxic trace elements in the local aquatic environment. Mummichogs (*Fundulus hereoclitus*), ribbed mussels (*Geukensia demissa*), and surface sediment were collected from five locations along the southern shoreline of Burton Island within Island Creek. Figure 1 shows the locations of the samples within Island Creek (BI-SS-1 through BI-SS-5). Sites were purposely selected to coincide with locations where previous sampling or observations indicated release from Burton Island through either erosion or shallow groundwater transport. Figure 1 also shows five locations within Pepper Creek (PC-RS-1 through PC-RS-5) that were sampled for sediment and biota to serve as controls against which the Burton Island results could be compared.

Each biota sample consisted of five separate animals. At each sampling location and for each species, five animals were combined to produce a station composite. Sediment samples consisted of surficial material containing fine-grained material. All sediment and biota samples were analyzed for selected trace elements by the Smithsonian Environmental Research Center (SERC) under contract with the CIB. Additional details concerning the sampling and analytical methods are covered in a project specific Quality Assurance Project Plan (Smithsonian Institute and Center for the Inland Bays, undated).

Analytical results for trace elements were distributed electronically on April 22, 2013 in an email from Mr. Chris Bason, Executive Director of the CIBs, to Marjorie Crofts, Division Director, Division of Waste and Hazardous Substances, Delaware DNREC. Subsequent email correspondence from Bart Wilson, CIB Project Manager, to Rick Greene, DNREC, confirmed that the sediment and biota data were reported on a dry weight basis. A separate email from Mr. Wilson later provided information on moisture content of the samples. Data on length and weight of the individual animals in the samples has been requested but has not yet been received. Finally with regard to data, it is unclear whether a grain size analysis was performed on the sediment samples.

In addition to the trace element results, Mr. Bason also submitted a letter to Director Crofts on April 22, 2013 which highlighted one particular finding of the CIB study. Specifically, the letter states that:

- *A two tailed t-test showed a statistically significant higher concentration of Selenium in the Ribbed Mussels and the Mummichogs at Burton Island than at the reference locations along Pepper Creek.*

Mr. Bason requests Director Crofts to consider this finding in determining an appropriate course of remediation for OU 2 of the Burton Island Ash Disposal Site. In light of this request and the special emphasis that Mr. Bason has placed on selenium, the assessment that follows focuses specifically on selenium. For reference, the selenium data provided by the CIBs are presented in Appendix 1 along with summary statistics. Although this assessment focuses on selenium, the same general approach presented herein should be considered by the CIB for the other trace elements in their study.

Objectives: The objectives of this assessment are to:

- Confirm or refute the CIB's finding concerning selenium.

- Compare the Burton Island ribbed mussel selenium data to NOAA's Mussel Watch data for the U.S. East Coast.
- Assess whether the selenium concentrations in the Burton Island mummichogs and ribbed mussels represent a significant ecological risk to those species.
- Predict the chemical partitioning of selenium in the sediment samples and assess whether the resulting dissolved selenium concentrations in the pore water are expected to exceed the chronic aquatic life criterion.
- Assess whether the selenium concentrations detected in the biota represent a significant human health risk.
- Integrate the findings into an overall summary.

Findings: The findings for each of the above-listed objectives are presented below.

1. **Confirm or Refute CIB's Finding:** The CIBs used a two sample t-test to reach their conclusion that selenium concentrations in mummichogs and ribbed mussels are higher at Burton Island than at the Pepper Creek reference area. All statistical tests have assumptions that should be tested prior to use. The key assumptions for a two sample t-test include: i) the data are continuous; ii) the two populations are independent of each other; iii) the samples were randomly selected among their respective populations; iv) the data are normally distributed; and v) the variances (or standard deviations) of the two populations are equal. It is not clear from the CIB's preliminary findings whether these assumptions were rigorously examined prior to asserting their finding. As such, that is done here.

The data are continuous variables and so the first assumption is met. Adult mussels are sessile organisms that colonize a fixed location. They do not migrate. As such, it is reasonable to assume that mussels along the shoreline of Burton Island are independent of those along the shoreline of Pepper Creek. Mummichogs are free-swimming fish. Although they demonstrate homing behavior, they are also known to leave an area if conditions become unfavorable. Despite this, the assumption is made that mummichogs from Burton Island are independent of those from Pepper Creek. The validity of the third assumption (i.e., that the samples were random) is debatable since samples collected along Burton Island where deliberately collected at locations where prior release was expected. This is a form of sample bias. This is not inherently bad but it needs to be recognized in light of assumptions made concerning a paired t-test. The broader implication is that the Burton Island samples that were collected may or may not be representative of overall conditions along the Burton Island shoreline and in Island Creek. The greater concern is that assumption iv (i.e., normality) and assumption v (equal variance) do not appear to hold as explained below.

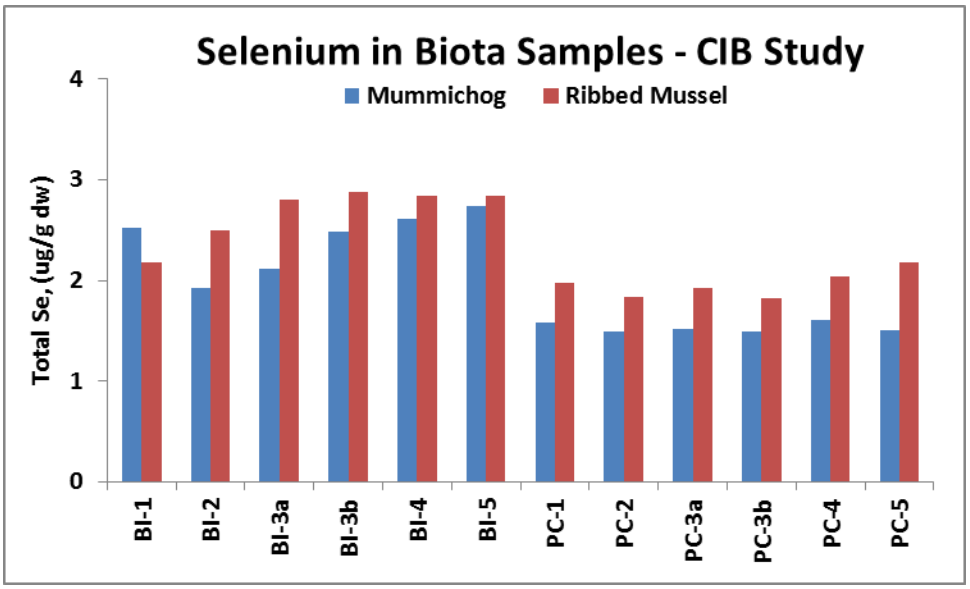
Appendix 2, Table 1 of this assessment presents the results of statistical tests performed on the selenium data to determine if those data are reasonably described as normal distributions. That

appendix also presents a comparison of standard deviations between Burton Island and Pepper Creek for selenium (Appendix 2, Table 2). Of note is that the mussel data from Burton Island are non-normal. This is also true for mummichogs in Pepper Creek, depending on the p-value chosen. These findings, especially for the Burton Island mussel data, invalidates assumption iv. With regard to assumption v, standard deviations were not equal for selenium in Burton Island and Pepper Creek mummichogs.

The important conclusion here is that not all of the underlying assumptions were met to justify a two sample t-test. This makes the CIB's conclusion concerning selenium premature at best and incorrect at worst. In such cases, there are three possible responses. The first is to ignore the fact that some assumptions were not met and simply take the results of the t-test at face value. This is not advisable. The second is to abandon parametric statistical methods (such as a t-test) in favor of non-parametric (distribution-free) statistical methods, the latter being generally less restrictive with regard to assumptions. The third approach is to not rely on statistics at all. Rather, one can present the individual results and indicates whether the concentrations in one group are ***nominally*** greater than the other group and by how much. Approach 2 and approach 3 are both reasonable for comparing selenium concentrations between Burton Island and Pepper Creek and so both approaches are pursued below.

Using the second approach, we can compare the medians (50^{th} percentile values) and the probability distributions of the data from Burton Island and Pepper Creek. The Mann-Whitney (Wilcoxon Rank Sum) test was used to compare the medians and the Kolmogorov-Smirnov (K-S) test was used to compare the probability distributions. The results of these tests are presented in Appendix 2, Tables 3 and 4. Summarizing, the median selenium concentration in mummichogs from Burton Island is statistically greater than the median in mummichogs from Pepper Creek. The same is true for selenium in ribbed mussels but not for selenium in sediments. The K-S test also indicates that there is a statistically significant difference between the probability distribution of selenium in the mummichogs in Burton Island and Pepper Creek. The same is true for the ribbed mussels but not for sediments. Overall, the results of the non-parametric statistical tests are consistent with those from the t-test but are more properly justified.

Additional perspective on the dataset is had through the third approach (i.e., a non-statistical comparison). This is best illustrated with the following simple data plot, where "BI" stands for Burton Island, "PC" stands for Pepper Creek, and 1 through 5 refers to the sample stations.



From the above plot, it is clear that the concentration of selenium in mummichogs from Burton Island is nominally greater than selenium in mummichogs from Pepper Creek. Based on the actual concentrations, the relative percent difference is, on average, 44.3%. Similarly, selenium in ribbed mussels from Burton Island is nominally greater than selenium in ribbed mussels from Pepper Creek. The relative percent difference in this case is 30.7%. Although there is a nominal difference for both species, the magnitude of that difference is not particularly large. Further, it's possible that the difference is actually due to a covariance effect associated with specimen length or weight. Body size (e.g., length/weight) and age are important factors in metal bioaccumulation in marine fish (Zhang and Wang, 2007; Ohlendorf, 2003). Length/weight data have been requested from the CIB but have not been received at the time of this writing. Upon receipt, selenium concentration will be cross-plotted against length and weight to assess apparent relationships.

One additional observation is made concerning the data plot. For Burton Island mummichogs, and to a lesser degree for Burton Island mussels, selenium concentrations tend to increase with sample number between stations 2 and 5. From the map at the end of this assessment, station numbers increase in the upstream direction in Island Creek. Hence, station 1 is closer to the open waters of Indian River and station 5 is closer to the actual power plant, including the active coal management area. This may or may not explain the subtle gradient in selenium concentrations.

The final point to be made in this section is that, regardless of which approach is used to compare Burton Island results to Pepper Creek results, it's important to recognize that a difference in concentration between 2 sites (whether based on statistics or not) is not the same as a biologically significant effect. The biological significance of the results will be addressed in Findings 3, 4, and 5 to follow. First however, we compare the results from the CIBs to a more extensive dataset to provide a broader perspective on the situation.

2. **Comparison to NOAA Mussel Watch Data:** The National Oceanic and Atmospheric Administration (NOAA) collects bivalves from coastal waters of the U.S. and analyzes the meats for various trace elements and organic contaminants. Those data were accessed online (NOAA, 2013) in late April of

2013. All bivalve data for the East Coast of the U.S. from Florida to Maine were downloaded. Selenium data were parsed out by species and year of collection (1986 through 2008). All toll, 1171 selenium results were retrieved for 5 separate species, most of which were for blue mussels (*Mytilus edulis*, n = 638) and oysters (*Crassostrea virginica*, n = 493). A small number of results were included for ribbed mussels (*Geukensia demissa*, n = 26), which is the same species analyzed in the CIB study. Summary statistics for selenium for all Mussel Watch samples, for oysters only, for blue mussels only, and for ribbed mussels only appear in Appendix 3, Table 1 of this assessment.

Note that the mean for all Mussel Watch data (2.66 ppm dw) is essentially identical to the mean for the Burton Island ribbed mussels (2.67 ppm dw). As discussed above, formally comparing means (say with a t-test) is probably not the best approach and so we compare medians and probability distributions as previously discussed. Those results are presented in Appendix 3, Tables 2 and 3 of this assessment. Summarizing, the median concentration of selenium in Burton Island ribbed mussels is not statistically different than the median for the entire East Coast bivalve dataset. This is also true if the comparison is restricted to blue mussels along the Eastern U.S. and if the comparison is restricted specifically to ribbed mussels along the Eastern U.S. Comparing distributions, there is not a statistically significant difference between the probability distribution of selenium in ribbed mussels from Burton Island and the probability distribution of selenium in bivalves collected along the entire East Coast. This is also true in comparing Burton Island ribbed mussels to East Coast blue mussels. In comparing the selenium distribution in ribbed mussels from Burton Island to that in ribbed mussels from the East Coast, the p-value for the test is right at 0.05. This means the distributions are at the breakpoint between being significantly different and not being significantly different at the 95% confidence level. In this case, it's important to consider that the range of selenium concentrations observed in the Burton Island ribbed mussels (2.18 to 2.88 ppm dw) falls squarely within the range of selenium in East Coast ribbed mussels (1.17 to 3.6 ppm dw).

To further this point, Ohlendorf (2003) notes that background concentrations of selenium in aquatic invertebrates (which includes bivalves) are 0.4 to 4.5 ug/g dw. Again, the Burton Island ribbed mussels fall in this range. In contrast, the selenium concentrations in Burton Island ribbed mussels are actually lower than concentrations observed in blue mussels from San Francisco Bay (SFB). Luoma and Rainbow (2005), in presenting data from other studies, indicate that selenium concentrations in blue mussels from SFB fall between 2.5 ug/g dw and 6.7 ug/g dw with a median of 4.6 ug/g dw.

Based on the above, it is concluded that selenium concentrations in ribbed mussels from Burton Island are not outside of expected background concentrations and in fact are not statistically different than concentrations in bivalves collected along the entire East Coast.

3. **Ecological Risk to Mummichogs and Mussels:** A key question is whether the concentrations of selenium in the mummichogs and ribbed mussels reported by the CIB represent an ecological risk to those species. This question is relevant because bioaccumulated metal is not necessarily toxic (Rainbow, 2002).

The critical exposure route of selenium to fish and bivalves is through the dietary pathway as opposed to uptake from water (DeForest and Adams, 2011; Luoma and Presser, 2009; Luoma et al., 1992). Selenium that accumulates in adult fish can be transferred maternally to eggs, which are thought to be

the most sensitive life stage. When the concentration is sufficiently high in the eggs, edema, deformities, or mortality in larval fish can occur (DeForest and Adams, 2011). For freshwater fish, a selenium threshold of 17 ug/g dw in eggs has been recommended when egg data are available and 8.1 ug/g dw in whole-body fish when egg data are not available or sparse (DeForest and Adams, 2011). The EPA, in draft revisions to their selenium water quality criteria (EPA, 2004), recommended a similar whole-body fish tissue selenium concentration of 7.91 ug/g dw as a chronic freshwater criterion. That document also states that, "Because selenium might be as chronically toxic to saltwater fishes as it is to freshwater fishes, the status of the fish community should be monitored if selenium exceeds 5.85 ug/g dw in summer or fall or 7.91 ug/g dw during any season in the whole-body of salt water fishes." So, existing literature, some of which is still draft, suggests that an appropriate threshold for selenium in whole-body salt water fish is approximately 8 ug/g dw.

There is some evidence that invertebrate species (which includes bivalves) are less sensitive to selenium than fish (Ohlendorf, 2003). Here we make the conservative assumption that ribbed mussels are as sensitive as fish to selenium. As such, we apply the threshold of 8 ug/g dw to the mussels as well.

The maximum whole body selenium concentration reported for mummichogs as part of the CIB study was 2.73 ug/g dw (detected at Burton Island sampling station 5). The maximum for ribbed mussels was 2.88 ug/g dw (detected at Burton Island sampling station 3). These concentrations are well below a threshold of 8 ug/g dw.

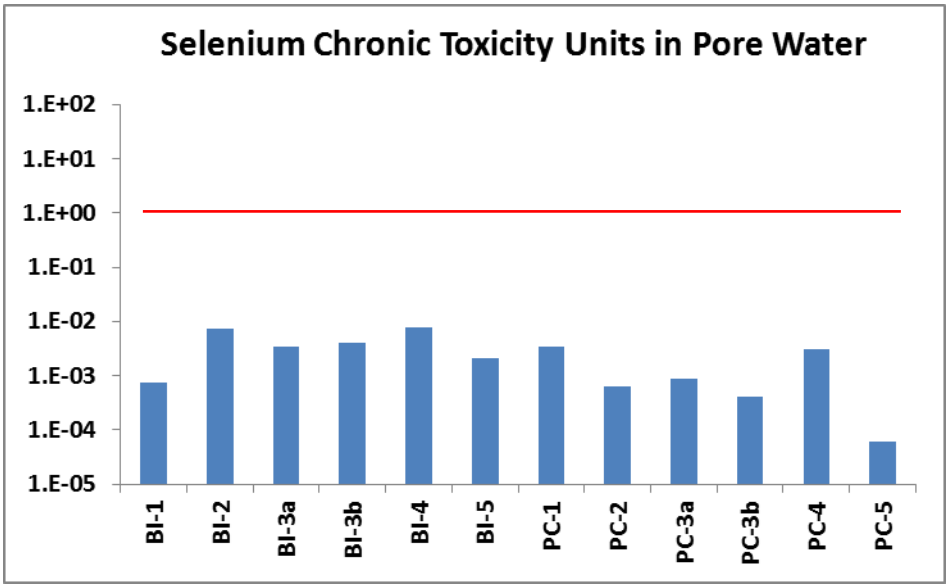
Ohlendorf (2003) notes that background concentrations of selenium in freshwater fish are 1 to 4 ug/g dw and that estuarine and marine fish tend to have higher selenium concentrations than freshwater fish. The selenium concentrations in the mummichogs are within expected background, without considering higher concentrations typical of marine and estuarine fish.

It is concluded that the selenium concentrations in the mummichogs from Burton Island are within the expected range of background. More importantly, the concentrations in the mummichogs and ribbed mussels are well below a concentration expected to cause reproductive effects in these species.

4. **Selenium Partitioning in Sediments and Ecological Risk to Benthic Invertebrates:** Another important question to ask is whether selenium in the sediments poses any special ecological risks. To answer this question, the bulk concentration of selenium reported for the sediments was partitioned between selenium sorbed to the sediment and selenium dissolved in the pore water. The motivation for doing this is that DNREC and EPA's aquatic life criteria for selenium are expressed on a dissolved basis to better account for bioavailability. Details of the partitioning calculations are contained in a spreadsheet that accompanies this assessment (Greene, 2013).

Predicted dissolved selenium concentrations in the pore water were compared to DNREC and EPA's chronic aquatic life criteria for the protection of marine aquatic life, which is 71 ug/L (dissolved). The predicted concentration was divided by the chronic criterion to produce so-called chronic toxic units. Chronic toxic units greater than 1 indicate increased potential for chronic toxic effects.

Chronic toxic units associated with selenium in the sediments are shown in the plot below.



The maximum chronic toxic unit value is 0.0077. The reciprocal of this value tells us how many times lower the predicted concentration is compared to the criterion. So, the maximum predicted dissolved selenium concentration is 130 times less than the chronic criterion. It is concluded that dissolved selenium in the sediments does not pose a risk to benthic organisms through conventional toxic action.

5. **Assess Human Health Risk Associated with Selenium in Biota Samples:** The final issue that is addressed in this assessment is whether the selenium concentrations in the biota samples have implications for human health risk. First, mummichogs and ribbed mussels are not consumed by humans. Hence, there is no exposure through consumption of these species and therefore no human health risk. As a conservative exercise however we might ask if there's a human health risk if commonly consumed species caught in the upper Indian River have similar concentrations of selenium as the mummichogs and ribbed mussels. Before we can answer that question, the dry weight results for the biota samples need to be converted to a wet weight basis to be consistent with "as consumed" fish/shellfish. The conversion is done with the following formula where % moisture was calculated from the raw laboratory data provided by the CIB.

$$Wet\ Weight\ Conc = Dry\ Weight\ Conc \times \frac{(100 - \%\,Moisture)}{100}$$

The dry weigh selenium results, moisture content, calculated wet weight selenium concentrations, and the ratio between dry and wet concentrations appear in the table below.

Sample ID	Species	Se (µg/g dw)	Moisture (%)	Se (ug/g ww)	Ratio (dw/ww)
BI-SS-Fh-1	Mummichogs	2.53	77.58	0.57	4.46
BI-SS-Fh-2	Mummichogs	1.92	76.25	0.46	4.21
BI-SS-Fh-3a	Mummichogs	2.11	78.46	0.45	4.64

BI-SS-Fh-3b	Mummichogs	2.49	78.03	0.55	4.55
BI-SS-Fh-4	Mummichogs	2.61	78.57	0.56	4.67
BI-SS-Fh-5	Mummichogs	2.73	77.43	0.62	4.43
PC-RS-Fh-1	Mummichogs	1.58	76.84	0.37	4.32
PC-RS-Fh-2	Mummichogs	1.49	77.02	0.34	4.35
PC-RS-Fh-3a	Mummichogs	1.51	79.76	0.31	4.94
PC-RS-Fh-3b	Mummichogs	1.49	79.71	0.30	4.93
PC-RS-Fh-4	Mummichogs	1.61	82.43	0.28	5.69
PC-RS-Fh-5	Mummichogs	1.51	85.97	0.21	7.13
BI-SS-Gd-1	Ribbed Mussel	2.18	91.37	0.19	11.58
BI-SS-Gd-2	Ribbed Mussel	2.50	91.10	0.22	11.24
BI-SS-Gd-3a	Ribbed Mussel	2.80	88.82	0.31	8.94
BI-SS-Gd-3b	Ribbed Mussel	2.88	86.93	0.38	7.65
BI-SS-Gd-4	Ribbed Mussel	2.84	88.25	0.33	8.51
BI-SS-Gd-5	Ribbed Mussel	2.84	87.88	0.34	8.25
PC-RS-Gd-1	Ribbed Mussel	1.97	93.22	0.13	14.75
PC-RS-Gd-2	Ribbed Mussel	1.83	92.38	0.14	13.13
PC-RS-Gd-3a	Ribbed Mussel	1.93	90.56	0.18	10.59
PC-RS-Gd-3b	Ribbed Mussel	1.82	89.64	0.19	9.66
PC-RS-Gd-4	Ribbed Mussel	2.04	90.21	0.20	10.22
PC-RS-Gd-5	Ribbed Mussel	2.18	88.74	0.25	8.88

The wet weight selenium concentrations in the above table, which range between 0.13 and 0.62 ug/g ww, are well below Delaware's fish tissue screening value of 10.8 ug/g ww meant to protect recreational anglers (DNREC and DHSS, 2005). The wet weight concentrations are even further below EPA's fish tissue screening value of 20 ug/g ww for selenium (EPA, 2000). EPA's screening value is also set at a level intended to protect recreational anglers.

But what if there is biomagnification of selenium at trophic levels above the mummichogs and ribbed mussels? The biomagnification factor (BMF) would need to be between 17 and 83 to yield selenium concentrations in higher trophic level sport that would exceed Delaware's conservative fish tissue screening value. As pointed out by Ohlendorf (2003), there is little evidence that selenium biomagnifies to any significant degree through successive trophic levels. Luoma and Presser (2009) support this position by listing selenium trophic transfer factors (TTFs) of approximately 1 for several marine fish species.

From the above, it is concluded that selenium concentrations in fish and shellfish from upper Indian River do not pose a significant human health risk to recreational anglers.

Summary of Findings: This assessment confirms that the concentration of selenium is statistically higher in mummichogs and ribbed mussels collected along the shoreline of Burton Island than from Pepper Creek. However, the increase is modest and may be due to the biased nature of the sampling along Burton Island. Alternatively or in addition, differences in selenium concentration between the two

areas may be due to differences in organism length/weight. More importantly, the selenium concentrations in the mummichogs and mussels are of no biological consequence, with peak concentrations being well below the threshold associated with reproductive effects (which is the critical effect for selenium). Further, the selenium concentrations in the ribbed mussels from Burton Island are not statistically different than selenium concentrations in bivalves collected along the entire East Coast of the U.S. This suggests that selenium concentrations in the Burton Island mussels aren't high, but rather that the selenium concentrations in the Pepper Creek mussels are on the low side.

With regard to sediments, equilibrium partitioning calculations were used to predict the dissolved phase concentration of selenium in the sediment pore water. The predicted concentrations were over 2 orders of magnitude less than Delaware's and EPA's chronic aquatic life criterion for the protection of marine aquatic life. However, for many organisms, selenium toxicity has less to do with dissolved phase exposure than it does with selenium associated with particulate matter that ends up as part of the animal's diet (Luoma and Presser, 2009). This is especially important for suspension filter feeders such as mussels. Unfortunately, no measurements of selenium in the water column were made as a part of the CIB's study. However, a worst case estimate of the particulate phase concentration of selenium in the water column can be made based on the bed sediment concentration and assuming strong particle mixing between the bed and the water column.

The peak selenium concentration reported for the sediments was 2.18 ug/g dw. For strong particle mixing, the solid phase, dry weight selenium concentration in the water column will be the same as that in the bed. Hence, a first estimate of the solid phase concentration of selenium in the water column is also 2.18 ug/g dw. For a typical TSS concentration of 20 mg/L in the water column, the associated particulate selenium concentration in the water column expressed on a wet weight basis would be 0.044 ug/L (i.e., 2.18 ug/g x 20 mg/L x 1 mg/1000 g). At a peak TSS concentration of 100 mg/L, the particulate selenium concentration in the water column would be 0.22 ug/L. These concentrations, which may represent what ribbed mussels ingest in their diet, are fairly low. Such low predicted water column concentrations are consistent with the non-detected results observed by DNREC in sampling performed in the fall of 2010. Total and dissolved selenium were both reported as non-detected at 2.4 ug/L for samples collected along a transect between the head of tide at Millsboro Pond, past the power plant, and out to the Indian River Inlet.

Low concentrations of selenium in the water column and sediments help to explain why the selenium concentrations in the ribbed mussels from Burton Island aren't particularly high (despite having statistically higher concentrations than the mussels from Pepper Creek). Again, a statistically higher concentration in one location versus another has nothing to do with whether body burdens are toxic.

Finally, this assessment has demonstrated that selenium in fish and shellfish from upper Indian River is almost certainly not a human health risk to recreational fishermen.

In summary, this assessment does not find that selenium concentrations in upper Indian River, including along Burton Island, pose a significant ecological or human health risk.

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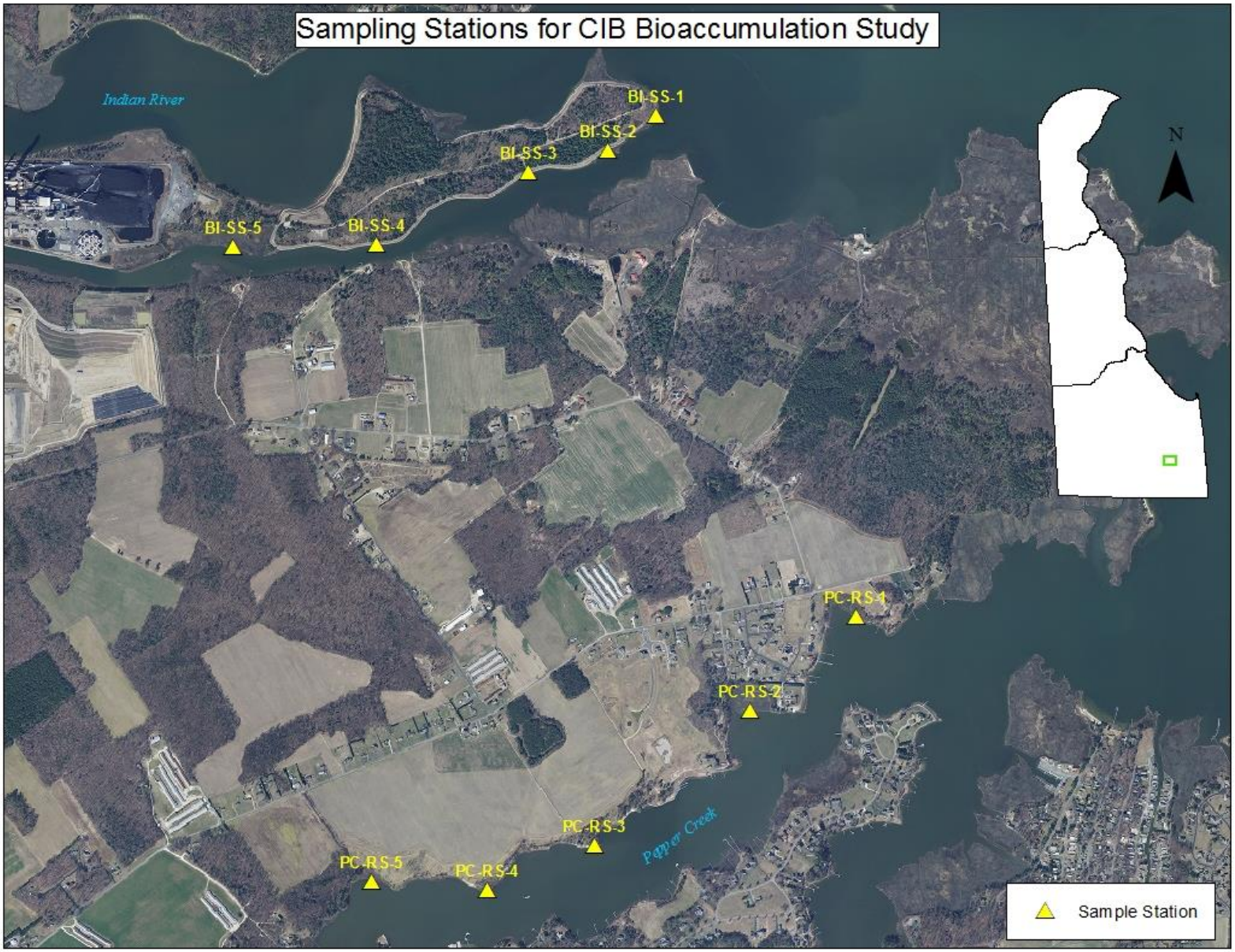
Sampling Stations for CIB Bioaccumulation Study
Indian River
BI-SS-1
BI-SS-2
BI-SS-3
BI-SS-4
BI-SS-5
PC-RS-1
PC-RS-2
PC-RS-3
PC-RS-4
PC-RS-5
Pepper Creek
N
Sample Station

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APPENDIX 1
Total Selenium Concentrations Reported by the Delaware Center for the Inland Bays

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Table 1. Total Selenium (Se) Concentrations and % Moisture in Biota and Sediment Samples

Station	Se Mummichog (µg/g dw)	Se Ribbed Mussel (µg/g dw)	Se Sediment (µg/g dw)	% Moisture Mummichog (%)	% Moisture Ribbed Mussel (%)	% Moisture Sediment (%)
BI-1	2.53	2.18	0.21	77.58	91.37	36.76
BI-2	1.92	2.50	2.11	76.25	91.10	53.67
BI-3a	2.11	2.80	0.98	78.46	88.82	35.69
BI-3b	2.49	2.88	1.12	78.03	86.93	37.88
BI-4	2.61	2.84	2.18	78.57	88.25	65.44
BI-5	2.73	2.84	0.59	77.43	87.88	76.36
PC-1	1.58	1.97	0.98	76.84	93.22	70.19
PC-2	1.49	1.83	0.17	77.02	92.38	46.56
PC-3a	1.51	1.93	0.25	79.76	90.56	49.22
PC-3b	1.49	1.82	0.11	79.71	89.64	40.34
PC-4	1.61	2.04	0.88	82.43	90.21	72.08
PC-5	1.51	2.18	0.02	85.97	88.74	34.48

Table 2. Summary Statistics for Total Selenium in Biota and Sediment Samples

	BI - Fish	*PC - Fish*	*BI - Mussels*	*PC - Mussels*	*BI - Sed*	*PC - Sed*
Mean	2.400	1.532	2.672	1.962	1.198	0.402
Standard Error	0.128	0.020	0.114	0.055	0.326	0.170
Median	2.508	1.510	2.817	1.950	1.050	0.210
Standard Deviation	0.313	0.050	0.279	0.134	0.799	0.417
Sample Variance	0.098	0.002	0.078	0.018	0.638	0.174
Kurtosis	-0.964	-0.949	1.250	-0.051	-1.604	-1.742
Skewness	-0.795	1.006	-1.475	0.699	0.300	0.847
Range	0.809	0.120	0.701	0.353	1.969	0.958
Minimum	1.925	1.489	2.176	1.824	0.214	0.017
Maximum	2.734	1.609	2.877	2.177	2.182	0.975
Sum	14.399	9.191	16.033	11.772	7.189	2.410
Count	6	6	6	6	6	6
Conf. Level (95.0%)	0.329	0.052	0.293	0.140	0.838	0.437

Notes:

1. BI = Burton Island; PC = Pepper Creek; Fish = Mummichogs; Mussels = Ribbed Mussels; Sed = sediments

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APPENDIX 2
Statistical Test Results for Selenium in Biota and Sediment Samples from Burton Island and Pepper Creek

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Table 1. Shapiro-Wilks Test for Normality (performed with STATGRAPHICS)

	Shapiro-Wilks Test		Normal Distribution
Variable Name	W statistic	p-value	(Y/N)?
BI_Fish_Se	0.8972	0.3489	Y at α = 0.05
BI_Mussels_Se	0.7776	0.0354	N at α = 0.05
BI_Sed_Se	0.9104	0.4225	Y at α = 0.05
PC_Fish_Se	0.8143	0.0724	Y at α = 0.05; N at α = 0.1
PC_Mussels_Se	0.9363	0.645	Y at α = 0.05
PC_Sed_Se	0.8112	0.0682	Y at α = 0.05; N at α = 0.1

Notes:

1. BI = Burton Island; PC = Pepper Creek; Fish = Mummichogs; Mussels = Ribbed Mussels

2. If p-value is > 0.05, then data are considered normally distributed at the 95% confidence level.

Table 2. F-Test to Compare Standard Deviations (performed with STATGRAPHICS)

	F-Test		Equal Standard Deviations
Groups Compared	F Statistic	p-value	(Y/N)?
BI_Fish_Se and PC_Fish_Se	38.2264	0.0011	N at α = 0.05
BI_Mussels_Se and PC_Mussels_Se	4.2016	0.1412	Y at α = 0.05
BI_Sed_Se and PC_Sed_Se	3.6701	0.1799	Y at α = 0.05

Notes:

1. BI = Burton Island; PC = Pepper Creek; Fish = Mummichogs; Mussels = Ribbed Mussels

2. If p-value is > 0.05, then the standard deviations are considered equal at the 95% confidence level.

Table 3. Mann-Whitney Test to Compare Medians (performed with STATGRAPHICS)

	Mann-Whitney Test		Medians Equal
Groups Compared	W Statistic	p-value	(Y/N)?
BI_Fish_Se and PC_Fish_Se	0	0.0049	N at α = 0.05
BI_Mussels_Se and PC_Mussels_Se	0.5	0.0063	N at α = 0.05
BI_Sed_Se and PC_Sed_Se	5.5	0.0542	Y at α = 0.05; N at α = 0.1

Notes:

1. BI = Burton Island; PC = Pepper Creek; Fish = Mummichogs; Mussels = Ribbed Mussels

2. If p-value is > 0.05, then the medians are considered equal at the 95% confidence level.

Table 4. Kolmogorov-Smirnov Test to Compare Distributions (performed with STATGRAPHICS)

	K-S Test		Distributions Equal
Groups Compared	Statistic	p-value	(Y/N)?
BI_Fish_Se and PC_Fish_Se	1	0.0050	N at α = 0.05
BI_Mussels_Se and PC_Mussels_Se	1	0.0050	N at α = 0.05
BI_Sed_Se and PC_Sed_Se	0.6667	0.13899	Y at α = 0.05

Notes:

1. BI = Burton Island; PC = Pepper Creek; Fish = Mummichogs; Mussels = Ribbed Mussels

2. If p-value is > 0.05, then the distributions are considered equal at the 95% confidence level.

APPENDIX 3
Statistical Test Results for Selenium in NOAA Mussel Watch Data for the Eastern U.S.

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Table 1. Summary Statistics for Total Selenium in Bivalves Collected along the U.S. East Coast

	All Species	*CV*	*ME*	*GD*
Mean	2.661	2.525	2.789	2.188
Standard Error	0.030	0.046	0.042	0.137
Median	2.500	2.430	2.590	2.075
Mode	1.900	2.700	1.900	2.040
Standard Deviation	1.042	1.014	1.060	0.697
Sample Variance	1.086	1.029	1.123	0.486
Kurtosis	5.206	9.907	2.657	-0.452
Skewness	1.367	1.774	1.128	0.551
Range	10.400	10.400	7.850	2.430
Minimum	0	0	0	1.17
Maximum	10.400	10.400	7.850	3.600
Sum	3115.860	1244.610	1779.089	56.893
Count	1171	493	638	26
Conf. Level (95.0%)	0.060	0.090	0.082	0.282

Notes:

1. CV = Crassostrea virginica (oysters); ME = Mytilus edulis (blue mussel); GD = Geukensia demissa (ribbed mussel)

2. Area of Sampling: East Coast of US, FL to ME

3. Period of Sampling: 1986 - 2008

Table 2. Mann-Whitney Test to Compare Medians (performed with STATGRAPHICS)

	Mann-Whitney Test		Medians Equal
Groups Compared	W Statistic	p-value	(Y/N)?
BI_Mussels_Se and MWEC_All_Se	3041.0	0.5702	Y at α = 0.05
BI_Mussels_Se and MWEC_ME_Se	1851.5	0.8913	Y at α = 0.05
BI_Mussels_Se and MWEC_GD_Se	38.0	0.0564	N at α = 0.05; Y at α = 0.1

Notes:

1. BI = Burton Island; MWEC = Mussel Watch East Coast

2. All = All Species from Mussel Watch East Coast; CV = Crassostrea virginica (oysters); ME = Mytilus edulis (blue mussel); GD = Geukensia demissa (ribbed mussel)

3. Mussels = ribbed mussels from Burton Island

Table 3. Kolmogorov-Smirnov Test to Compare Distributions (performed with STATGRAPHICS)

	K-S Test		Distributions Equal
Groups Compared	Statistic	p-value	(Y/N)?
BI_Mussels_Se and MWEC_All_Se	0.3442	0.4898	Y at α = 0.05
BI_Mussels_Se and MWEC_EC_Se	0.4060	0.2823	Y at α = 0.05
BI_Mussels_Se and MWEC_GD_Se	0.6154	0.0500	On the bubble

Notes:

1. BI = Burton Island; MWEC = Mussel Watch East Coast

2. All = All Species from Mussel Watch East Coast; CV = Crassostrea virginica (oysters); ME = Mytilus edulis (blue mussel); GD = Geukensia demissa (ribbed mussel)

3. Mussels = ribbed mussels from Burton Island

Appendix B: Comments on Study by Citizens Advisory Committee

Burton Island Bioaccumulation Study-CAC Feedback

June 7, 2013

Four reviewers from the Citizens' Advisory Committee (CAC) were selected to make recommendations on the *Burton Island Bioaccumulation* Study: John Austin, Bob Batky, Nancy Cabrera-Santos, and Steve Callanen.

General comments: The review team found the study's description of study methodology, including collection techniques, sample analysis & preparation to be excellent. Additionally, the use of an extensive list of tables and figures added layers of information that complemented the text. The background summary of problems associated with the Indian River Generating Station is helpful to the reader. However, the report needs refinement with regard to being understandable by the lay audience. The authors' names need to be included in the title page. Additionally there **should be an Executive Summary** at the beginning of the report.

The CAC reviewers **recommend a clear, concise, statement of findings** addressing: (1) Whether the material (either sediment, ash, and/or trace toxins) is being eroded or transported from Burton Island to the Indian River; (2) And, if "yes", is this material contributing to trace toxins in nearby marshes and biota? If the study's authors believe the findings are insufficient to address these issues, they should explain their findings, including limitations, and recommendations for possible follow-up studies.

Scope of the Study-The review team found the scope of the study to be narrow. Two locations were chosen (Burton Island and Pepper Creek), each with five sites. At each location, 25 samples were taken, for a total of 50 samples. At each of the ten sites, the organisms selected for the study were mummichogs and ribbed mussels. The report should offer a rationale as to **why mummichogs and mussels were chosen** for the study.

Use of Acronyms-The study is geared to a scientific audience. However, it is expected that the lay public, including journalists, educators, and others will be interested in the contents of this study. It is standard procedure that an **acronym (or trace element) be spelled out at first mention** in the study. Thereafter, the acronym can be freely used. A mystifying sample of the study's acronyms includes SERC, DRC, FIAS, ICP-MS, RSD, ICP, and OES. **The CAC recommends a separate page at the end of the report with a list of acronyms and scientific terms.**

A2-B2-Language Usage-- (page 5) "Any prospective **exposure of pollutants around Pepper Creek likely resulted from contaminant sources other than Burton Island disposal site** (e.g. industry or housing). The reviewers recommend striking or revising this statement, given the fact that Island and Pepper Creeks are linked by tidal action.

B3-The write up on sample analysis is incomprehensible to the lay audience.

C1-The write up on results of the organisms and sediment samples does not start with a statement of results. Rather, it directs readers to review mathematical tables.

- (Page 13), The reader sees one result.—"For *fundulus*, only one element-- **Se has a highly significant difference between the two sites.** This important study result should be highlighted in some way. In addition, the lay audience does not understand the term "highly significant" (e.g. 95% confidence level).
- (Page 14), Unclear sentence: "Summary results for trace elements found in higher concentration in organisms, **mostly, but not solely, essential trace** elements by ICP.
- (Page 17) The explanation on Table 5 is not understandable. "In a few cases, the differences between Burton Island and Pepper Creek become significant at the 95% level. However, it made the difference of **AS between the two regions, which was borderline** 95% significant without normalization less significant." Are the authors saying the differences are or ARE NOT significant?
- (page 18) The report mentions **"further work would be necessary to prove that excess SE in organisms found in Island Creek originates from the Burton Island ash disposal area."** The authors need to elaborate on the term "further work".
- (page 20) The explanation asks more questions than it answers. "The difference between organisms **could result in some difference between the sites not due to the ash disposal at Burton Island."** This statement is dissatisfying, given the evidence.

CAC Recommends Further Study

The *Burton Island Bioaccumulation Study* points to higher concentrations of arsenic and selenium near Burton Island. Therefore, the CAC reviewers recommend a follow-up study of potential heavy metal contamination in additional locations, and possibly other shellfish (1).

Such a study could be co-sponsored by DNREC and other interested parties. DNREC recently made a presentation (to the STAC) on locations with large clam concentrations in the Indian River Bay (2). A new study of heavy metal concentrations in clams could add to the scientific understanding of transport from multiple sources, including Burton Island—especially in light of Sea Level Rise.

Appendix C: Comments on Study by John Austin (CAC)

John Austin

Comments on "Accumulation of Toxic Elements in Biota near Burton Island Disposal Site Indian River Bay, Delaware."

Thank you for the opportunity to review the Draft Final Report.

Page 5 reads:

"Any prospective exposure of pollutants along Pepper Creek likely resulted from contaminant sources other than Burton Island disposal site (e.g. industry or housing) and will be representative of background conditions of the Western Indian River Bay system."

This statement should be stricken or revised. Pepper Creek and Island Creek are linked by tidal action. Release of dissolved and particulate material could be transported from Island Creek and be deposited in or absorbed on to sediments in Pepper Creek. Ambient water quality reports have documented spikes of arsenic moving progressively down the Indian River and into both Rehoboth Bay and Little Assawoman Bay, and to the inlet.

Page 11 - Figure 6 – The land mass of Burton Island has been obscured.

Page 14 – The spreadsheet accompanying the DNREC letter I believe indicated the arsenic was also significantly different for *Geukensia*. Arsenic is listed as nominally different at 14.

Page 20 – "…, although the results of the sediment analysis provide equivocal evidence for erosion as a major source hypothesis." Where\what is this equivocal evidence? This needs clarification.

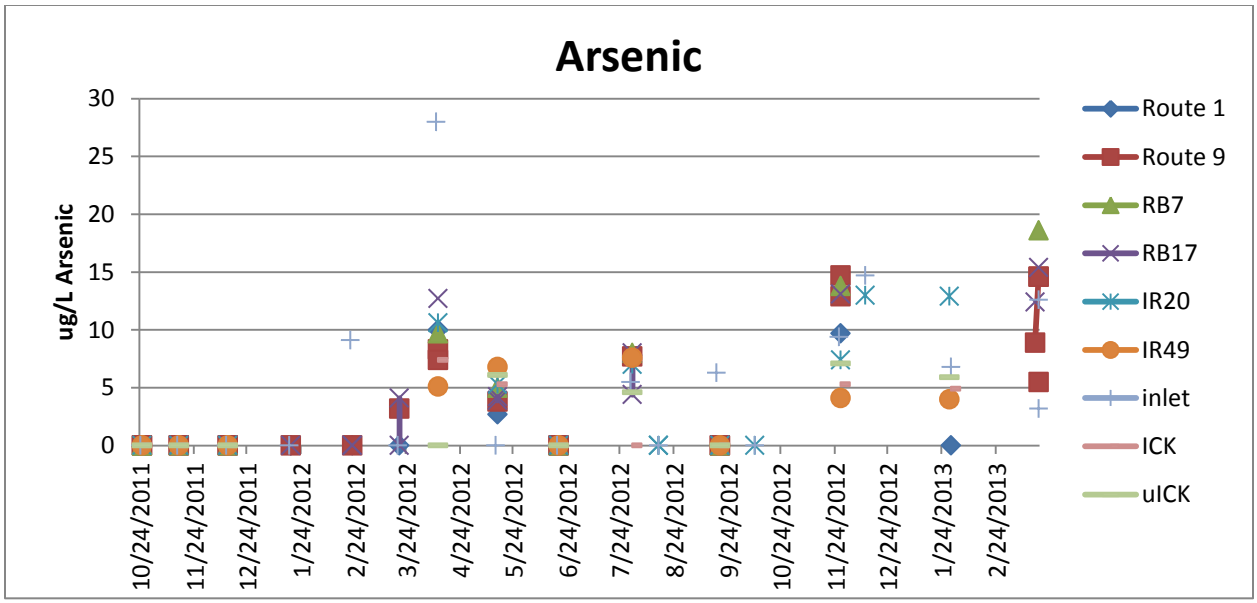
Elevated levels of aluminum, antimony, arsenic, iron, lead, manganese, selenium, thallium, and vanadium leaching from coal ash deposited on Burton Island and the Phase I landfill have previously been reported in the groundwater under these sites and sediments adjacent to Burton Island. (Shaw 2008, NRG 2011) This study was not designed to detect the mode or the extent of transport of materials from the NRG facility, but rather to document if there were differences in the contaminants in sediments and organisms taken from adjacent the disposal sites and a control site some distance removed.

There remain many unanswered questions that go beyond this narrow study. Focusing on arsenic and selenium both are known to be present and to leach from coal ash resulting in the contamination of the groundwater beneath both Burton Island and the unlined Phase I landfill on the opposite shore of Island Creek. Prior studies by NRG (Shaw, 2008) and NRG monitoring well reports have all confirmed this and detected the elevation of arsenic and selenium at the NRG permit monitoring site SG-2 in Island Creek.[1]

Parameter (ug/L)	**4/24/2007**	**10/30/2007**	**4/15/2008**	**2/11/2009**	**4/17/2009**	**10/19/2009**	**4/20/2010**	**10/11/2010**	**4/5/2011**	**10/5/2011**	**Fish + Water Ingestion**	**Marine Chronic Criterion**	**Marine Acute Criterion**
Arsenic (total)	**19**	9	5	**30**	<15	**46**	<30	**42**	4	**27**	10	36 As(III)	69 As (III)
Selenium	17	8	7	**120**	54	**160**	**110**	**160**	13	14	50	71	290
Iron	50	100	50	<60	84	<180	360	<300	<120	<120	-	-	-
Sulfate mg/L	608	1613	1241	1570	632	1260	1360	2330	1150	1890	-	-	-

Both arsenic and selenium may have been released in the vicinity of Island Creek by prior wave erosion of Burton Island, or surface runoff and groundwater inflow from either or both sites. Also, there are other potential additional sources for arsenic. A food additive in chicken feed (roxarsone) contains arsenic and the use of chicken manure as fertilizer has released some additional arsenic to the watershed, as did the reported use of arsenic containing herbicides. However, ambient water quality testing of the Inland Bay tributaries has not detected significant levels of arsenic entering the Inland Bays. This testing has however detected significant spikes of arsenic being transported within the Bays and ultimately being dissipated to the ocean.

[1] NRG is required in its permit to analyze the waters of Island Creek at Station SG-2 adjacent to the Phase I/II Landfill. Station SG-2 consists of a staff gage in Island Creek near the region of groundwater discharge from the Phase I/II Landfill site. Samples are to be taken on the outgoing tide as per the permit.



The question of how has the biota of the Inland Bays been impacted goes beyond the scope of the current study. The CIB effort looked only to dectect differences between the contaminants in sediments and organisms taken from the shoreline of the disposal site and a control site in an adjacent watershed. However, the Pepper Creek sites could still be impacted by potential tidal transport from the disposal areas.

Levels of some metals in sediments and organisms were detected to be elevated relative to the control area. Was this due to the higher levels of contaminates found nearer the disposal site, natural varibality, salinity differences, or some other host of reasons is simply beyond the scope of the effort.

There simply remain more important questions beyond the scope of the current study.

What causes the spikes in concentration observed in arsenic concentrations observed in ambient testing?

Part of the answer may lie in spikes in pH. Storet data records a range since 2011 of pH 6.19-9.23. The intatanious recorder at the Millsboro Dam has recorded levels spiking above pH 10.[2] I cannot explain the causes of the pH changes, but highly alkaline pH conditions would spur the dissolution of arsenic and selenium oxyanions from sediments and coal ash.

What frequency of arsenic levels being detected above Delaware's ambient water quality standards should trigger further testing for evaluation of shellfish and consideration of additional consumption advisories?

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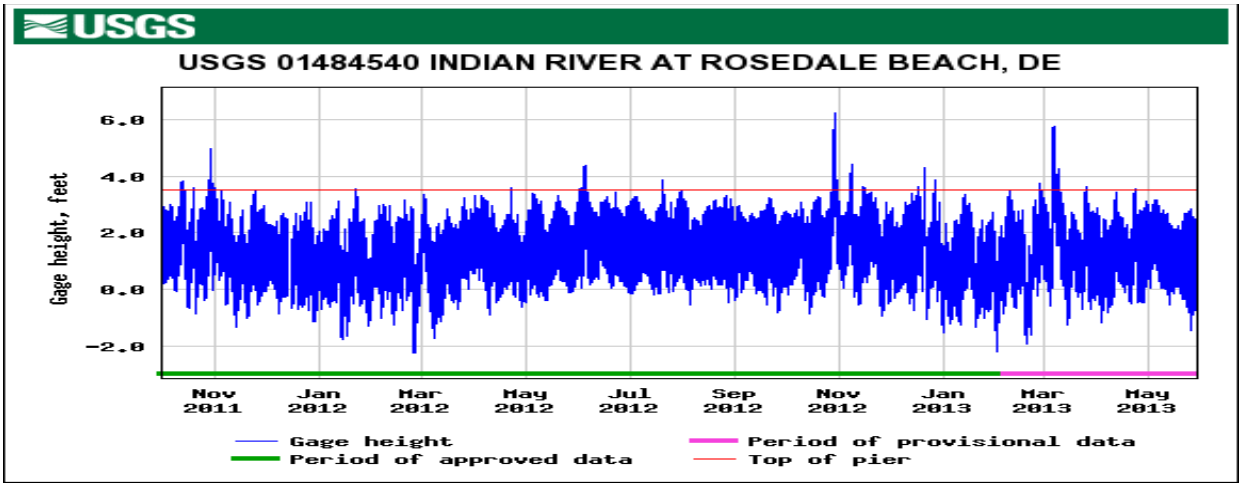
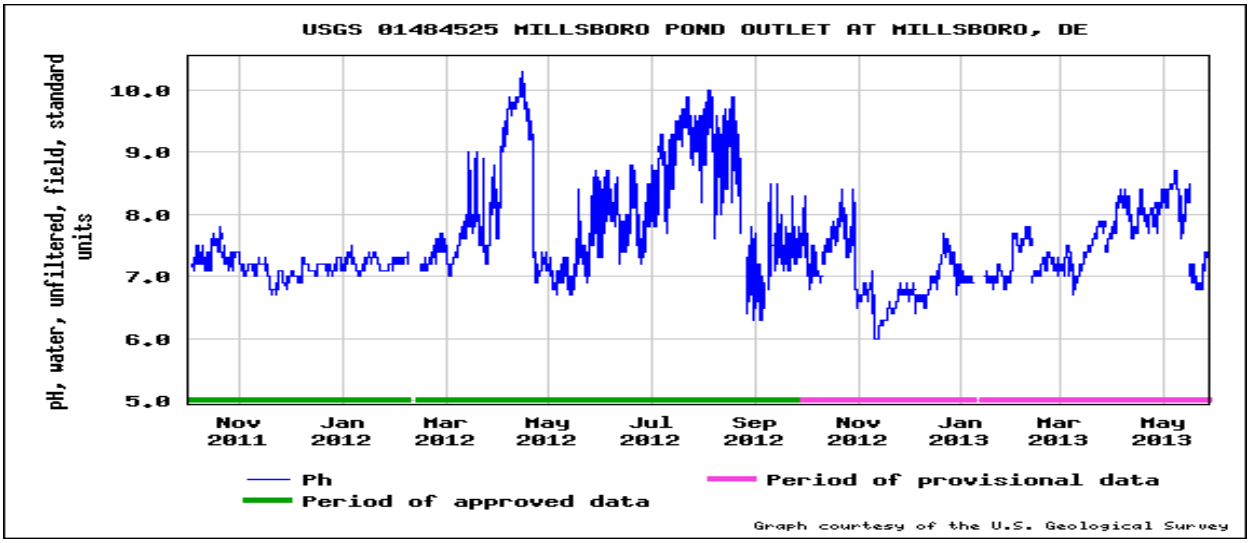
2 http://nwis.waterdata.usgs.gov/de/nwis/uv?cb_00060=on&cb_00065=on&cb_00400=on&cb_00095=on&cb_00010=on&cb_00300=on&cb_00301=on&format=gif_stats&period=&begin_date=2010-01-01&end_date=2013-05-22&site_no=01484525

DNREC conducted ambient water quality testing at Indian River buoy stations from August 1998 until February 2008. Testing resumed in October 2011. Ambient water quality criteria of 10 ug/L arsenic was found to be exceed in four sample sets between 1998 & 2008, and four more since 2011 (All in the last 12 months) in Indian River/Bay (five if you also include Rehoboth Bay). The last time clams were tested was by DNREC in 2002. One site in Indian Run Bay and one site in Rehoboth Bay were sampled.

Recently DNREC completed a survey of where the clams are distributed in the Inland Bays. However, that effort presented to STAC did not include the measurement of heavy metals. http://www.inlandbays.org/wpcontent/documents/HARD%20CLAM%20%28Mercenaria%20mercenaria%29%20Presentation.pdf


USGS
USGS 01484540 INDIAN RIVER AT ROSEDALE BEACH, DE
Gage height, feet
6.0
4.0
2.0
0.0
-2.0
Nov 2011
Jan 2012
Mar 2012
May 2012
Jul 2012
Sep 2012
Nov 2012
Jan 2013
Mar 2013
May 2013
Gage height
Period of approved data
Period of provisional data
Top of pier


USGS 01484525 MILLSBORO POND OUTLET AT MILLSBORO, DE
pH, water, unfiltered, field, standard units
10.0
9.0
8.0
7.0
6.0
5.0
Nov 2011
Jan 2012
Mar 2012
May 2012
Jul 2012
Sep 2012
Nov 2012
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May 2013
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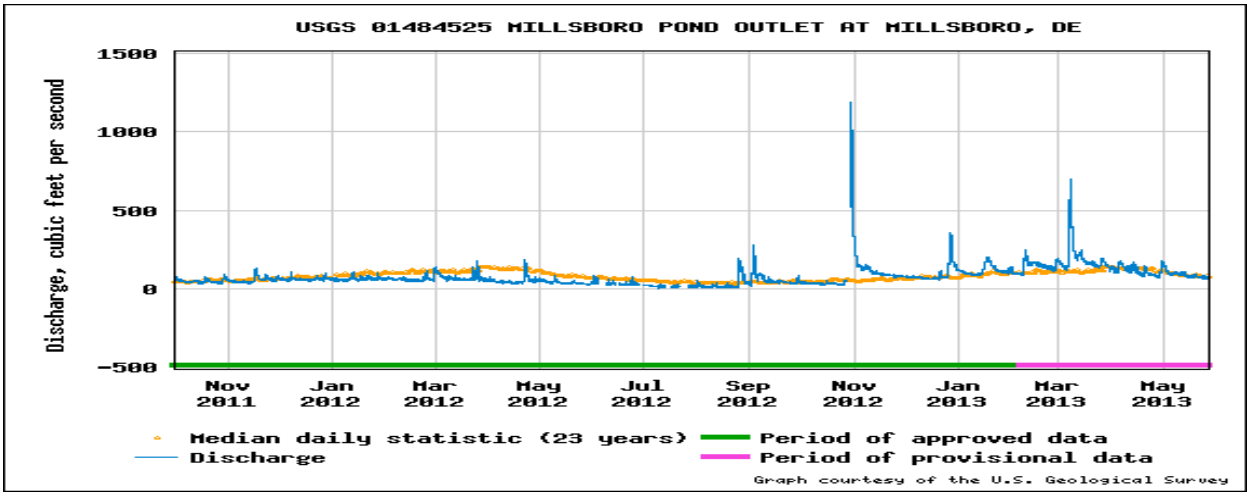
Period of approved data
Period of provisional data
Graph courtesy of the U.S. Geological Survey


USGS 01484525 MILLSBORO POND OUTLET AT MILLSBORO, DE
Discharge, cubic feet per second
1500
1000
500
0
-500
Nov 2011
Jan 2012
Mar 2012
May 2012
Jul 2012
Sep 2012
Nov 2012
Jan 2013
Mar 2013
May 2013
Median daily statistic (23 years)
Discharge
Period of approved data
Period of provisional data
Graph courtesy of the U.S. Geological Survey

Appendix D: Comments on Study by David Bacher (NRG)

Title Page

- The title indicates accumulation in biota. This study did not measure "accumulation" in biota. Nowhere in this report do the authors show accumulation from sediment-to-biota.
- Inaccurate use of the term toxic. "The dose makes the poison". Selenium and other constituents are essential micro-nutrients and are only toxic at elevated concentrations. In fact too little selenium causes toxicity as well as too much. The title of this report pre-supposes that trace elements are accumulated in biota at toxic levels. In fact the report shows just the opposite.
- The report was not prepared "for" NRG or with any association with NRG.

Page 5

- Were both organisms and sediment samples collected from the same locations? Each sediment and organism sample should be co-located. It isn't clear if that is the case or not.

Page 11

- On the map, Burton Island does not show up.

Page 12

- You note the SERC, I assume this is the Smithsonian Environmental Research Center, but it isn't defined anywhere.
- It was noted the composite samples for tissue were thawed, if the samples were not depurated post-collection and prior to analysis could the chemical composition of the tissue sample be significantly affected by the gut contents of the organism and possibly tend to skew the tissue concentrations higher, making it appear that the bioaccumulation is greater than it actually is.

Page 13

- Should the report put the data, specifically Se in terms of the calculated HI which would be well below the level of concern.

Page 14

- What is ICP-OES.
- It would provide greater clarity if the data were presented such that you could see the max detected conc. and the minimum detected concentration.

Page 17

- While the Se levels are higher on one site, not sure if the term "excess' is correct since all measured tissue conc. of Se are less than levels protective of human health and the environment. Maybe this should be noted.

Page 18

- Ash heaps is not a correct term.
- Don't agree with the assumption that "the results suggest" exposure from "ash heaps". They do state it is not proven, however the implication is not supported by the study or valid.

Page 19

- It is good the study notes the difference in salinity. However they should further discuss how salinity can impact bioaccumulation and the correlation on the data from of the two sites. Salinity is a very important factor in the process of bioaccumulation. If there were multiple biota samples, it would be interesting to plot salinity vs bioaccumulation to see what kind of correlation there was.

- The comment on the Remedial Investigation is not accurate. The following sentence better reflects the report.

  Correction The Remedial Investigation Report (2011), showed that the *water table aquifer within Burton Island is characterized by a subtle mounding of the water table in the interior of the peninsula all of the time, and the periods of inward and outward flow of groundwater were controlled by the water levels in the surrounding surface water bodies. Outward flow of fresh groundwater from Burton Island was documented as occurring less than 10 percent of the time, resulting in a net inward flow.*
- The last statement on Page 19 *"This study was not designed to answer this question, although the results of the sediment analysis provide equivocal evidence for the erosion as a major source of input hypothesis."* is not supported by the data. Sediment and biota data from Island Creek are similar to sediment and biota data reported by the Mussel Watch
- Page 20 Figure 7 is from 2008, The conceptual site model for groundwater was significantly revised and refined based on the results of the OU-2 RI. This report should reflect the most recent findings regarding groundwater at Burton Island. A good diagram that shows this is Figure 3.3-9 from the OU-2 RI report.

Page 23

- On recovery it is noted Se is high and in the table it is 142%. Would this indicate the methodology may result in high biased results for tissue analyses and perhaps they should add more detail on this. My understanding is this represents the percent recovery for standards that they analyze in the lab to determine the accuracy of their analytical methods. They have a standard tissue sample (NIST 1566b - National Institute of Standards and Technology) with a known concentration of selenium and the lab analyzes it along with the samples collected from the site for quality control purposes. Because the selenium recovery is 142%, which means the lab results for selenium in the NIST sample were greater than the actual sample concentration (e.g. the NIST sample is known to contain 100 mg/kg selenium and the lab detected 142 mg/kg), this result indicates the lab method is biased high for selenium.