Assessment of Impacts from the Hart-Miller Island Dredged Material Containment Facility, Maryland Year 32 Exterior Monitoring Technical Report (September 2013-August 2014)











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# Prepared by: Environmental Assessment And Standards Program Maryland Department of the Environment





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### **DEFINITION OF TERMS**

Aliquot	A portion of a larger whole, (e.g., a small portion of a sample taken for chemical analysis or other treatment).
Amalgamation	In the chemical context amalgamation is the binding or dissolving of two metals to form an alloy with mercury typically being one of the metals.
Amphipod	Crustacean order containing laterally compressed members such as the sand hoppers.
Anion	A negatively charged ion, (e.g., $\text{Cl}^-$ and $\text{CO}_3^{2^-}$ ).
Anoxic	Deplete of oxygen, (e.g., groundwater that contains no dissolved oxygen).
Bathymetric	Referring to contours of depth below the water's surface.
Benthic	Referring to the bottom of a body of water.
Benthos	The organisms living in or on the bottom of a body of water.
Bioaccumulation	The accumulation of contaminants in the tissue of organisms through any route, including respiration, ingestion, or direct contact with contaminated water, sediment, pore water or dredged material.
Bioaccumulation factor	The degree to which an organism accumulates a chemical compared to the source. It is a dimensionless number or factor derived by dividing the concentration in the organism by that in the source.
Bioassay	A test using a biological system. It involves exposing an organism to a test material and determining a response. There are two major types of bioassays differentiated by response: toxicity tests which measure an effect (e.g., acute toxicity, sublethal/chronic toxicity) and bioaccumulation tests which measure a phenomenon (e.g., the uptake of contaminants into tissues).
Biogenic	Resulting from the activity of living organisms. For example, bivalve shells are biogenic materials.
Biomagnification	Bioaccumulation up the food chain, e.g., the route of accumulation is solely through food. Organisms at higher trophic levels will have higher body burdens than those at lower trophic levels.

Biota	The animal and plant life of a region.
Bioturbation	Mixing of sediments by the burrowing and feeding activities of sediment-dwelling organisms. This disturbs the normal, layered patterns of sediment accumulation.
Box and Whisker Diagram	A graphical summary of the presence of outliers in data for one or two variables. This plot, which is particularly useful for comparing parallel batches of data, divides the data into four equal areas of frequency. A box encloses the middle 50 percent, where the median is represented as a vertical line inside the box. The mean may be plotted as a point.
	Horizontal lines, called whiskers, extend from each end of the box. The lower (left) whisker is drawn from the lower quartile to the smallest point within 1.5 interquartile ranges from the lower quartile. The other whisker is drawn from the upper quartile to the largest point within 1.5 interquartile ranges from the upper quartile.
	Values that fall beyond the whiskers, but within 3 interquartile ranges (suspect outliers), are plotted as individual points. Far outside points (outliers) are distinguished by a special character (a point with a + through it). Outliers are points more than 3 interquartile ranges below the lower quartile or above the upper quartile.
Brackish	Salty, though less saline than sea water. Characteristic of estuarine water.
Bryozoa	Phylum of colonial animals that often share one coelomic cavity. Encrusting and branching forms secrete a protective housing (zooecium) of calcium carbonate or chitinous material. Possess lophophore feeding structure.
Bulk sediment chemistry	Results of chemical analyses of whole sediments (in terms of wet or dry weight), without normalization (e.g., to organic carbon, grain-size, acid volatile sulfide).
Cation	A positively charged ion, (e.g., $Na^+$ and $Mg^{2+}$ ).
Congener	A term in chemistry that refers to one of many variants or configurations of a common chemical structure (e.g., polychlorinated biphenyls [PCBs] occur in 209 different forms with each congener having two or more chlorine atoms located at specific sites on the PCB molecule).

Contaminant	A chemical or biological substance in a form that can be incorporated into, onto or be ingested by and that harms aquatic organisms, consumers of aquatic organisms, or users of the aquatic environment, and includes but is not limited to the substances on the 307(a)(1) list of toxic pollutants of the Clean Water Act promulgated on January 31, 1978 (43 FR 4109).
Contaminated material	Material dredged from Baltimore Harbor, originating to the northwest of a line from North Point to Rock Point. Material shows high concentrations of metals, PCBs, organics, etc.
Dendrogram	A branching, diagrammatic representation of the interrelations of a group of items sharing some common factors (as of natural groups connected by ancestral forms).
Depurate	To cleanse or purify something, especially by removing toxins.
Desiccation	The process of drying thoroughly; exhausting or depriving of moisture.
Diversity index	A statistical measure that incorporates information on the number of species present in a habitat with the abundance of each species. A low diversity index suggests that the habitat has been stressed or disturbed.
Dominant (species)	An organism or a group of organisms that by their size and/or numbers constitute the majority of the community.
Dredge	Any of various machines equipped with scooping or suction devices used in deepening harbors and waterways and in underwater mining.
Dredged material containment	A disposal method that isolates the dredged material from the environment. Dredged material containment is placement of dredged material within diked confined disposal facilities via pipeline or other means.
Dredged Material Containment Facility (DMCF)	A diked area, either in-water or upland, used to contain dredged material. The terms confined disposal facility (CDF), dredged material containment area, diked disposal facility, and confined disposal area are used interchangeably.
Effluent	Something that flows out or forth; an outflow or discharge of waste, as from a sewer.
Effects Range Low (ERL)	Concentration below which effects are rarely observed or predicted among sensitive life stages and (or) species of biota for Sediment Effect

	Concentrations used to evaluate sediment concentrations of trace elements and sediment concentrations of trace elements and synthetic organic compounds.
Effects Range Median (ERM)	Concentration above which effects are frequently or always observed among most species of biota for Sediment Effect Concentrations used to evaluate sediment concentrations of trace elements and synthetic organic compounds.
Enrichment factor	A method of normalizing geochemical data to a reference material, which partially corrects for variation due to grain size.
Epifauna	Benthic animals living on the surface of the bottom.
Fine-grained inmaterial	Sediments consisting of particles less than or equal to 0.062 mm diameter.
Flocculation	An agglomeration of particles bound by electrostatic forces.
Flocculent layer	The transition zone between water column and sediment column. The material in the layer is gelatinous and highly mobile; composed primarily of water with organic matter and fine Clay sized particles. The thickness of the layer varies seasonally and as a function of the flow of water over the sediment-water interface. In the Chesapeake Bay, the flocculent layer is generally less than a centimeter thick, and can be absent in areas of high flow.
Freshet	A sudden overflow of a stream resulting from a heavy rain or a thaw. A stream of fresh water that empties into a body of salt water.
Gas chromatography	A method of chemical analysis in which a sample is vaporized and diffused along with a carrier gas through a liquid or solid adsorbent differential adsorption. A detector records separate peaks as various compounds are released (eluted) from the column.
Gravity core	A sample of sediment from the bottom of a body of water, obtained with a cylindrical device, used to examine sediments at various depths.
Gyre	A circular motion. Used mainly in reference to the circular motion of water in each of the major ocean basins centered in subtropical high-pressure regions.
Hydrodynamics	The study of the dynamics of fluids in motion.

Hydrography	The scientific description and analysis of the physical condition, boundaries, flow, and related characteristics of oceans, rivers, lakes, and other surface waters.
Hydrozoa	A class of coelenterates that characteristically exhibit alternation of generations, with a sessile polypoid colony giving rise to a pelagic medusoid form by asexual budding.
Hypoxic	A partial lack of oxygen.
Infauna	Benthic animals living within bottom material.
Isopleths	Lines on a graph or map connecting points that have equal or corresponding values with regard to certain variables.
Leachate	Water or any other liquid that may contain dissolved (leached) soluble materials, such as organic salts and mineral salts, derived from a solid material.
Least-Squares fit	A method to choose the "best" line fit through a cluster of data points. It is possible to fit many different lines through a set of data points. A line that results in the smallest value of the sum of the squares of the differences between observed and expected values is considered the best fit.
Ligand	Lewis bases that bind by coordinate covalent bonds to transition metals to form complexes.
Littoral zone	The benthic zone between the highest and lowest normal water marks; the intertidal zone.
Mesohaline	Moderately brackish estuarine water with salinity ranging from $5 - 18$ parts per thousand
Metalloid	An element with properties intermediate between non-metals and metals. There are seven metalloids; Boron, Silicon, Germanium, Arsenic, Antimony, Tellurium, Polonium.
Mixing zone	A limited volume of water serving as a zone of initial dilution in the immediate vicinity of a discharge point where receiving water quality may not meet quality standards or other requirements otherwise applicable to the receiving water. The mixing zone may be defined by the volume

	and/or the surface area of the disposal site or specific mixing zone definitions in State water quality standards.
Nephelometric turbidity unit (NTU)	A unit of measurement of the amount of light scattered or reflected by particles within a liquid.
Oligohaline	Water with salt concentrations ranging from 0.5 to 5.0 parts per thousand, due to ocean-derived salts
Open water disposal	Placement of dredged material in rivers, lakes or estuaries via pipeline or surface release from hopper dredges or barges.
Polycyclic aromatic hydrocarbons	Polycyclic aromatic hydrocarbons (PAHs) are a group of over 100 different chemicals that are formed during the incomplete burning of coal, oil and gas, garbage, or other organic substances like tobacco or charbroiled meat.
Pollution Sensitive Taxa	Organisms that are sensitive to pollution.
Pore Water	The water filling the space between grains of sediment.
QA	Quality assurance, the total integrated program for assuring the reliability of data. A system for integrating the quality planning, quality control, quality assessment, and quality improvement efforts to meet user requirements and defined standards of quality with a stated level of confidence.
QC	Quality control, the overall system of technical activities for obtaining prescribed standards of performance in the monitoring and measurement process to meet user requirements.
Radiograph	An image produced on a radiosensitive surface, such as a photographic film, by radiation other than visible light, especially by x-rays passed through an object or by photographing a fluoroscopic image.
Reflux	A technique involving the condensation of vapors in a closed system, and the return of this condensate to the system from which it originated. The process allows a solvent and reagent to be heated continuously at or near the boiling point without the loss of the solvent or reagent.

Salinity	The concentration of salt in a solution. Full strength seawater has a salinity of about 35 parts per thousand (ppt). Normally computed from conductivity or chlorinity.		
Secchi depth	The depth at which a standard, black and white Secchi disk disappears from view when lowered into water.		
Sediment	Material, such as sand, silt, or clay, suspended in or settled on the bottom of a water body.		
Seine	A large fishing net made to hang vertically in the water by weights at the lower edge and floats on the top.		
Sigma	A measure of standard deviation away from the mean of a normally distributed data set. One sigma accounts for approximately 68 percent of the population that makes up the set. Two sigma accounts for approximately 95 percent of the population while three sigma accounts for 99 percent.		
Slag	The fused vitreous material left as a residue by the smelting of metallic ore.		
Spectrophotometer	An instrument used in chemical analysis to measure the intensity of color in a solution.		
Spillway	A channel for an overflow of water.		
Standard Deviation	A statistical measure of the variability of a population or data set. A high standard deviation indicates greater variance around the mean of a data set where as a low standard deviation indicates little variance around the mean.		
Substrate	A surface on or in which a plant or animal grows or is attached.		
Supernatant	The clear fluid over sediment or precipitate.		
Total suspended solids (TSS)	A measurement (usually in milligrams per liter or parts per million) of the amount of particulate matter suspended in a liquid.		
Trace metal	A metal that occurs in minute quantities in a substance.		
Trawl	A large, tapered fishing net of flattened conical shape, towed along the sea bottom. To catch fish by means of a trawl.		

Turbidity	The property of the scattering or reflection of light within a fluid, as caused by suspended or stirred-up particles.
Turbidity maximum	A zone in a water body where turbidity is typically the greatest, resulting from the influx of river-borne sediments, and flocculation of clay particles due to prevailing salinity patterns.
Water Quality Certification	A state certification, pursuant to Section 404 of the Clean Water Act, that the proposed discharge of dredged material will comply with the applicable provisions of Sections 301, 303, 306 and 307 of the Clean Water Act and relevant State laws.
Water quality standard	A law or regulation that consists of the beneficial designated use or uses of a water body, the numeric and narrative water quality criteria that are necessary to protect the use or uses of that particular water body.

# PROJECT I: SUMMARY REPORT FOR THE HART-MILLER ISLAND DREDGED MATERIAL CONTAINMENT FACILITY YEAR 32

(September 2013– August 2014)

Prepared by The Environmental Assessment and Standards Program

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The Hart-Miller Island Dredged Material Containment Facility (HMI DMCF) is a large and complex operation and its success goes to the credit of many individuals within numerous organizations.

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MDE thanks Darlene Wells, Elizabeth Sylvia, and Stephen Van Ryswick, PIs for Project II with Maryland Geological Survey (MGS); and Dr. Andrew Heyes, PI for Project IV with the Chesapeake Biological Laboratory.

MDE would like to thank all the members of the HMI Exterior Monitoring Program's Technical Review Committee, especially Mr. Thomas Kroen, Chairmain of the HMI Citzens Oversight Committee, for their useful comments and suggestions throughout the project year. Special thanks also to the Maryland Port Administration (MPA) for their continued commitment and financial support of the Exterior Monitoring Program. Last but not least, a special appreciation goes to Mr. David Peters, Ms. Cassandra Carr and their staff with Maryland Environmental Service (MES) for their invaluable work in managing all necessary dredging operations of HMI.

#### **INTRODUCTION**

The HMI DMCF (Hart-Miller Island Dredged Material Containment Facility) was designed to receive dredged material from navigation channel maintenance and improvement activities in the Baltimore Harbor and its approaches. Construction of HMI, which entailed building a diked area connecting the remnants of Hart and Miller Island, began in 1981 and was completed in 1983. The facility, encompassing approximately 1,100 acres, is divided by a 4,300 foot interior cross-dike resulting in a North and South Cell. In the early years, material was mainly placed in the South Cell, which was completed on October 12, 1990 after which efforts were initiated to convert it into an upland-wetland wildlife refuge. Placement of dredged material was then diverted to the North Cell and continued until December 31, 2009 at which time all inflow of dredged material ceased.

Because the North Cell is now no longer receiving dredged material while design plans are being finalized, dewatering and crust management will be minimal. The goal is to shape the area creating upland habitat around the northwest side with a gradual slope to the southeast producing a pond ranging in depth from one and a half to six feet in depth with occasional mudflats similar to, but not to the extent of, the South Cell. The current scheduled plan is to use the existing water collected from precipitation events in the cell to form the pond, which allows for minimal discharge during crust management. During this truncated phase of crust management, dredged material could potentially be exposed to air resulting in sulfides becoming oxidized creating acidic conditions during rainfall events. Acidic conditions can mobilize metals, which is cause for concern if discharged to the exterior environment through the spillways. Discharge will continue to be monitored to comply with the permit requirements, and water is not discharged if it does not comply with permit limits. Post closure exterior monitoring will continue to occur to see if any possible concerns do arise during this period.

The first sampling cruises for monitoring Year 28 took place in September 2009, while HMI was still receiving dredged material. The April 2010 sampling cruises marked the first sampling after closure. Thus, only the April 2010 monitoring results can be considered post-closure baseline data. Year 32 marks the fourth full year of post-closure monitoring. It is important that monitoring continues for at least 5 years post-closure during this crucial period of dewatering and crust management, and habitat development of the North Cell to establish a robust post-closure data set. These 5 years of data can then be compared to the thirty years of data collected during dredged material placement. This comparison of pre- and post-closure data will allow the scientists to determine differences, if any, in the exterior environment, and whether the differences were a result of HMI operations. The information learned can be applied to future dredged material containment facilities.

Throughout this Year 32 Exterior Monitoring Technical report, the companion *Year 32 Data Report* is referenced. This report contains the detailed information in regards to sampling locations, field description of samples which includes and is not limited to the number of specimens collected and the detailed results of findings.

Year 32 represents the fourth year of post-closure monitoring, and unlike previous sampling years, no spring samples were taken. Further, monitoring will continue but with a reduced sampling grid (15 sampling sites), which will be conducted every other year beginning in the fall of 2014. The final bi-annual sampling is scheduled to be collected in fall of 2018. The biannual data will be reviewed with the citizens. MGS will continue to evaluate ground water data collected by MES on a quarterly basis. This monitoring schedule is also adaptive depending on future findings, which includes taking into account the occurrence of any unusual events. In 2019, the frequency of monitoring will be reevaluated based on the findings in Project II, Project III, and Project IV. Close cooperation with MPA and MES will continue to be important in this endeavor.

#### HMI EXTERIOR MONITORING DESIGN

The HMI DMCF Exterior Monitoring Program is modeled after the Sediment Quality Triad developed in the mid-1980s (Long and Chapman, 1985). This approach consists of three separate components: sediment chemistry, sediment toxicity, and benthic community composition. The sediment chemistry project (Project II) assesses contamination by evaluating metal concentrations in exterior sediments. Project III, benthic community studies, monitors animal communities living in sediments surrounding HMI. As a surrogate for toxicity, Project IV looks at benthic tissue concentrations of both metals and organics in the brackish-water clam *Rangia cuneata*. Whereas sediment contamination thresholds, benthic toxicity benchmarks, and benthic macroinvertebrate indices alone may not conclusively identify pollution impacts, combining them into a triad approach provides a body of evidence for pollution determinations. Summary Table 1-1 below illustrates the triad concept.

Scenario	Sediment Contamination (Project II)	Toxicity (Project IV)	Benthic Community Impacts (Project III)	Possible Conclusions
1	+	+	+	Strong evidence for pollution
2	-	_	-	Strong evidence that there is no pollution
3	+	-	-	Sediment pollutants are elevated but not affecting biota
4	-	+	-	Pollutant levels increasing through food chain
5	-	-	+	Benthic community impacts not a result of pollution
6	+	+	-	Pollutants are stressing the system
7	-	+	+	Pollutants increasing through the food chain and altering the benthic community
8	+	-	+	Pollutants are available at chronic, non-lethal levels

# Summary Table 1-1: Differential Triad Responses



Summary Figure 1-1: Shows the sampling design and the parameters which were monitored. For Year 32, MGS analyzed sediment for physical and chemical properties from all 43 sites, MDE sampled the benthic organisms at 22 sites, and CBL collected the brackish water clam *Rangia cuneata* from 10 sites in the fall for tissue and sediment analysis of metals and metalloids.

#### HMI PROJECT SUMMARIES

#### **PROJECT II: Sedimentary Environment and Groundwater Monitoring**

The Coastal and Environmental Geosciences Program of the MGS has been involved in monitoring the physical and chemical behavior of near-surface sediments around HMI DMCF from the initial planning stages of construction of the facility to the present. The facility stopped receiving dredged material in December 2009. As part of the 32<sup>nd</sup> year exterior monitoring program, MGS collected bottom sediment samples from 43 sites on September 10, 2013; there was no spring sampling this year. The sediment samples were analyzed for various physical and chemical properties of the samples: (1) grain size composition (relative proportions of sand, silt, and clay) and (2) total elemental concentrations of iron (Fe), manganese (Mn), zinc (Zn), copper (Cu), chromium (Cr), nickel (Ni), cadmium (Cd), lead (Pb), phosphorous (P), carbon (C), nitrogen (N), and sulfur (S).

An analysis of grain size distribution of Year 32 does not display any clear trends in sedimentation patterns from the previous year. The utilization and findings of the sedimentological procedures described in Kerhin et al. (1988) shows a depositional environment that was similar during the last five monitoring years. The general sediment distribution is consistent with the findings of previous monitoring years dating back to 1988.

Sediment metal data was interpreted by taking into account grain size induced variability and references the data to a regional norm. This method involves correlating metal levels with grain size composition on a data set that can be used as a reference for comparison. Samples collected in Year 32 showed no abberant behavior in metal levels. At most sampling sites, concentrations of Cr, Cu, and Pb in the sediment exceed the ERL (Effects Range Low) values, while concentrations of Ni exceed the ERM (Effects Range Median) values at some sites. In addition, at some sites, the concentrations of Zn exceed the ERM values. Concentrations between the ERL and ERM may have adverse impacts to benthic organisms, while values greater than the ERM have probable adverse biological effects. These criteria are based on a statistical method of termed preponderance of evidence. The method does not allow for unique basin conditions and does not take into account grain size induced variability in metal concentrations in the sediment. Therefore, through the grain size normalization procedure that corrects the deficiencies and normalizes the data, findings reveal that Pb and Zn are significantly enriched in some samples compared to the baseline.

Presented in Appendix 1A, the groundwater monitoring report is a summary of the HMI well data collected on September 24, 2013, December 17, 2013, March 21, 2014 and June 10, 2014. These wells are part of 34 wells installed around the facility dike between 2001 and

February 2002 for a groundwater study (US, 2003). The purpose of the study was to identify 1) the direction and rate of groundwater flow from the facility to the surrounding Bay, and 2) physical and chemical reactions controlling the mobilization of contaminants from the facility.

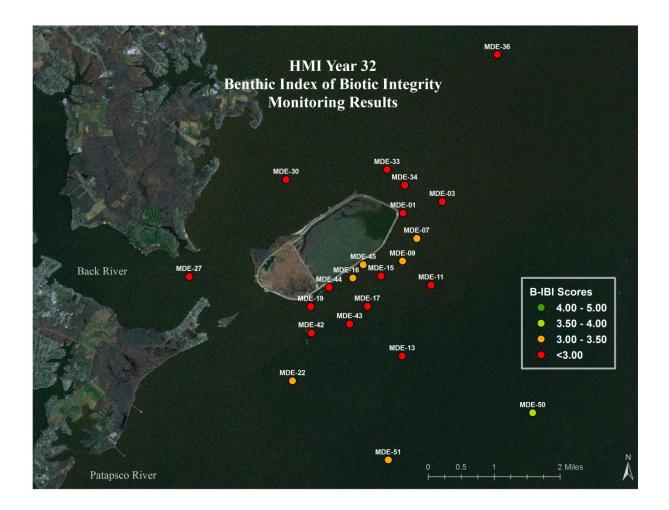
MES analyzed the water samples for the following parameters: pH, temperature, conductivity, dissolved oxygen (DO), oxygen-reduction potential (ORP), salinity, alkalinity, chloride (Cl<sup>-</sup>), sulfate, total Kjeldahl nitrogen (TKN), total nitrogen (TN), nitrates/nitrites (NO<sub>3</sub><sup>-</sup>/NO<sub>2</sub><sup>-</sup>), P (Phosphorus), aluminum (Al), arsenic (As), cadmium (Cd), calcium (Ca), Chromuim (Cr), Copper (Cu), Iron (Fe) Lead (Pb), magnesium (Mg), Manganese (Mn)potassium (K), silver (Ag), sodium (Na), and Zinc (Zn). The Maryland Geological Survey (MGS) evaluated the results of the MES analyses of the water samples.

Results show that the North Cell Well 2A is the only well that continues to have a reducing environment, whereas Wells 4A, and to a lesser degree, 6A, are more similar to the oxidizing environment seen in the South Cell wells. Multiple field and metal parameters in all wells began to show irregular fluctuations after October 2012. These fluctuation in water chemistry are thought to be seasonal as well as delayed responses to operation activities in the North Cell and to weather events; the degree of responses affected by a number of factors including well location, depth and differences in infill (sediment) and dike wall composition. Nevertheless, the metal concentrations in both the North and South Cell wells showed a decreasing trend this monitoring year. Copper and lead remain below the detection limit in both cells. Fe and Mn are the only metals with concentration that exceed the EPA Secondary Maximum Concentration Levels (SMCL).

#### **PROJECT III: Benthic Community Studies**

The benthic macroinvertebrate community in the vicinity of the HMI DMCF was studied for 32<sup>nd</sup> consecutive year under Project III of the HMI Exterior Monitoring Program. The water quality parameters measured *in situ* included dissolved oxygen concentrations, salinity, temperature, pH conductivity, and Secchi depth. Twenty-two stations were sampled on September 19, 2013. Unlike previous years, there was no spring cruise conducted due to the scaling back of the monitoring efforts. The salinity regime was in its historical average range.

The Chesapeake Bay Benthic Index of Biotic Integrity (B-IBI), a multi-metric index of biotic condition that evaluates summer populations of benthic macro-invertebrates, was calculated for all stations. The B-IBI's and derivative metrics (Total Infaunal Abundance, Pollution Indicative Taxa Abundance, Pollution Sensitive Taxa Abundance, and ShannonWeiner Diversity Index) were compared to historical data and were analyzed both spatially and statistically.



Summary Figure 1-2: Year 32 B-IBI Monitoring Results

Similar to Year 31, findings in Year 32 showed that the health of the benthic macroinvertebrate community was worse than historical averages. B-IBI's around the island were at or near historical lows. Out of 22 stations, 14 failed to meet the benchmark criteria of 3.00. This finding is similar to Year 31 where 11 stations failed to meet the criteria. Also, 19 out of the 22 performed below their historical averages. The four year decline in B-IBI's can be attributed to fluctuations in the invertebrate community, which included decreases in the relative abundance of the pollution sensitive polychaete worm *M. viridis* and the bivalves *R. cuneata* and *M. balthica*. Another fluctuation was the high average abundance of the pollution indicative

polychaete worm, *S. benedicti*. The abundance of all organisms was especially high, causing the decreases in the Total Infaunal Abundance metric scores and the relative Pollution Sensitive Taxa Abundance metric. The resultant dilution of pollution indicative species was not as influential on the Pollution Indicative Taxa Abundance metric scores.

The statistical analyses did not indicate that the stressed benthic invertebrate communities measured at stations in September 2013 were due to any adverse localized impacts from HMI operational discharges. Stressed benthic communities throughout the monitoring area were likely the result of large-scale Bay-wide and regional factors.

#### **PROJECT IV: Analytical Services**

As part of the HMI annual exterior sediment survey for Year 32, the University of Maryland for Environmental Science Chesapeake Biological Laboratory (UMCES) measured and evaluated the levels of sediment contaminants in the vicinity of HMI. A minimum of 10 sites were selected from the larger pool, where sediments and clams were collected and analyzed for mercury (Hg), methylmercury (MeHg), silver (Ag), selenium (Se), arsenic (As), lead (Pb) and cadmium (Cd). The concentrations of target trace elements in surface sediments in a number of stations were also determined, including polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs). The results of quality assurance (QA/QC) were acceptable. In the past, stations have shown to not have enrichments of more than one trace element when compared to a sites running mean. In general, concentrations were very close to the sites running mean for 1998-2012 with the one exception. In 2013, only one site, MDE-48, had enrichment in As, Hg, and MeHg relative to their respective previous means. Site 48 is one of the two sites not in the zone of influence of Baltimore Harbor and could warrant further monitoring. In some sites, concentrations of As in sediment have been trending upward at a large number of sites since 2005, and this trend continues in 2013. Conversely, concentrations of Se appear to be trending downward, as concentrations in 2013 appear similar to 2012. Concentrations of MeHg were lower than the site means at all sites. The one exception that was not consistent with the running mean was T-Hg (total mercury). T-Hg is different from the other trace elements and is not well correlated with Se, As, or Ag as T-Hg appears more dependent on organic matter and clay content of sediment than the other elements. T-Hg was elevated in concentration at more than half of the sites.

Additionally, the clam *Rangia Cuneata* was collected from 10 stations in the fall, and similarly, concentrations in these clams were similar to the running mean determined from previous years with some exceptions. Concentrations of PCBs in sediment collected in September 2013 were generally similar to or below the historical site averages, being within the

standard deviation of the mean. The total concentrations of PAHs in sediment collected in 2013 from sites were similar to or below historical levels. Concentrations of PAHs in clams were well below historic levels at all sites, including the reference sites.

#### **PROJECT 1 SUMMARY AND RECOMMENDATIONS**

As part of the 32<sup>nd</sup> year exterior monitoring program, MGS collected bottom sediment samples from 43 sites on September 10, 2013; there was no spring sampling this year. The sediment samples were analyzed for various physical and chemical properties of samples, which included grain size composition. The grain size distribution did not show any clear trends in sedimentation patterns from the previous year. The clay:mud ratios show that the depositional environment was similar during the last five monitoring years. The general sediment distribution pattern is consistent with the findings of previous monitoring years dating back to 1988 (the second year after the start of release from HMI) and no significant changes occurred during Year 32. This year's monitoring documents a slight increase over the previous year in enrichment of Ni, Pb and Zn around the HMI facility. Although in regards to water management, all discharged water meets the State Discharge Permit Regulations and is discharged within limits, this persistent enriched level indicates a need for continued monitoring due to the water quality issues which have been exacerbated by unusual weather events, which contributed a significant volume of fresh, oxygenated water to the facility. ERL and ERM for the concentrations of the elements are similar to the previous three years' findings. Most sampling sites exhibited concentrations of Cr, Cu, and Pb in the sediment, which exceeded ERL values, while concentrations of Ni exceed the ERM values. Additionally, concentrations of Zn exceed the ERM values at some sites.

Similar to the previous year, MES documented a very low pH as well as high metals in the North Cell on several occasions during this monitoring year. Therefore, no water was discharged directly from the North Cell spillways, nor was water transferred to the South Cell as it was done during the previous year. Consequently, over 500 million gallons of water still remain in the North Cell at the end of the monitoring year. Due to fragile pond conditions and efforts to control pH in the South Cell, minimal water was discharged from the South Cell. Monitoring should continue in order to document the effect that operations has on the exterior environment and to assess the effectiveness of any amelioration protocol implemented by MES to counteract the effects of crust and water management inside the facility.

The health of the benthic macroinvertebrate community around HMI in Year 32 was worse than historical averages. B-IBI's around the island were at or near historical lows. Seven stations set new historic lows; four tied their historic lows. No stations met their historic highs. Year 32 marks the fourth consecutive year where B-IBI's have been trending downward. The four year decline in B-IBI's and the Year 32 low B-IBI's were attributable to several variations in the invertebrate community. Total infaunal abundances were exceptionally high for most organisms (both pollution tolerant, pollution indicative, and non-designated species). These high abundances depressed the total infaunal abundances metric slightly throughout the region. As in most years with poor B-IBI's, the abundances of some pollution sensitive taxa were below average. Among these, the bivalves, *M. balthica* and *R. cuneata*, while rebounding from recent die-offs, were still below average in abundance. The abundances of pollution indicative taxa were also above historic averages. Future monitoring plans will be the continuation of benthic monitoring at a reduced level until stabilization of the island is complete. This involves sampling fifteen select sites every fall, starting in 2014.

For analytical services, sediments of a few sites have been enriched in more than one trace element to a degree well above the historic means, but this was not the case in 2013. In general, concentrations were close to the sites running median for 1998-2012 with the exception of T-Hg, which was elevated in concentration at more than half of the sites. Concentrations of As have been trending upwards in recent years, but this may be simply part of an oscillation seen in previous years. Some deviations in the relationships between trace elements in sediment suggest changes in source or are the result of differences in diagenetic behavior. Concentrations of trace elements in clams were similar to or below concentrations in previous years. Bioaccumulation of some traces such as MeHg occurred as anticipated. The pattern in metal bioaccumulation was similar in both years, and no site appeared to stand apart from the other sites. In the case of organic contaminants, concentrations of PCBs in sediment were similar to historic values and the concentration in clams was below historic levels. The majority of PAHs in sediment was similar to that of the past years consisting of the following: 2-methylnapthalene, phenanthrene, fluoranthene, pyrene, benzo[b]fluoranthene, and perylene. Although naphthalene was present, the compound was lower in concentration compared to previous years. PAHs were seldom detected in the clams, which has been the case in past. Due to this being only the fourth full year of post-closure exterior monitoring for HMI, monitoring needs to continue for a number of years to further evaluate changes, trends, and impacts in the environment surrounding HMI.

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# APPENDIX 1: SEDIMENTARY ENVIRONMENT YEAR 32

## (PROJECT II)

(September 2013-June 2014)

## **Technical Report**

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#### **EXECUTIVE SUMMARY**

The Coastal and Environmental Geosciences Program of the MGS has been involved in monitoring the physical and chemical behavior of near-surface sediments around the Hart-Miller Island Dredged Material Containment Facility (HMI DMCF) from the initial planning stages of construction of the facility to the present. The Facility stopped receiving dredged material in December, 2009. As part of the 32<sup>nd</sup> year exterior monitoring program, MGS collected bottom sediment samples from 43 sites on September 10, 2013; there was no spring sampling this year. The sediment samples were analyzed for various physical and chemical properties of the samples: (1) grain size composition (relative proportions of sand, silt, and clay) and (2) total elemental concentrations of iron (Fe), manganese (Mn), zinc (Zn), copper (Cu), chromium (Cr), nickel (Ni), cadmium (Cd), lead (Pb), phosphorous (P), carbon (C), nitrogen (N), and sulfur (S).

The grain size distribution of the Year 32 sediment samples does not show any clear trends in sedimentation patterns from the previous year. Effects from Hurricane Sandy, which occurred at the end of October, 2012, were minimal around the exterior of the HMI DMCF. The clay:mud ratios show that the depositional environment was similar during the last five monitoring years. The general sediment distribution pattern is consistent with the findings of previous monitoring years dating back to 1988 (the second year after the start of release from HMI) and no significant changes occurred during Year 32.

Elemental analyses data indicate that the sediments are similar to the previous year including the anomalously high Cr value measured at a sampling site in the Baltimore Harbor Zone of influence; this Zone has consistently been high in metals in previous years. Based on summary statistics, the elemental data show that:

- 1. At most sampling sites, concentrations of Cr, Cu, and Pb in the sediment exceed the Effects Range Low (ERL) values; and
- 2. At most sampling sites, concentrations of Ni exceed the Effects Range Median (ERM) values; and at some sites, Zn exceeds the ERM values.

ERL and ERM are proposed criteria put forward by NOAA (Buchman, 2008) to gauge the potential for deleterious biological effects. Sediments with concentrations below the ERL are considered baseline concentrations with no expected adverse effects. Concentrations between the ERL and ERM may have adverse impacts to benthic organisms, while values greater than the ERM have probable adverse biological effects. These criteria are based on a statistical method of termed preponderance of evidence. The method does not allow for unique basin conditions and does not take into account grain size induced variability in metal concentrations in the sediment. The grain size normalization procedure outlined in the previous section is a means to correct the deficiencies of the guidelines by taking into account the unique character of Chesapeake Bay sediments and eliminating grain size variability. When the data are normalized, Pb, and Zn are significantly enriched in some samples compared to the baseline.

In regard to potential adverse benthic effects the overlap of enrichment and concentration can be used as an indicator of potential biological impacts: based on the intensity of the effect

(enrichment based on sigma level, and concentrations exceeding ERL or ERM), and in regard to the number of samples, Pb>Zn>Ni. Within the HMI Zone of influence (both distal and proximal), the sediments containing multiple metals (primarily Ni, Pb or Zn) exceeding ERLs or ERMs, and sigma levels greater than 2 include sites MDE-9, -11, -13, -14, -18, and -45. From the preliminary toxicology work done in Year 25, enrichments of Zn and Pb are probably the most significant in influencing benthic communities as a result of HMI operations. Pb enriched samples are associated with the three local sources HMI, Baltimore Harbor and Back River. Zn on the other hand shows enrichment from Baltimore Harbor and a decreasing enrichment from HMI. The two sampling sites in Back River showed no enrichment for Zn.

Prior to Year 28 monitoring, most of the samples with potential benthic effects due to high concentrations of Ni were in the Back River and Baltimore Harbor Zones of Influence. Between Monitoring Years 28 and 30, sigma levels of Ni steadily increased in the HMI Zone. In Year 31, sigma levels of Ni were within normal ranges in the HMI Zone. This year, two sites in the HMI Zone showed significant enrichment in Ni. In terms of absolute concentration, Ni continues to exceed ERL at most sites and ERMs at some sites.

This year's monitoring documents slight increase over the previous year in enrichment of Ni and Zn around the HMI facility. Enrichment of Pb continues to be above background levels. These enriched levels indicate a need for continued monitoring, particularly since the facility has experienced water quality issues related to crust management operations and to unusual weather events resulting in high influx of fresh water to the facility. Similar to the previous year, MES documented very low pH as well as high metals in the North Cell on several occasions during this monitoring year. Therefore, no water was discharged directly from the North Cell spillways, nor was water transferred to the South Cell as it was done during the previous year. Consequently, over 500 million gallons of water still remain in the North Cell. Due to fragile pond conditions and efforts to control pH in the South Cell, minimal water was discharged from the South Cell. Monitoring should continue in order to document the effect that operations has on the exterior environment and to assess the effectiveness of any amelioration protocol implemented by MES to counteract the effects of crust and water management inside the facility. Close cooperation with MES is important in this endeavor.

#### INTRODUCTION

Since 1981, the MGS has monitored the sedimentary environment in the vicinity of HMI DMCF. HMI is a man-made enclosure in northern Chesapeake Bay, named for the two natural islands that form part of its western perimeter.

Designed specifically to contain material dredged from Baltimore Harbor and its approach channels, the oblong structure was constructed of sediment dredged from the facility interior. The physical and geochemical properties of the older, "pristine" sediment used in dike construction differed from those of modern sediments accumulating around the island. Likewise, material dredged from shipping channels as well as channels in Baltimore Harbor, near commercial docks, which generally have local sources of material of concern, and deposited inside the facility also differ from recently deposited sediments in the region. Much of the material generated by channel deepening is fine-grained and enriched in trace metals and organic constituents. In addition, oxidation of the sediment placed in the facility produces effluent enriched in metals. Oxidation occurs when the sediments are exposed to aerated conditions; this occurs during periods of dewatering and crust management. These differences in sediment properties and discharge from the facility have allowed the detection of changes attributable to construction and operation of the facility. All effluent discharged from HMI facility must meet water quality permit limits for metal concentrations.

### **Previous Work**

Events in the history of the facility can be meaningfully grouped into the following periods:

- 1. Preconstruction (Summer 1981 and earlier)
- 2. Construction (Fall 1981 Winter 1983)
- 3. Post-construction
  - a. Pre-discharge (April 1984 Fall 1986)
  - b. Post-discharge (Fall 1986 present).
- 4. Closing of South Cell to new dredged material (Oct. 1990)
- 5. Closing of North Cell to new dredged material (Dec. 2009).

The nature of the sedimentary environment prior to and during dike construction has been well documented in earlier reports (Kerhin *et al.*, 1982a, 1982b; Wells and Kerhin 1983; Wells *et al.*, 1984; Wells and Kerhin 1985). This work established a baseline against which changes due to operation of the facility could be measured. The most notable effect of dike construction on the surrounding sedimentary environment was the deposition of a thick, light gray to pink layer of "fluid mud" immediately southeast of the facility (Wells and Kerhin, 1983; 1985).

For a number of years after HMI began operating, no major changes were observed in the surrounding sedimentary environment. Then, in April 1989, more than two years after the first release of effluent from the facility, anomalously high Zn values were detected in samples collected near Spillway 007 (Hennessee *et al.*, 1990). Zn levels rose from the regional average

enrichment factor of 3.2 to 5.5; enrichment factors are normalized concentrations, referenced to a standard material. Enrichment factors are the ratios of concentrations, in this case Zn to Fe, which are in turn normalized to the same ratio in a standard reference material; this number is dimensionless. Effluent discharged during normal operation of the facility was thought to be the probable source of the enrichment of Zn accumulating in the sediments. This was confirmed by use of the Upper Bay Model (Wang, 1993), a numerical, hydrodynamic model, which was used to predict the dispersion of discharge from the facility, coupled with discharge records from the spillways. From the discharge records it was noted that there is a significant increase in metal loading to the exterior sediments during periods of low discharge [<10 million gallons per day (MGD)]; periods of higher discharge rates corresponded to lower metal levels in the exterior sediments.

The factors that influence the metals loadings to the exterior sediments are circulation patterns in the northern Bay (Figure 1-1) and the rate and the nature of discharge from the facility. The results of the hydrodynamic model pertinent to a discussion of contaminant distribution around HMI follow (see the *Year 10 Technical Report* for details):

- 1. A circulation gyre exists east of HMI (Figure 1-1). The gyre circulates water in a clockwise pattern, compressing the discharge from the facility against the eastern and southeastern perimeter of the dike.
- 2. Releases from Spillways 007 and 009 travel in a narrow, highly concentrated band up and down the eastern side of the dike. This explains the location of areas of periodically high metal concentrations east and southeast of the facility.
- 3. Releases from Spillway 008 are spread more evenly to the north, east, and west. However, dispersion is not as great as from Spillways 007 and 009 because of the lower shearing and straining motions away from the influence of the gyre.
- 4. The circulation gyre is modulated by fresh water flow from the Susquehanna River. The higher the flow from the Susquehanna, the stronger the circulation pattern and the greater the compression against the dike. Conversely, the lower the flow, the less the compression and the greater the dispersion away from the dike.
- 5. Discharge from the HMI spillways has no influence on the circulation gyre. This was determined by simulating point discharges of 0-70 MGD from three different spillways. Changes in discharge rate only affect the rate of dilution of species released from the facility; the higher the discharge, the higher the concentration in the plume outside the facility.

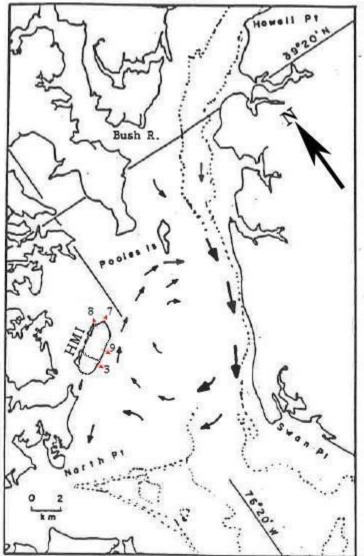


Figure 1- 1: Schematic surface gyre circulation in the upper Chesapeake Bay and relation to HMI DMCF (modified from Wang, 1993). Red arrows indicate approximate location of the HMI DMCF spillways; numbers 3, 7, 8 and 9 identify spillways 003, 007, 008 and 009, respectively.

The 3-D hydrodynamic model explains the structure of the plume of material found in the exterior sediments, but it does not explain why the level of Zn in the sediments increases at lower discharges. To account for this behavior, the chemistry of the effluent discharged from the facility was examined, as reported in the *Year 11 Technical Report*. As a result of this examination, a model was constructed to predict the general trend in the behavior of Zn as a function of discharge rate from the facility. The model has two components: (1) loading due to material similar to the sediment in place and (2) loading of enriched material as predicted from a regression line based on discharge data supplied by MES. The behavior of this model supports the hypothesis of metal contamination during low flow conditions. Sediments discharged from the facility are one of the sources of metals that enrich the exterior sediments. When exposed to the atmosphere, these sediments oxidize in a process analogous to acid mine drainage (i.e.,

sulfide minerals oxidize to produce sulfuric acid, which leaches acid-soluble metals, nutrients, and organic compounds that are released with the discharged waters). Since the initial detection of Zn, the size of the affected area has fluctuated, as have metal concentrations within the area. Nonetheless, higher than expected levels of Zn and Pb have persisted in the vicinity of the facility. Figure 1-2, in addition to showing the sampling sites for Year 32, shows zones which indicate influence of sources of material to the exterior sedimentary environment based on elevated metal levels from previous years' studies. These influences are noted in the figure as:

- 1. Reference representing the overall blanketing of sediment from the Susquehanna River;
- 2. *Back River* Gradients showing the sewage treatment plant as a source carried by the river have varied through time; the sites in this zone encompass the area that has shown the influence from this source. Further documentation of this source was done in the *Year 16 Technical Report*, where samples were collected upstream beyond the sewage treatment plant. These samples clearly showed a continuous gradient from the plant down Back River approaching HMI;
- 3. *HMI* The area of influence from the facility is divided into two zones, (a) the proximal zone, which shows the most consistent enrichment levels through time, and (b) the distal zone, which is affected primarily during extended periods of dewatering and crust management, and;
- 4. *Baltimore Harbor* Sites in the southern portion of the area have consistently shown a gradient, indicating that Baltimore Harbor is a source of metals in the area south of HMI. The consistent pattern seen in the monitoring studies is base level values near HMI, which increase towards Baltimore Harbor. This pattern supports the results of a hydrodynamic model analyses performed in conjunction with the 1997 sediment characterization of Baltimore Harbor and Back River (Baker *et al.*, 1998). During Year 22 monitoring, near record rainfall levels in the area strongly influenced the hydrodynamic flow, resulting in the incursion of Baltimore Harbor material into the HMI zone. This sampling period was the only time in the 32 years of monitoring that this occurred. Surprisingly, the record rainfall from back-to-back storms in Year 30 monitoring (*i.e.*, Hurricane Irene, and Tropical Storm Lee) and Year 31 (Hurricane Sandy) did not result in any incursion of Baltimore Harbor material (MDE, 2013).

HMI stopped accepting dredged material after December 31, 2009 and facility operations shifted to dewatering and long-term crust management in the North Cell in preparation for environmental restoration activities. Past monitoring studies have shown that, during periods of extended crust management and dewatering when discharge volume is decreasing, metal concentrations in the discharge tend to increase. Therefore, metals concentrations in the sediments in the region of HMI influence to the east of the facility are expected to increase during the post-closure operation phase. In anticipation of these changes, a modified sediment sampling scheme was implemented during the 27<sup>th</sup> monitoring year, to provide better coverage in targeted areas south and east of the facility (Rowe and Hill, 2008). The modified sampling

scheme has been continued during this 32<sup>nd</sup> monitoring year (Figure 1-2). This year represents the fourth year of post-closure monitoring phase and covers only the fall sampling (Cruise 67). Monitoring after this year will be at a reduced effort both in areal coverage and frequency of sampling.

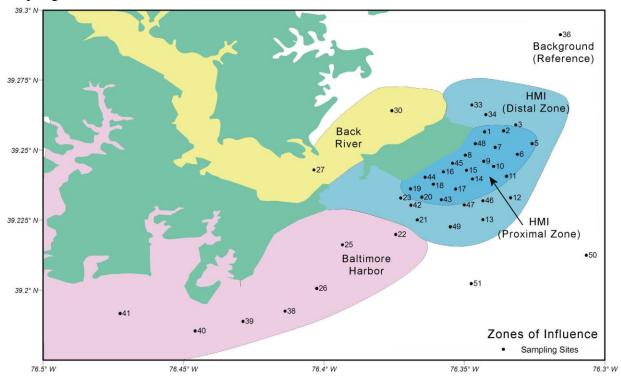


Figure 1- 2: Sampling locations for Year 32. Color areas show zones of influence found in previous studies. Stations 38 – 41 were added in Year 18 to measure the influence of Baltimore Harbor. Starting in Year 27, four stations in the Back River zone were dropped and additional stations added in the proximal zone and southeast of the facility, beyond the HMI zone of influence.

#### **Facility Operations**

Certain activities associated with the operation of HMI have a direct impact on the exterior sedimentary environment. Local Bay floor sediments are sensitive, both physically and geochemically, to the release of effluent from the facility. Events or operational decisions that affect the quality or quantity of effluent discharged from the facility account for some of the changes in exterior sediment properties observed over time. For this reason, facility operations during the periods preceding Year 32 cruise (67) are summarized below. Information, which was provided by Carolyn Blakeney, Cassandra Carr, Rachel O'Shea, and Amanda Peñafiel of MES, covered the period from September 1, 2012 to September 30, 2013.

The facility stopped accepting new dredged material at the end of 2009, after which operations in the North Cell focused on dewatering activities and long-term crust management in preparation for environmental restoration efforts. Precipitation accounted for almost all of the water input in the North and South Cells. The South Cell also received water that flows into the holding pond used for controlling the interior waterfowl pond and spray irrigation.

Figure 1-3 compares the monthly rainfall for HMI and Baltimore Washington International Airport (BWI) for the period between September 2012 and September 2013. The trend in monthly total precipitation recorded at HMI generally tracked that of BWI. The differences in HMI and BWI monthly amounts illustrate the variations in precipitation on a local scale. Hurricane Sandy (unofficially called "Super Storm Sandy"), which made landfall near Brigantine, New Jersey on Oct. 29, 2012, contributed significant rainfall to the Maryland-Delaware region, but not in the upper Susquehanna River Basin (Figure 1-4). HMI received 8.5 inches of rain from Sandy over a two day period (October 29 and 30), representing a significant influx of water into the facility. Precipitation amounts for BWI were at or below normal during the winter and following spring. In June 2013, several significantly high rain events occurred, accounting for the high rainfall total of 9 inches for the month for HMI. For the northeast U.S., June 2013 was ranked among the top 10 wettest since recordkeeping began (NRCC, 2013).

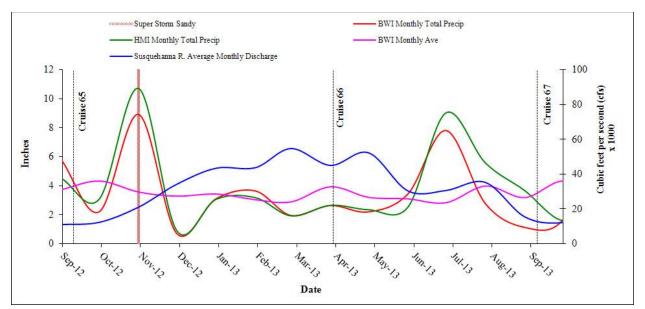


Figure 1- 3: Comparison of monthly precipitation data collected at HMI Facility and at the National Weather Service (NWS) Station at BWI (NOAA, 2014) with the average monthly discharge of the Susquehanna River. BWI monthly averages were based on monthly precipitation data from 1983 to 2012. Susquehanna River data were obtained from the USGS website (U.S.G.S, 2014).

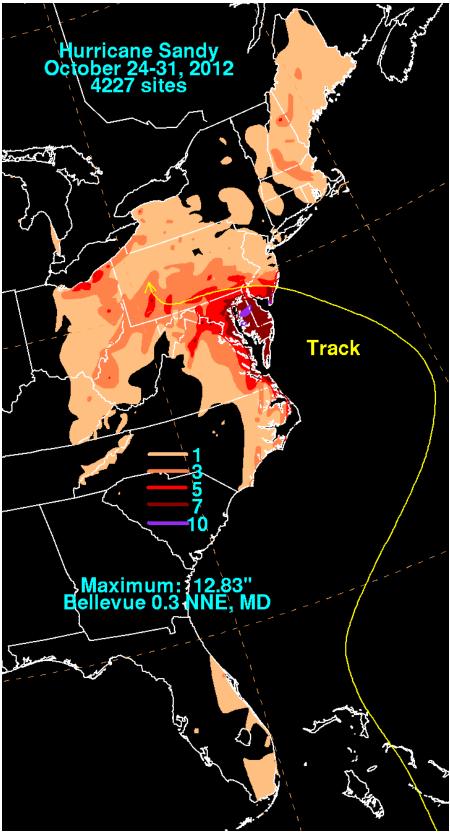


Figure 1- 4: Map showing areal extent and amounts of rainfall produced by Hurricane Sandy during October 2012. Note that the highest rainfall totals were recorded on Maryland's eastern shore. The map was downloaded from NOAA's Weather Prediction Service web site (Roth, 2012). Also shown in Figure 1-3 is the average monthly discharge for the Susquehanna River at the Conowingo Dam. As noted earlier, flow from the Susquehanna River influences the dispersion of material around HMI. During this monitoring year, the River flow was largely seasonal, with higher flow during the winter and spring (wet) and low flow during the summer and fall (dry). Unlike during Year 31 when rainfall from Tropical Storm (TS) Lee contributed to record high flow at Conowingo Dam, the Susquehanna River flow rate this year was not significantly influenced by Hurricane Sandy. For this monitoring period, the October-March average, which represents the high flow or wet season, was 40,377 cfs, and the April-September average, representing the dry, or low flow season, was 29,385 cfs. While the high flow average is similar to the rate (40,878 cfs) used in the hydrodynamic model, the low flow average is much higher than the 9,376 cfs used in the model to predict the dispersion of discharge from the facility (Wang, 1993).

During the 32<sup>nd</sup> year monitoring, there were no discharges from the North Cell into the Bay due to continued water quality issues within the cell (Amanda Peñafiel, pers. comm. 10/1/2014). MES continued to monitor pH, metal and alkalinity concentrations at the North Cell spillways. At the end of June, 2013, the pH at all three North Cell spillways continued to remain below permit limit of 6.0 and metal concentrations for Zn and Cu were above permit limits (MES, 2013). Water quality improved at Spillways 007 and 008 to pH levels meeting permit limits by August, 2013, but the pH at Spillway 009 continued to be very low (pH ranging between 2 and 3). No lime treatments to mitigate the low pH have taken place in either Cell since November, 2012 (Amanda Peñafiel, pers. comm. 9/30/2014).

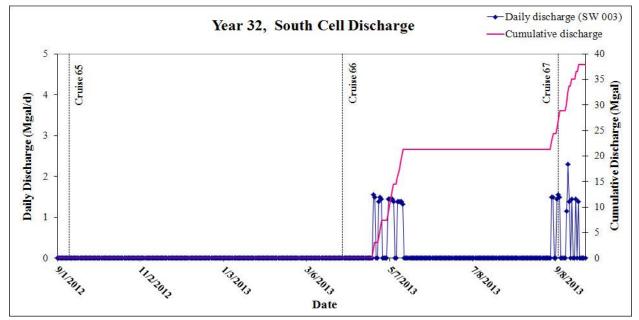


Figure 1- 5: Daily and cumulative discharge from the South Cell for the 13 month period covered in this report. The discharge from the South Cell is from SW003, which is the only discharge point for the Cell. The two discharges from SW003 were done to maintain the pond level (refer to Figure 1-6). Exterior sediment sampling events (*i.e.* sampling cruises) are marked by the vertical line

There were two periods of very low flow (*i.e.*, < 2.5 mgd) discharges from the South Cell (Figure 1-5). Both discharges were done to reduce the pond level (Figure 1-6). Both discharges were within the discharge permit criteria. Also, the Year 32 sampling took place during the second discharge. Between Cruise 65 (September 10, 2012) and Cruise 67 (September 10, 2013), total cumulative discharge from the South Cell into the Bay was 25.8 million gallons.

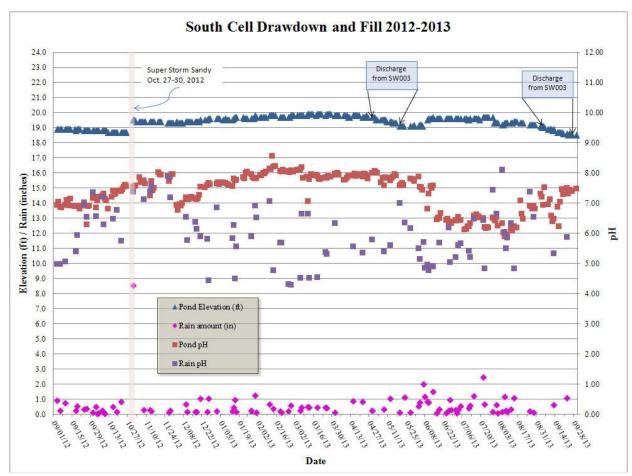


Figure 1- 6: Graph showing the South Cell pond elevation (blue triangles) and pond pH (red squares) for the 32<sup>nd</sup> monitoring year. Also shown are daily precipitation amounts and rain pH collected at the HMI DMCF.

#### **OBJECTIVES**

As with previous monitoring years, the main objectives of the Year 32 monitoring were (1) to measure specific physical and geochemical properties of near-surface sediments around HMI and (2) to assess detected changes in the sedimentary environment. Tracking the extent and persistence of the area of historically elevated metals concentrations was again of particular interest.

#### METHODS AND MATERIALS

#### **Field Methods**

The information presented in this report is based on observations and analyses of surficial sediment samples collected around HMI on September 10, 2013 (Cruise 67) aboard the R/V *Kerhin.* No samples were collected in the following spring.

Sampling sites (Figure 1-2) were located in the field by means of a Leica Model MX412B differential global positioning system (GPS) with a built-in beacon receiver. According to the captain, Rick Younger, the repeatability of the navigation system, that is, the ability to return to a location at which a navigation fix has previously been obtained is between 5-10 m (16-33 ft). Where replicates were collected, the captain repositioned the vessel between samples to counteract drifting off the station during sample retrieval. The captain recorded station coordinates and water depth at each site. Target and actual coordinates (latitude and longitude - North American Datum of 1983, or NAD83) of Year 32 sample locations are reported in the companion *Year 32 Data Report*.

Using a dip-galvanized Petersen sampler (maximum depth of penetration = 38 cm or 15 inches), crew members collected undisturbed samples, or grabs, of surficial sediments at 43 stations. The stations were identical to those sampled during previous four monitoring years.

At 39 stations, a single grab sample was collected, described lithologically, and representative sample taken of the grab. Triplicate grab samples were collected at the remaining four stations (MDE-2, MDE-7, MDE-9 and MDE-30) and, likewise, described and subsampled. Triplicate samples are identified by 'a, b, or c' after the station number. MGS analyzed each sample for grain size composition, a suite of trace metals, and total nitrogen, carbon and sulfur. A second subsample was taken from each grab, including the replicate grab, at all stations and analyzed by the Chesapeake Biological Laboratory (CBL) for a different suite of trace metals. Field descriptions of samples are included as appendices in the *Year 32 Data Report* 

Using plastic scoops cleaned with deionized water, the crew took sediment sub-samples from below the flocculent (floc) layer, usually several centimeters from the top, and away from the sides of the sampler to avoid possible contamination by the sampler itself. MGS's sub-

samples were placed in 18-oz Whirl-Pak<sup>TM</sup> bags and refrigerated. They were maintained at 4°C until they could be processed in the laboratory. CBL's splits were handled in much the same way, except that they included the floc layer and were frozen instead of refrigerated.

#### **Laboratory Procedures**

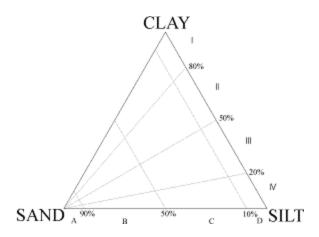
#### **Textural Analyses**

In the laboratory, sediment samples were analyzed for water content and grain size composition (sand-silt-clay content). Water content was calculated as the percentage of the water weight to the total weight of the wet sediment:

 $Wc = \frac{Ww}{Wt} \times 100$ Equation (1) where: Wc = water content (%) Ww = weight of water (g) Wt = weight of wet sediment (g)

Water weight was determined by weighing approximately 25 g of the wet sample, drying the sediment at 65°C, and reweighing it. The difference between total wet weight (Wt) and dry weight equals water weight (Ww). Bulk density was also determined from water content measurements.

The relative proportions of sand, silt, and clay were determined using the sedimentological procedures described in Kerhin *et al.*, (1988). The sediment samples were pre-treated with hydrochloric acid and hydrogen peroxide to remove carbonate and organic matter, respectively. Then the samples were wet sieved through a 62- $\mu$ m mesh to separate the sand from the mud (silt plus clay) fraction. The finer fraction was analyzed using the pipette method to determine the silt and clay components. Each fraction was weighed; percent sand, silt, and clay were determined; and the sediments were categorized according to Pejrup's (1988) classification (Figure 1-7).



#### Figure 1-7: Pejrup's Diagram (1988) classification of sediment type.

Pejrup's diagram, developed specifically for estuarine sediments, is a tool for graphing a three-component system summing to 100%. Lines paralleling the side of the triangle opposite the sand apex indicate the percentage of sand. Each of the lines fanning out from the sand apex represents a constant clay:mud ratio (the proportion of clay in the mud, or fine, fraction). Class names consist of letter-Roman numeral combinations. Class D-II, for example, includes all samples with less than 10% sand and a clay:mud ratio between 0.50 and 0.80.

The primary advantage of Pejrup's classification system over other schemes is that the clay:mud ratio can be used as a simple indicator of hydrodynamic conditions during sedimentation. (Here, hydrodynamic conditions refer to the combined effect of current velocity, wave turbulence, and water depth.) The higher the clay:mud ratio, the quieter the depositional environment. Sand content cannot be similarly used as an indicator of depositional environment; however, it is well suited to a rough textural classification of sediment.

Although the classification scheme is useful in reducing a three-component system to a single term, the arbitrarily defined boundaries separating classes sometimes create artificial differences between similar samples. Samples may be assigned to different categories, not because of marked differences in sand-silt-clay composition, but because they fall close to, but on opposite sides of, a class boundary. To avoid that problem, the results of grain size analysis are discussed in terms of percent sand and clay:mud ratios, not Pejrup's classes themselves.

#### **Elemental Analysis**

The sediment samples were analyzed for elements by *Activation Laboratories Inc*. (ActLabs). The quality assurance and quality control of ActLabs has proved to meet MGS standards and requirements. In addition to the nine elements historically measured by MGS (Fe, Mn, Zn, Cu, Cr, Ni, Pb, Cd, and total P), forty-one (41) additional elements were analyzed. Samples were prepared and ground in-house and sent to ActLabs for analyses using both Neutron Activation Analysis (NAA) and a four acid "near total" digestion technique followed by analysis on an Inductively Coupled Argon Plasma Spectrometer (ICAP). In addition to the standards and blanks used by ActLabs, National Institute for Standards and Technology (NIST) and Canadian Research Council (CRC) standard reference materials (SRM) were inserted as blind samples for analyses; one in every eight samples.

Results of the analyses of the SRMs reported by ActLabs are presented in the *Year 32 Data Report*. Both the accuracy and precision of the Actlabs analyses are in good agreement with the SRMs.

#### Carbon-Sulfur-Nitrogen Analysis

Sediments were analyzed by MGS for total carbon, nitrogen, and sulfur (CNS) contents using a Carlo Erba NA1500 analyzer. This analyzer uses complete combustion of the sample followed by separation and analysis of the resulting gasses by gas chromatographic techniques employing a thermal conductivity detector. The NA1500 Analyzer was configured for CNS analysis using the manufacturer's recommended settings. As a primary standard, sulfanilamide was used. Blanks (tin capsules containing only vanadium pentoxide) were run at the beginning of the analyses and after 12 to 15 unknowns (samples) and standards. Replicates of every seventh sample were also run. As a secondary standard, one of several NIST SRMs was run after every six to seven sediment samples. The recovery of the SRMs was good with the agreement between the NIST certified values and MGS's results well within the two standard deviations of replicate analyses. Results of the SRMs are presented in the *Year 32 Data Report*.

#### **RESULTS AND DISCUSSION**

#### **Sediment Distribution**

The monitoring effort around HMI is based on the identification of long-term trends in sediment distribution and on the detection of changes in those trends. The sampling scheme, revised in Year 17 and expanded in Year 18, established a new baseline against which any future changes in the sedimentary environment will be measured. Through Year 19, results of all cruises beginning with Year 17 were reported and compared. Starting with Year 20, results of the current year were discussed with respect to the preceding year. For this report, the current Year 32 results are discussed with respect to the preceding Year 31 results, and where appropriate, with references to earlier monitoring year results.

All sampling sites visited during Year 32 yielded results that can be compared to those measured during Year 31. The grain size composition (proportions of sand, silt, and clay) of the samples is depicted as a series of Pejrup's diagrams in Figure 1-8. Within a diagram, each solid circle represents one sediment sample. Related statistics, by cruise, are presented in Table 1-1.

Variable	Sept 2012 Year 31, Cruise 65	Apr 2013 Year 31, Cruise 66	Sept 2013 Year 32, Cruise 67				
Sand (%)							
Mean	22.08	19.34	21.38				
Median	4.53	4.22	3.35				
Minimum	0.66	0.82	0.70				
Maximum	96.76	98.26	95.36				
Range	96.09	97.43	94.66				
Count	43	42	43				
Clay:Mud							
Mean	0.54	0.55	0.53				
Median	0.55	0.56	0.53				
Minimum	0.31	0.45	0.38				
Maximum	0.62	0.62	0.65				
Range	0.31	0.16	0.26				
Count	43	42	43				

 Table 1-1: Summary statistics for Years 31 and 32, for 43 sediment samples common to all three cruises.

The ternary diagrams show very similar distributions of sediment type compared to the previous year. The samples range widely in composition, from very sandy (>95% sand) to very muddy (<1% sand). Muddy sediments predominate; approximately two-thirds of the samples contain less than 10% sand. All of the points fall fairly close to the line that extends from the

sand apex and bisects the opposite side of the triangle (clay:mud = 0.50 or 50%). For all three samplings (Cruises 65 through 67), most points lie above the 50% line (clay-silt boundary), indicating that the fine (muddy) fraction of the sediments contains more clay than silt.

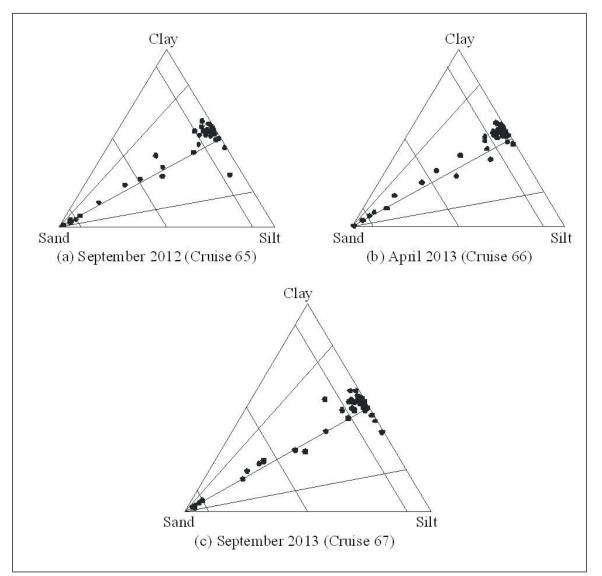


Figure 1-8: Pejrup's diagrams showing the grain size composition of sediment samples collected in Years 31 and 32 from the 43 sampling sites common to all three cruises: (a) September 2012, (b) April 2013, and (c) September 2013. Grain size compositions were adjusted to exclude any gravel component.

Based on the summary statistics (Table 1-1), average grain size composition, reported as % sand and as clay:mud ratios, varied little over the three sampling periods. The mean percentage of sand varied approximately 3 % for the three samplings.

Sandy sediments are associated with the shallower areas around the diked facility (Figure 1-9). The grain-size distribution of bottom sediments around HMI is depicted in contour maps

showing (1) the percentage of sand in bottom sediments and (2) the clay:mud ratios. In Figures 1-10 and 1-11, three contour levels represent 10%, 50%, and 90% sand, coinciding with the parallel lines in Pejrup's diagram (Figure 1-7). Generally, sand content diminishes with distance from the containment facility. Scattered around the perimeter of the dike, the sandiest sediments (>50% sand) are confined to relatively shallow (<15 ft) waters.

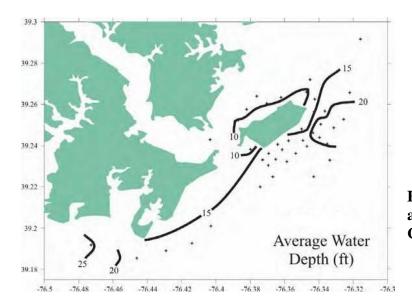


Figure 1- 9: Average water depths around HMI and vicinity. Contour interval = 5 ft.

Broadest north and west of the facility, the shoals are the erosional remnants of a larger neck of land. The once continuous landmass has been reduced to a series of islands, including Hart and Miller Islands, extending from the peninsula that now forms the south shore of Back River. However, not all shallow water samples are sandy. In particular, several of the shallow water samples from Hawk Cove (*e.g.*, MDE-30) contain less than 10% sand. Sand distribution map for Year 32, shown in Figure 1-10, is almost identical in appearance to that of the previous September (Cruise 65) (Wells *et al.*, 2014). Sand contents continue to be highest near the perimeter of HMI in shallow water depths. At the northeast end of the facility, the broad sand area, as defined by the 90% contour, underwent subtle seasonal shifts. The sand area defined by the 90% contour had shrank by April 2013 due to seasonal conditions, but also as a result of more fine grained material being moved and deposited as a result of Hurricane Sandy. In general though, the distribution of sand around HMI has remained largely unchanged since November 1988, two years after the first release of effluent from the dike.

Compared to the distribution of sand, the distribution of clay:mud ratios has tended to be slightly more variable over time. The fine (mud) fraction of the sediments around HMI is generally richer in clay than in silt. That is, the clay:mud ratio usually exceeds 0.50, as shown in the ternary diagrams in Figure 1-8. However, slight variations in the most clay-rich (clay:mud ratio  $\geq 0.60$ ) and in the most silt-rich (clay:mud ratio < 0.50) of the fine fractions are evident at the mouth of Baltimore Harbor, which continued to be clay-rich (Figure 1-11). The areas of higher silt seen along the south perimeter of HMI are probably related to high turbulence associated with the dike wall, preventing the settling of the finer clay size sediment These patterns are most likely due to the combined effects of the storms and seasonal changes. In

previous monitoring years, the April samplings occur during a period of higher turbulence due to weather, whereas the September samplings take place after a comparatively quiet, low flow summer during which more clay size sediment accumulated on the bottom. The small area of clay-rich adjacent to Spillway 003 is curious. The effluent may be contributing some clay sized sediment although TSS concentrations in discharges from Spillway 003 were within permitted levels.

Based on the overall similarities between the fine fraction results from the past five years, one may conclude that the depositional environment in the vicinity of HMI has not changed significantly over this period. The depositional environment continues to be very stable despite the major storm events.

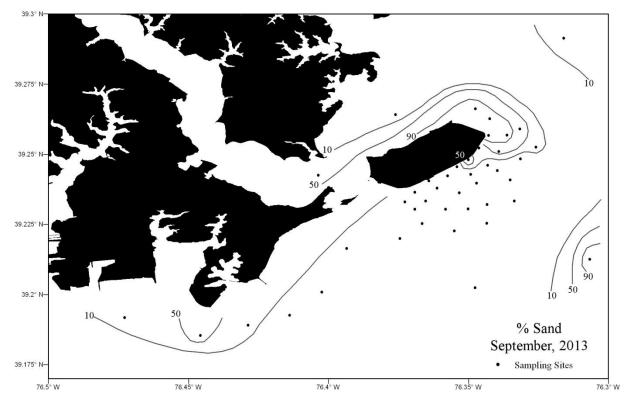


Figure 1-10: Sand distribution for Monitoring Year 32 which included one sampling cruise: September 2013 (Cruise 67). Contour intervals are 10%, 50%, and 90% sand.

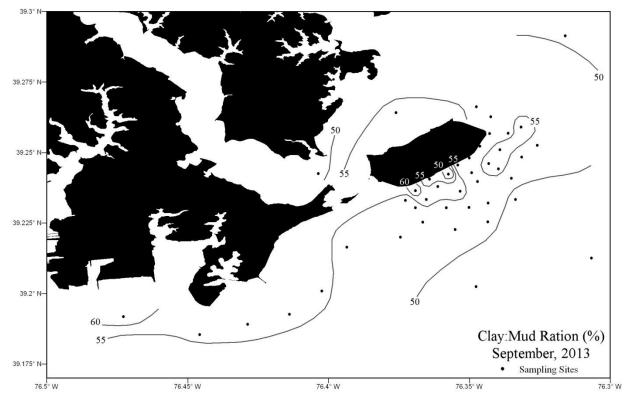


Figure 1-11: Clay:Mud ratios for September 2013 (Cruise 67). Contour intervals are 50%, 55%, and 60% (clay:mud ratio expressed as %).

#### **Elemental Analyses**

#### Interpretive Technique for Metals

Previous monitoring years have focused on eight metals as part of the ongoing effort to assess the effects of operation of the containment facility on the surrounding sedimentary environment. The method used to interpret changes in the observed metal concentrations takes into account grain size induced variability and references the data to a regional norm. The method involves correlating metal levels with grain size composition on a data set that can be used as a reference for comparison. For the HMI study area, data collected between 1983 and 1988 are used as the reference. Samples collected during this time showed no aberrant behavior in metal levels. Normalization of grain size induced variability of metal concentrations was accomplished by fitting the data to the following equation:

 $\mathbf{X} = \mathbf{a}(\mathbf{Sand}) + \mathbf{b}(\mathbf{Silt}) + \mathbf{c}(\mathbf{Clay})$  Equation (2)

where X = the metal of interest

a, b, and c = the determined coefficients Sand, Silt, and Clay = the grain size fractions of the sample A least squares fit of the data was obtained by using a Marquardt (1963) type algorithm. The results of this analysis are presented in Table 1-2. The correlations are excellent for Cr, Fe, Ni, Pb, and Zn, indicating that the concentrations of these metals are directly related to the grain size of the sediment. The correlations for Mn and Cu are weaker, though still strong. In addition to being part of the lattice and adsorbed structure of the mineral grains, Mn occurs as oxy-hydroxide chemical precipitate coatings. These coatings cover exposed surfaces, that is, they cover individual particles as well as particle aggregates. Consequently, the correlation between Mn and the disaggregated sediment size fraction is weaker than for metals, like Fe, that occur primarily as components of the mineral structure. The behavior of Cu is more strongly influenced by sorption into the oxy-hydroxide than are the other metals. The poor relationship with regard to Cd is due to the baseline being established at or near the detection limit; however, the relationship is still significant. Baseline levels for Cd and Pb were determined from analyses of 30 samples collected in a reference area on the eastern side of the Northern Bay. The baseline was established as part of a study examining toxic loading to Baltimore Harbor.

	X = [a*Sand + b*Silt + c*Clay]/100			Equation (2)				
	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
a	0.32	25.27	12.3	0.553	668	15.3	6.81	44.4
b	0.14	71.92	18.7	1.17	218	0	4.1	0
с	1.373	160.8	70.8	7.57	4158	136	77	472
$\mathbf{R}^2$	0.12	0.733	0.61	0.91	0.36	0.82	0.88	0.77

Table 1-2: Coefficients and  $R^2$  for a best fit of metal data as a linear function of sediment grain size around HMI. The data are based on analyses of samples collected during eight cruises, from May 1985 to April 1988.

The strong correlation between the metals and the physical size fractions makes it possible to predict metal levels at a given site if the grain size composition is known. A metal concentration can be predicted by substituting the least squares coefficients from Table 1-2 for the constants in equation 2, and using the measured grain size at the site of interest. These predicted values can then be used to determine variations from the regional norm due to deposition; to exposure of older, more metal-depleted sediments; or to loadings from anthropogenic or other enriched sources.

The following equation was used to examine the variation from the norm around HMI.

Note: Zn is used in the equation because of its significance in previous studies; however, any metal of interest could be used.

In Equation 3, the differences between the measured and predicted levels of Zn are normalized to predicted Zn levels. This means that, compared to the regional baseline, a value of zero percent excess metal is at the regional norm, positive values are enriched, and negative values are depleted. Direct comparisons of different metals in all sediment types can be made due to the method of normalization. As useful as the % Excess Metal values are, alone they do not give a complete picture of the loading to the sediments; natural variability in the samples as well as analytical variations must be taken into account. As result of the normalization of the data, Gaussian statistics can be applied to the interpretation of the data. Data falling within  $\pm 2\sigma$ ( $\pm 2$  standard deviations) are within normal background variability for the region. Samples with a value of  $\pm 3\sigma$  can be within accepted background variability, but are considered marginal depending on the trends in the distribution. Any values falling outside this range indicate a significant perturbation to the environment. The standard deviation ( $\sigma$ ) of the baseline data set (the data used to determine the coefficients in Equation 2) is the basis for determining the sigma level of the data. Each metal has a different standard deviation, as reflected in the R<sup>2</sup> values in Table 1-2. The sigma level for Zn is ~30% (e.g.  $1\sigma = 30\%$ ,  $2\sigma = 60\%$ , etc.).

## General Results

The summary statistics for the concentrations of the elements analyzed are given in Table 1-3. Generally, the statistics are very similar to the previous three years. Station MDE-41 consistently yields the maximum value for Cr. This sampling site is the upstream-most sample in the Baltimore Harbor Zone of influence and often has been high in one or more metals. The sample collected at this site in September 2013, contained the highest gravel content (4.4%), a portion of which may have been 'slag' from Sparrows Point, which would explain the high Cr content.

With regard to Effects Range Low (ERL) and Effects Range Median (ERM) values list in Table 1-3, the following statistics, which are very similar to the previous three years' findings, should be noted:

- 1. At most sampling sites, concentrations of Cr, Cu, Ni, Pb, and Zn in the sediment exceed the ERL values; and
- 2. At most sampling sites, concentrations of Ni exceed the ERM values; and concentrations of Zn exceed the ERM values at some sites.

ERL and ERM are proposed criteria put forward by NOAA (Buchman, 2008) to gauge the potential for deleterious biological effects. Sediments with concentrations below the ERL are considered baseline concentrations with no expected adverse effects. Concentrations between the ERL and ERM may have adverse impacts to benthic organisms, while values greater than the ERM have probable adverse biological effects. These criteria are based on a statistical method of termed preponderance of evidence. The method does not allow for unique basin conditions and does not take into account grain size induced variability in metal concentrations in the sediment. The values are useful as a guide, but are limited in applicability due to regional differences. The grain size normalization procedure outlined in the previous section is a means to correct the deficiencies of the guidelines by taking into account the unique character of Chesapeake Bay sediments and eliminating grain size variability. When the data are normalized, certain samples are significantly enriched in Pb and to a lesser extent in Zn and Ni, compared to the baseline.

	Cd	Cr	Cu	Fe (%)	Mn	Ni	Pb	Zn
Ave	0.6	97	42	4.19	2524	74	51	306
Std	0.3	39	19	1.60	1306	34	24	165
Min	0.2	11	4	0.34	431	7	7	22
Max	1.5	226	84	5.96	5830	167	103	742
N	25	43	43	43	43	43	43	43
ERL	1.3	81	34	n/a	n/a	21	47	150
#>ERL	1	33	29			39	27	37
ERM	9.5	370	270	n/a	n/a	52	218	410
#>ERM	0	0	0			32	0	8

Table 1-3: Summary statistics for elements analyzed for Year 32. All concentrations are in ug/g (ppm) unless otherwise noted. 'N' is the total number of values reported above detection limits and represents the number of values used in calculating the average.

The values presented in Table 1-3 are the measured concentrations of metals in the sediment, not normalized with respect to grain size variability, as outlined in the preceding *Interpretive Techniques* section. Figure 1-12 shows the variation of the data from the predicted baseline behavior for each of the elements measured for the last three cruises (65, 66 and 67). The values are in units of multiples of standard deviations from the norm; zero values indicate measurements that are identical to the predicted baseline behavior, values within plus or minus two (2) sigma (indicated by grey lines in Figure 1-12) are considered to be within the natural variability of the baseline values. Cd, Cr, Cu, Fe, Mn and Ni at most sites for the three sampling cruises are within the range expected for normal baseline behavior in the area (i.e., between +/-2 sigma). Approximately 21% of the samples contain Pb significantly exceeding the baseline levels (*i.e.*, >3 sigma levels, indicated by red line) and 5% of the samples contain Zn levels significantly exceeding the baseline. Three samples (MDE-18, -26 and -34) contained Ni levels exceeding 3 sigma levels, an increase in overall enrichment of Ni compared to the previous fall (September 2012), but similar to fall 2010 and 2011 cruises. Most of the samples with elevated Pb and Zn sigma levels are in the Baltimore Harbor and Back River Zones of Influence.

Based on work done by the University of Maryland during Year 25 monitoring year, the most probable conditions where the metals affect the infaunal communities are:

- 1. When the sigma level exceeds +2 [indicating enriched metals concentrations over baseline] and;
- 2. When the metals level exceeds the ERL with increased probability as the level exceeds the ERM [showing absolute concentrations that have exhibited adverse effects in other systems].

Sediments from several sites met these conditions. Samples for the September 2013 cruise from sites MDE-26, -38, and -39, all within the Baltimore Harbor Zone of Influence, and MDE-27 within the Back River Zone contained more than one target metal exceeding the ERL or ERM and sigma greater than 2. Within the HMI Zone of influence (both distal and proximal), the sediments containing multiple metals exceeding ERLs or ERMs, and sigma levels greater than 2 include sites MDE-9, -11, -13, -14, -18, and -45.

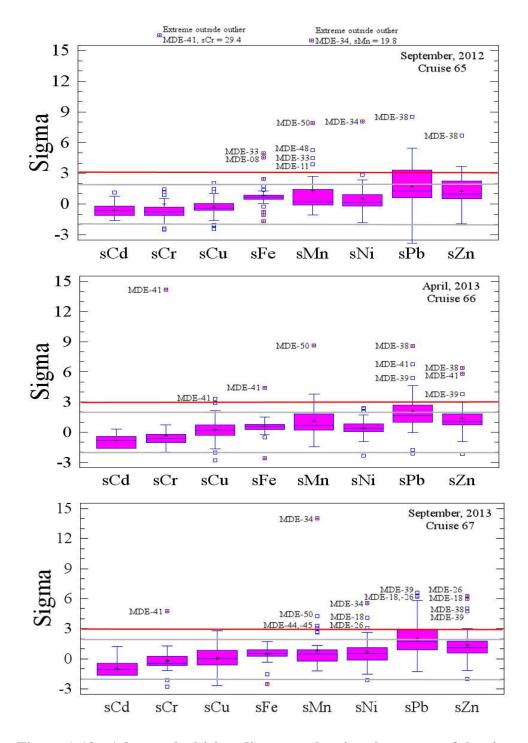


Figure 1-12: A box and whisker diagrams showing the ranges of the sigma levels for the September and April cruises for Year 31 and September cruise for Year 32. The box encloses the middle 50% of the sigma level values for each metal (interquartile range or IQR); the median is indicated by the horizontal blue line within each box; the mean is indicated by the black +. The vertical lines, or whiskers, bracket the +/- 1.5 IQR. Inside outliers (between 1.5 and 3 IQR) and outside outliers (> 3 IQR), are plotted as individual points (shown as open blue squares, and blue squares with red +, respectively). Outliers greater than +3 sigma are identified by site number.

### Metal Distributions

Beginning Year 8, increased metal sigma levels (specifically Zn) have been noted in bottom sediments east and south of Spillway 007; similarly since the Pb was added to the monitoring protocol (Year 15), elevated levels of Pb have been found in the same areas, but with generally higher relative loadings. The results of earlier HMI monitoring studies have shown that the areal extent and magnitude of metals loadings to the exterior sedimentary environment is controlled by three primary factors. These factors are:

- Discharge rate Controls the amount of metals discharged to the external sedimentary environment. Discharge from HMI at flows less than 10 MGD contribute excess metals to the sediment (see *Year 12 Interpretive Report*). The high metal loading to the exterior environment may be the result of a low pond level, which allows exposure of the sediment to the atmosphere. When the sediments are exposed to atmospheric oxygen, naturally occurring sulfide minerals in the sediment oxidize to produce sulfuric acid, which leaches metals and other acid-soluble chemical species from the sediment. At discharge rates greater than 10 MGD, the water throughput (input from dredge disposal to release of excess water) submerges the sediment within the facility, minimizing atmospheric exposure, and dilutes and buffers any acidic leachate. As a result, higher discharge rates produce metal loadings that are close to background levels.
- 2. Flow of freshwater into the Bay from the Susquehanna River The hydrodynamic environment of the Bay adjacent to HMI is controlled by the mixing of freshwater and brackish water south of the area. Details of the hydrodynamics of this region were determined by a modeling effort presented as an addendum to the Year 10 Interpretive Report (Wang, 1993). The effects of Susquehanna flow to the contaminant distribution around HMI follow;
  - a. A circulation gyre exists east of HMI (Figure 1-1). The gyre circulates water in a clockwise pattern, compressing the discharge from the facility against the eastern and southeastern perimeter of the dike;
  - b. The circulation gyre is modulated by fresh water flow from the Susquehanna River. The higher the flow from the Susquehanna, the stronger the circulation pattern and the greater the compression against the dike. Conversely, the lower the flow, the less the compression and the greater the dispersion away from the dike; and
  - c. Discharge from the facility has no influence on the circulation gyre. This was determined by simulating point discharges of 0-70 MGD from three different spillways. Changes in discharge rate only modulated the concentration of a hypothetical conservative species released from the facility; the higher the discharge, the higher the concentration in the plume outside the facility.
- 3. *The positions of the primary discharge points from the facility* The areal distribution of the metals in the sediment also depends on the primary discharge locations to the

Bay. The effects of discharge location were determined as part of the hydrodynamic model of the region around HMI. The effects of discharge location are:

- a. Releases from Spillways 007 and 009 travel in a narrow, highly concentrated band up and down the eastern side of the dike. This explains the location of the areas of periodic high metal enrichment to the east and southeast of the facility; and
- b. Releases from Spillway 008 are spread more evenly to the north, east, and west. However, dispersion is not as great as from Spillways 007 and 009 because of the lower shearing and straining motions.

The 3-D hydrodynamic model explains the structure of the plume of material found in the exterior sediments, and the functional relationship of contaminants to discharge rate accounts for the magnitude of the loading to the sediments.

Figures 1-13, 1-14, and 1-15 show the distribution of significant sigma levels for Ni, Pb and Zn, respectively, for Year 32 monitoring in the study area adjacent to HMI. Sigma levels are the multiple of the standard deviation of the baseline data set. Data that fall within +/-2 sigma are considered within normal baseline variability. Data within the 2 -3 sigma range are transitional; statistically one sample in 100 would normally be expected to occur, in a small data set. The occurrence of two or more spatially contiguous stations in this range may be significant. Samples having >3 sigma are considered significantly elevated above background. As shown in Figure 1-2, there are three primary areas of interest that will be referred to as: Back River, Baltimore Harbor, and HMI Zones of Influence.

*Back River* - The Back River influence is seen for Pb even though only two sites within this zone were sampled this monitoring year. As with previous years, Pb continues to be discharged by Back River during both of the sampling periods. Ni and Zn concentrations were less than 3 sigma for Year 32, consistent with the previous three years monitoring.

*Baltimore Harbor* - Elevated levels of Pb and Zn extend into the area southwest of HMI. In spite of the major storms to have affected the area in the past three years, the distribution of the levels for these metals remain separated from the HMI Zone of Influence adjacent to the island. Maximum enrichment values for Pb and Zn decreases slightly from the previous two years, but continue to be significantly elevated.

*HMI* – Elevated levels of Ni, Pb and Zn are seen at isolated sites southeast of HMI. Whether the absolute number of sites having elevated levels has decreased or increase since the previous fall depends on the metal. However, the degree of elevated levels of Ni, Pb and Zn have increased compared to Year 31 (refer to outliers in Figure 1-12). Also there appears to be a subtle southward shift in distribution of the elevated sites since September 2012. The source of the enrichment of Ni, Pb and Zn is attributed to the effluent discharged from the South Cell (Spillway 003), since there have been no discharges directly from the North Cell since February, 2011. Discharge from the South Cell occurred during relatively low flow of the Susquehanna River, but during a period of higher than normal rainfall locally, which resulted in higher flow out of the Patapsco River. This higher flow could have modified the flow of the circulation gyre, accounting for the distribution of the sites with elevated levels of metals.

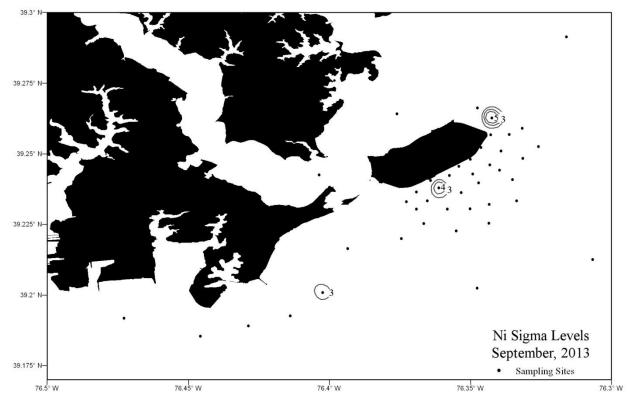


Figure 1-13: Distribution of Ni sigma levels in the study area for the September 2013 sampling cruise. Units are in multiples of standard deviations - Sigma levels: 0 = baseline, +/- 2 = baseline, 2-3 = transitional (contour intervals less than 3 not shown), >3 = significantly enriched.

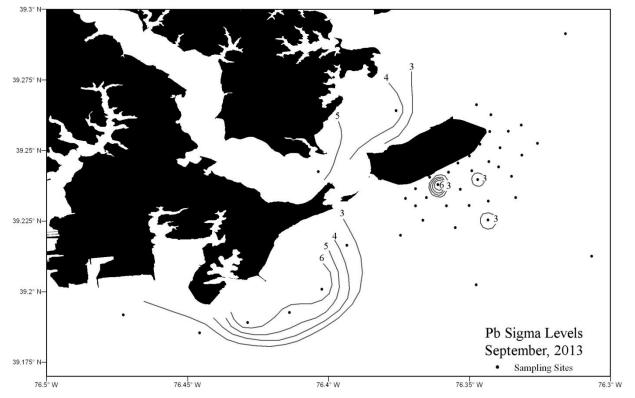


Figure 1-14: Distribution of Pb in the study area for the September 2013 sampling cruise. Units are in multiples of standard deviations - Sigma levels: 0 = baseline, +/- 2 = baseline, 2-3 = transitional (contour intervals less than 3 not shown), >3 = significantly enriched.

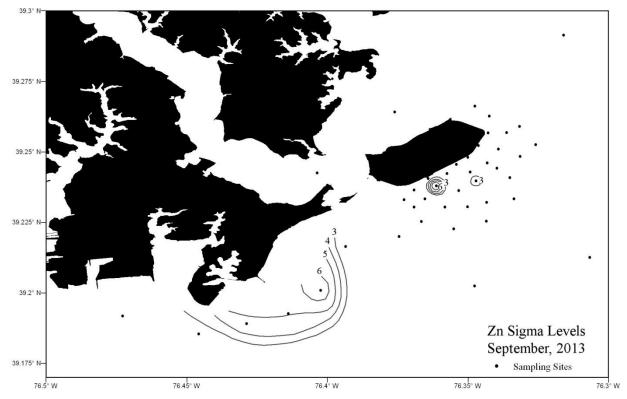


Figure 1-15: Distribution of Zn in the study area for the September 2012 and April 2013 sampling cruises. Units are in multiples of standard deviations - Sigma levels: 0 = baseline, +/- 2 = baseline, 2-3 = transitional (contour intervals less than 3 not shown), >3 = significantly enriched.

#### CONCLUSIONS AND RECOMMENDATIONS

The general sediment distribution pattern is consistent with the findings of previous monitoring years dating back to 1988 (the second year after the start of release from HMI) and no significant changes occurred during Year 32. The depositional environment continues to be very stable despite the major storm events occurring in past two years.

Elemental analyses data indicate that the sediments are similar to the previous year including the anomalously high Cr value measured at a sampling site in the Baltimore Harbor Zone of Influence; this Zone has consistently been high in metals in previous years. Based on summary statistics, the elemental data show that:

1. At most sampling sites, concentrations of Cr, Cu, and Pb in the sediment exceed the ERL values; and2. At most sampling sites, concentrations of Ni exceed the ERM values; and at some sites, Zn exceeds the ERM values.

ERL and ERM are proposed criteria put forward by NOAA (Buchman, 2008) to gauge the potential for deleterious biological effects. Sediments with concentrations below the ERL are considered baseline concentrations with no expected adverse effects. Concentrations between the ERL and ERM may have adverse impacts to benthic organisms, while values greater than the ERM have probable adverse biological effects. These criteria are based on a statistical method of termed preponderance of evidence. The method does not allow for unique basin conditions and does not take into account grain size induced variability in metal concentrations in the sediment. The grain size normalization procedure outlined in the previous section is a means to correct the deficiencies of the guidelines by taking into account the unique character of Chesapeake Bay sediments and eliminating grain size variability. When the data are normalized, Ni, Pb, and Zn are significantly enriched in some samples compared to the baseline.

From the preliminary toxicology work done in Year 25, enrichments of Zn and Pb are probably the most significant in influencing benthic communities as a result of HMI operations. Pb enriched samples are associated with the three local sources HMI, Baltimore Harbor and Back River. Pb showed lower enriched levels, both in terms of the number of sites and extended spatial distribution, compared to the previous year. Sediments were slightly enriched (3 sigma levels) with Zn at two sites in the HMI zone, representing a slight increase since Year 31. Zn shows enrichment from Baltimore Harbor and HMI, but not from Back River. The two sampling sites in Back River showed no enrichment for Zn. Prior to Year 28 monitoring, most of the samples with potential benthic effects due to high concentrations of Ni were in the Back River and Baltimore Harbor Zones of Influence. Between Monitoring Years 28 and 30, sigma levels of Ni steadily increased in the HMI Zone. During Year 31, sigma levels of Ni were within normal ranges in the HMI Zone. This year, two sites within the HMI Zone of Influence were enriched with Ni. In terms of absolute concentration, Ni continues to exceed ERL threshold at most sites and ERM at some sites.

To illustrate the long-term trend of the data, the highest levels of Zn enrichment (% excess Zn) in the HMI Zone of Influence for all monitoring sampling events (cruises) are plotted in Figure 1-16. The data from this monitoring year, shown as the solid point, show a pronounced fluctuation over the past several monitoring years, but the overall trend is a slight increase in enrichment that began in 2011 (Year 29).

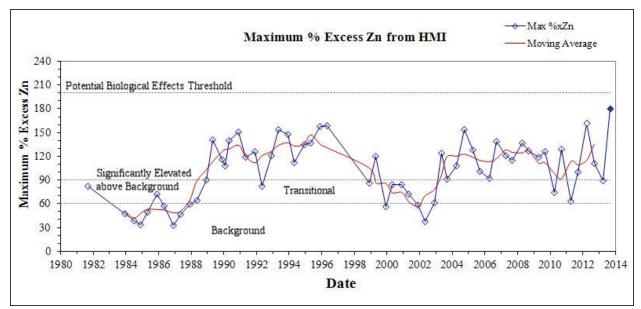


Figure 1-16: Record of the maximum % excess Zn for all of the cruises for which MGS analyzed the sediments. The filled point is the maximum from this year's study (Cruise 67).

In regard to potential adverse benthic effects the overlap of enrichment and concentration can be used as an indicator of potential biological impacts: based on the intensity of the effect (enrichment based on sigma level, and concentrations exceeding ERL or ERM), and in regard to the number of samples, Pb>Zn>Ni. Within the HMI Zone of Influence (both distal and proximal), the sediments containing multiple metals (primarily Ni, Pb or Zn) exceeding ERLs or ERMs, and sigma levels greater than 2 include sites MDE-9, -11, -13, -14, -18, and -45 (Figure 1-17).

This year's monitoring documents enrichment of Ni, Pb and Zn around the HMI facility. This persistent enriched level indicates a need for continued monitoring, particularly since the facility has experienced water quality issues which have been exacerbated by unusual weather events contributing a significant volume of fresh, oxygenated water to the facility. Similar to the previous year, MES documented very low pH as well as high metals in the North cell on several occasions during this monitoring year. Therefore, no water was discharged directly from the North Cell spillways, nor was water transferred to the South Cell. Consequently, over 500 million gallons of water still remain in the North Cell. Due to fragile pond conditions and efforts to control pH in the South Cell, minimal water was discharged from the South Cell. Exterior sediment monitoring at the current level (*i.e.*, using present sampling grid) should continue in order to document the effect that operations has on the exterior environment, particularly in the

case of future discharge from the North Cell, and to assess the effectiveness of any amelioration protocol implemented by MES to counteract the effects of crust and water management inside the facility. Close cooperation with MES is important in this endeavor.

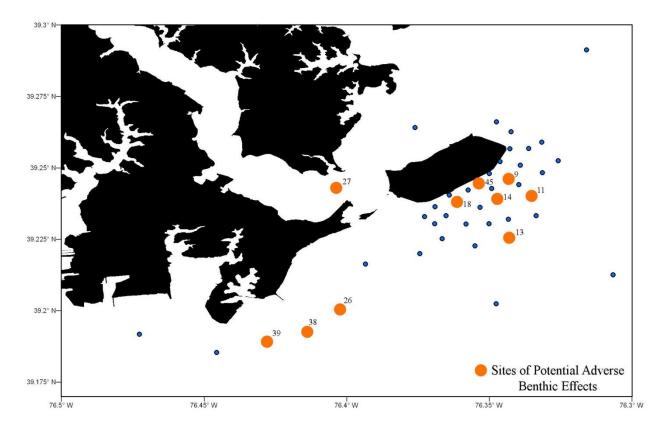


Figure 1-17: Distribution of sites of potential adverse benthic effects for September 2013 (Cruise 67). At the sampling sites shown in orange, sediments contained multiple metals (primarily Ni, Pb or Zn) exceeding ERLs or ERMs, and sigma levels greater than 2.

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# APPENDIX 1A: HMI GROUNDWATER MONITORING WELLS 2013-2014 (PROJECT II)

#### **INTRODUCTION**

Groundwater samples from six wells were collected on September 24, 2013, December 17, 2013, March 21, 2014 and June 10, 2014. MES analyzed the water samples for the following parameters: pH, temperature, conductivity, dissolved oxygen (DO), oxygen-reduction potential (ORP), salinity, alkalinity, chloride (Cl<sup>-</sup>), sulfate (SO42-), total Kjeldahl nitrogen (TKN), total nitrogen (TN), nitrates/nitrites (NO<sub>3</sub><sup>-</sup>/NO<sub>2</sub><sup>-</sup>), phosphorus (P), aluminum (Al), arsenic (As), Cadmium (Cd), calcium (Ca), Chromuim (Cr), Copper (Cu), Iron (Fe) Lead (Pb), magnesium (Mg), Manganese (Mn), potassium (K), silver (Ag), sodium (Na), and Zinc (Zn). The groundwater sampling and analyses are done as part of the on-going HMI external monitoring effort and as a continuation of the groundwater studies completed in 2003 (URS, 2003), and 2005 (Hill, 2005). As part of the monitoring effort, the Maryland Geological Survey (MGS) evaluated the results of the MES analyses of the water samples.

The monitoring wells are equally divided between the North and South Cells as seen in Figure 1A-1: North Cell 2A, 4A & 6A; South Cell 8A, 10A & 12A. These wells are part of 34 wells installed around the facility dike between 2001 and February 2002 for a groundwater study (URS, 2003). The purpose of that study was to identify 1) the direction and rate of groundwater flow from the facility to the surrounding Bay, and 2) physical and chemical reactions controlling the mobilization of contaminants from the facility. The 6 wells (*i.e.*, 'A' wells) were installed to depths to monitor the shallow saturated groundwater zone; depths of the wells range from -4 ft to -16.6 ft North America Vertical Datum of 1988 (NAVD88) (Table 1A-1).

Table 1A-1: Elevation and depth of well data for the HMI Wells sampled for groundwater monitoring. Data is from URS, 2003. Elevation is referenced to NAVD88 datum which is approximately mean sea level.

Well ID	Date	Elevation, ft (Top	Depth of	Elevation,
	Installed	of well casing)	well, ft	ft (Bottom
				of well)
2A	12/12/2001	19.28	35	-15.72
4A	1/6/2002	21.48	30	-8.52
6A	1/4/2002	21.41	30	-8.59
8A	12/19/2001	21.07	30	-8.93
10A	12/18/2001	20.98	25	-4.02
12A	12/15/2001	13.6	25	-11.4

The South Cell, which was closed to new dredged material in 1990, has been converted to upland and wetlands. Activities within the South Cell are specific to the management of the

different habitats. The North Cell was closed to dredged material in December 2009. Since then, activities within the North Cell consisted primarily of crust management as part of habitat development. In the last two years, several significant storms, the most recent being Hurricane Sandy (Oct. 29-30, 2012), contributed an enormous volume of water to the Facility, resulting in water quality issues (MES, 2012). Consequently, discharge from the Facility was limited to the South Cell during this monitoring year. To mitigate low pH conditions, MES installed and operated lime dosers in both cells in 2012. Since November 2012, no lime treatments to mitigate the low pH have taken place in either cell (Amanda Peñafiel, pers. comm. 9/30/2014). At the end of 2013, the North Cell contained over 500 million gallons of water. Areas within the North Cell continued to have extremely low pH (Figure 1A- 2) and high metal concentrations. A more detailed summary of the facility operations for the Year 32 monitoring period is presented in the Technical Report for Sedimentary Environment.

Presented in this groundwater monitoring report is a summary of the well data collected from the quarterly sampling during the 32<sup>nd</sup> monitoring year. Discussion of data includes comparison with previous data collected since June 2006 when MES had adopted new protocols for sampling groundwater monitoring wells (MES, 2010). Data analyses are based on the interpretive methods detailed in the HMI well monitoring report (Hill, 2005).

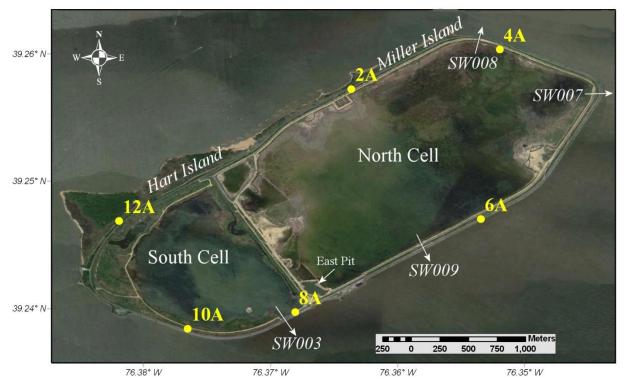


Figure 1A-1: Aerial photograph of the HMI DMCF, taken on May 5, 2013, showing the locations of the groundwater monitoring wells (yellow dots) and the spillways (*SW; white arrows*). Aerial photography from Google Earth (2014).

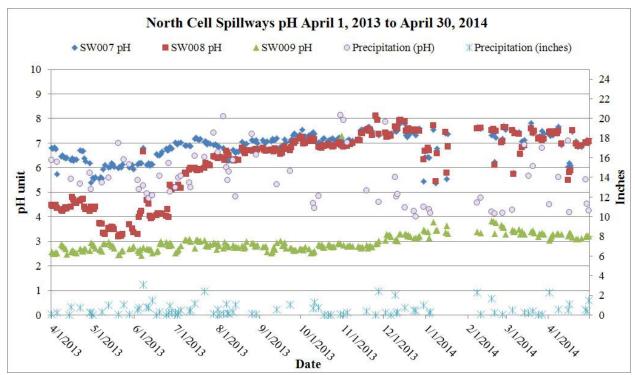


Figure 1A-2: Graph showing the North Cell spillways pH from April 1, 2013 to April 30, 2014. Also shown are daily precipitation amounts and rain pH collected at the HMI DMCF. Locations of the spillways are shown in Figure 1A-1.

#### SUMMARY OF WELL DATA

Trend plots of select field parameters and metal concentrations measured in well water samples collected since 2006 are presented in Figures 1A-3 through 1A-6. The vertical lines in the plots correspond to several major events affecting operations and water quality within the Facility. All of the wells continue to be anoxic or hypoxic with DO levels less than 2.0 mg/L until the March 2013 sampling, when DO levels spiked in wells 2A, 8A and 12A (Figures 1A-3 and 1A-4. The following March (2014) DO levels spiked in all the wells except 2A. The DO spike would also explain the redox (OPR) spike in the same wells for the March 2013 sampling. However, there was inconsistent spiking of redox for the March 2014 sampling.

Due to limitations in the instrumentation used to get *in-situ* measurements, no sulfide measurements were taken. These measurements are not necessary, but their absence limits the information on the degree of anoxia and the processes occurring. URS (2003) found that sulfide concentrations in HMI groundwater were consistently at or below detection. The low levels were attributed to loss by precipitation, based on the relatively high Fe concentrations (Figures 1A-5 and 1A-6). Dissolved sulfide binds with many metals and restricts their mobility, and is preferentially used as a metal ligand releasing mineralized phosphate into the water.

The dominant form of nitrogen in all of the wells appears to be ammonium, since most nitrate readings are below detection. Nitrate is used preferentially once oxygen is consumed as the primary oxidant, and ammonium ion is a by-product of anaerobic respiration. This is consistent with the anoxic/hypoxic nature of the groundwater.

#### North Cell Wells 2A, 4A and 6A

Figure 1A-7 shows the chloride (Cl<sup>-</sup>) concentration from the September 24, 2013, December 17, 2013, March 21, 2014 and June 10, 2014 samplings as a function of the amount of excess sulfate, either removed from the water as a result of sulfate reduction (- excess sulfate) or added to the water as the result of sulfide oxidation in the sediment solids (+ excess sulfate). The predicted sulfate levels are calculated from the chloride concentration based on conservative mixing between rainwater and seawater. This years' plot appears different from 31<sup>st</sup> year's plot primarily because Cl<sup>-</sup> is plotted on a logarithmic scale, rather than a linear scale. Based on the depletion in sulfate in comparison to predicted concentrations, North Cell Well 2A is the only well that continues to have a reducing environment, whereas Wells 4A, and to a lesser degree, 6A, are more similar to the oxidizing environment seen in the South Cell wells. Well 2A, which is the deepest of the six monitoring wells (Table 1A-1), is located on the remnant of Miller Island. Well 2A also is the only well exhibiting seasonal fluctuations in alkalinity, total nitrogen, pH, phosphorus (not shown) and, to a lesser extent, Fe concentrations (Figures 1A-3 and 1A-5). These seasonal fluctuations become obvious starting at the end of 2009, about the same time the North Cell stopped receiving dredged material and operations focused on crust management (dewatering) activities. After October 2012, multiple field and metal parameters in all wells show irregular fluctuations, but they are not necessarily seasonal. These fluctuations in water chemistry are interpreted to be delayed responses to operation activities in the North Cell and to weather events; the degree of responses affected by a number of factors including well location, depth and differences in infill (sediment) and dike wall composition.

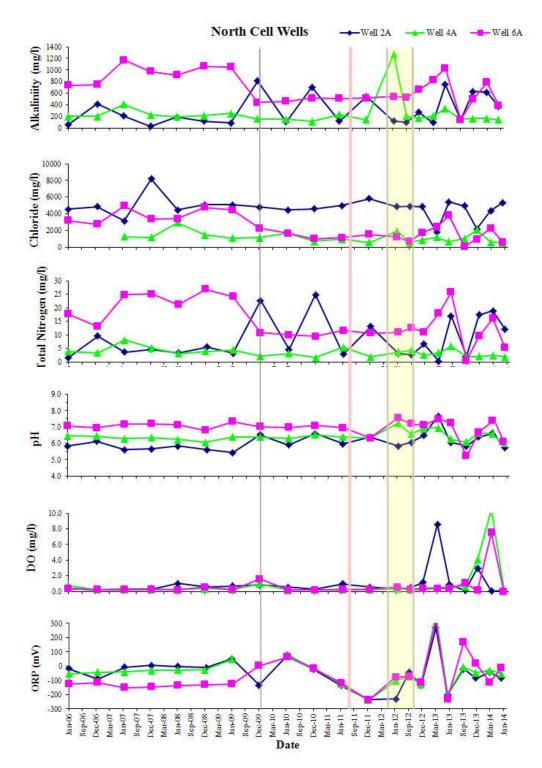


Figure 1A- 3: Trend plots for field parameters measured in groundwater samples collected since 2006 from North Cell wells. The vertical lines in the plots mark several notable events having an impact on the Facility: 1) Dec-09 (gray line) when North Cell was closed to dredge material; 2) Aug-Sept-11 (pink) Hurricane Irene and TS Lee; 3) Apr-12 to Oct-12 (yellow shading) marking the period when liming took place in North Cell; 4) Hurricane Sandy occurred at the end of the liming period (end of Oct. 2012 coincides with end of liming).

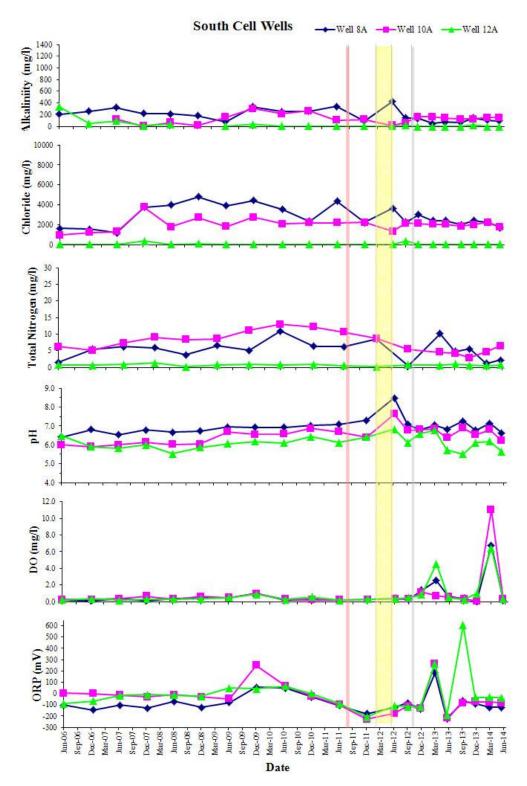


Figure 1A- 4: Trend plots for field parameters measured in groundwater samples collected since 2006 from South Cell wells. The vertical lines in the plots mark several notable events having an impact on the Facility: 1) Aug-Sept-11 (pink) Hurricane Irene and TS Lee; 2) Feb-12 to Jun-12(yellow shading) marking the period when liming took place in South Cell; 3) Oct-12 (gray) Hurricane Sandy.

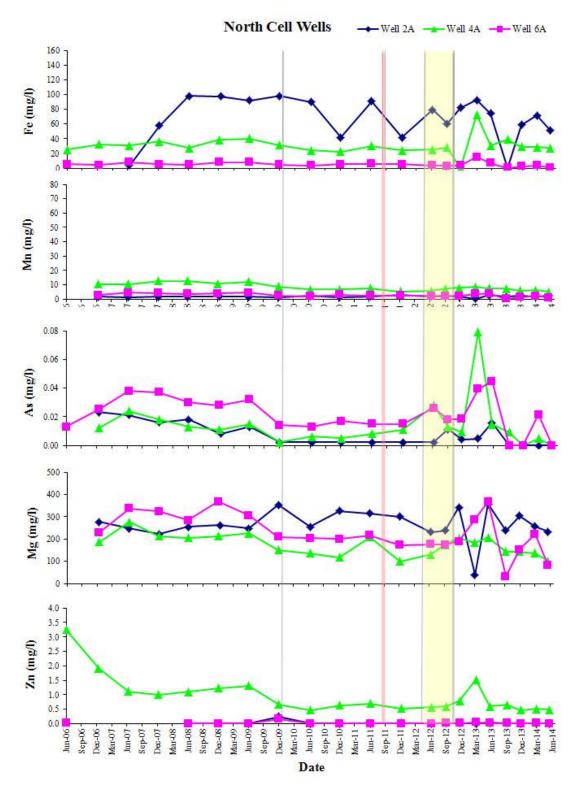


Figure 1A- 5: Trend plots for select metals measured in groundwater samples collected since 2006 from North Cell wells. The vertical lines in the plots mark several notable events having an impact on the Facility (refer to caption for Figure 1A-2 for explanation).

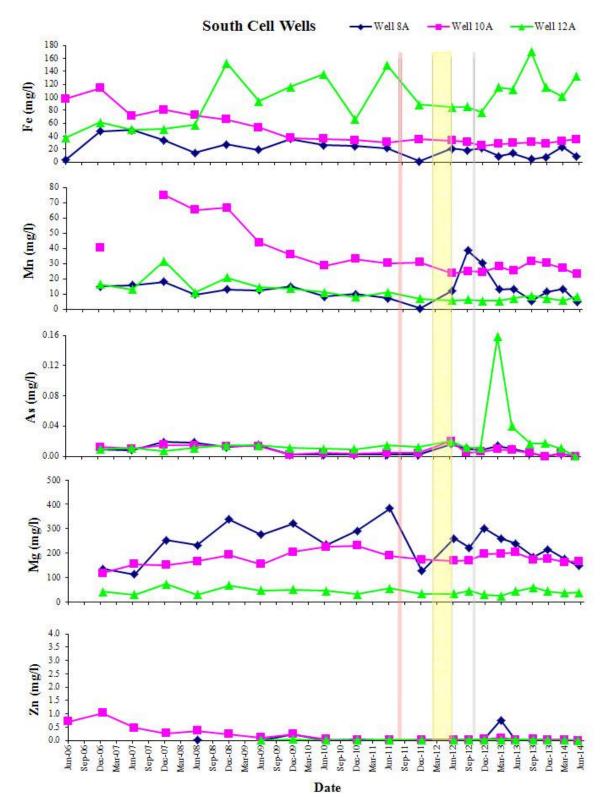


Figure 1A- 6: Trend plots for select metals measured in groundwater samples collected since 2006 from South Cell wells. The vertical lines in the plots mark several notable events having an impact on the Facility (refer to caption for Figure 1A-3 for explanation).

Figure 1A-8 shows ratios of  $K^+/Cl^-$  and  $Ca^{++}/Cl^-$  as a function of the amount of excess sulfate. The major cations are near the predicted conservative mixing concentrations. Since acid generally is not being generated in the vicinity of Well 2A, there is minimum mineral dissolution (specifically calcium carbonate) or ion exchange. In the rest of the wells, the hydrogen ion from acid is preferentially bound on ion exchange sites in the sediment releasing other adsorbed cations (e.g.  $K^+$ ,  $Ca^{++}$ ). The linear relation in the positive excess sulfate region is due to the process of acid production being directly related to neutralization and ion exchange. Prior to December 2009, alkalinity in Well 6A had been consistently higher compared to other wells. After December 2009, alkalinity dropped and leveled off but continued to be higher than the other two wells in the North Cell (except for December 2009, 2010 and 2011 samplings for Well 2A and June 2012 for Well 4A) and the wells in the South Cell (Figures 1A-2 and 1A-3). The higher concentrations suggest that the alkalinity in this well still had not been neutralized by acid production and may be buffered somewhat, particularly during and after the liming period. This is supported by the pH values for Well 6A, which generally have been higher than the other wells (both North and South Cell wells). Also, the behavioral trend of alkalinity in Well 6A matches those of total nitrogen and arsenic. In June 2012, pH increased to highest levels in all wells except Well 2A. After June 2012, pH in all wells, both North Cell and South Cell, fluctuated seasonally, reaching high in March and low in September.

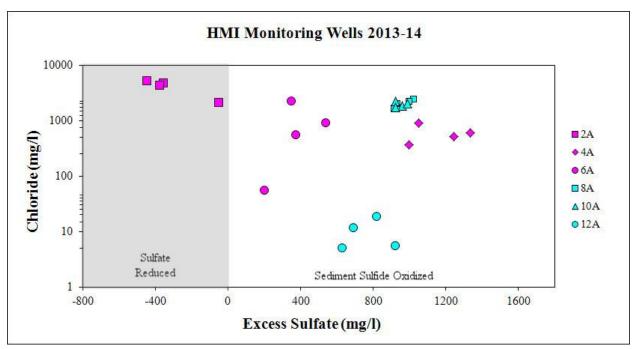


Figure 1A-7: Groundwater chloride concentrations as a function of excess sulfate (the difference of the measured sulfate concentrations minus the predicted concentrations). Monitoring wells are grouped by general location; North Cell (pink) or South Cell (light blue).

The groundwater from the North Cell Well 2A continues to exhibit behavior typical of anoxic pore waters that have minimum exposure to oxidized sediment. It may be that Well 2A is the least affected by operations in the North Cell compared to Wells 4A and 6A due to its location and depth. Generally the behavior of measured parameters in each of the North Cell wells is different reflecting a number of factors. The recharge area for the monitoring wells is the North Cell, the surface conditions of which have been constantly changing due to crust management and dewatering operations and the influx of fresh, oxygenated rainwater. Another factor is the heterogeneous material contained in the dike wall and the North Cell substrate, both of which affect transport rates and chemistry of the groundwater.

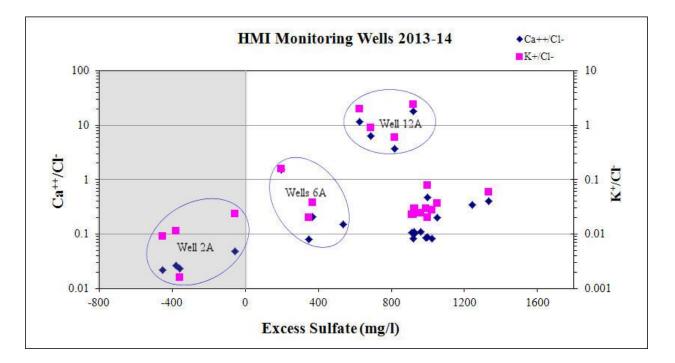


Figure 1A- 8: The ratios of  $K^+/C\Gamma$  and  $Ca^{++}/C\Gamma$  as a function of excess sulfate. For reference, the ratio for both of these cations in seawater is ~0.02. Note that scale of the y-axes are logarithmic to accommodate the relatively large ratios calculated for Well 12A; the ratios were very high due the extremely low chloride concentrations.

#### South Cell Wells 8A, 10A & 12A

The waters in these wells have been exposed to oxidized sediments, thus the higher levels of excess sulfate (Figure 1A-7). Chloride concentrations are high in Wells 8A and 10A. However, rainwater appears to be a major source of water to Well 12A, the waters of which appear to be entirely fresh water. The lowest level of chloride was observed in June, 2012 ( $Cl^{-}$  = 4.1 mg/L). Well 12A is located in a stand of mixed hardwood and conifer trees on a portion of the dike underlain by a remnant of Hart Island.

Total nitrogen (ammonium) and alkalinity are slightly lower, while some metals and cations are higher than in the waters in the North Cell wells. Since the sediments in the South Cell had been exposed to the atmosphere, one time or another, much of the sulfide in the sediments has been oxidized, accounting for the higher excess sulfate and metals in the groundwater. Until June 2012, water chemistry in the South Cell wells tended to be more stable, showing less fluctuation, compared to the North Cell wells. Starting in June 2012, some wells began to exhibit fluctuations in some field parameters and metal concentrations, although not to the same degree as seen in the North Cell wells (Figures 1A-4 and 1A-6). As with the North Cell wells, the fluctuations in chemistry seen in the South Cell wells after June 2012 are attributed to operations activities in the cell (e.g., liming to adjust pond pH) and extreme weather events.

#### **PROCESSES OPERATING IN HMI GROUNDWATER**

Figure 1A-9 shows a hypothetical cross section of HMI at the South Cell. Hydrodynamically, there are four areas to consider:

1. The surface sediments of the interior of the cell. Here if the sediment is kept inundated, the sediment and the associate pore fluids would be anoxic and would have the characteristics of normal Bay sediments. This is the situation in the North Cell, especially after the influx of rainwater from the major storms. However, in the South Cell circumstance, a large area is sub-areal with rain water being the primary source of water to the system. The occluded water native to the dredged material is diluted by the fresh rain water; this lowers the dissolved load derived from dilution of sea water in the Bay waters. Since the hydrated sediment is exposed to atmospheric oxygen, the aerobic process is in operation. One of the most significant reactions is the oxidation of the naturally occurring sulfide minerals (primarily iron monosulfides and pyrite) that produces sulfuric acid. The acidified waters have sulfate concentrations in excess of conservative mixing. The oxidation of the sulfide minerals significantly increases the levels of Fe and Mn, and the free acid can react with the sediment to release other metals, acid soluble nutrients, and trace organic compounds. This acidified water is either entrained in surface water runoff or infiltrates into the sediment in the dike forming the groundwater flow through the dike. The surface water is monitored and controlled by MES.

- 2. Dredged sediment in the dike. When the acidified waters infiltrate into the dredged sediment they enter an organic rich environment that is isolated from the atmosphere. Here several processes occur: the acid is neutralized by naturally occurring material such as shell material which contains calcium carbonate; acid and metals are bound by ion exchange processes; the reduction in acidity causes precipitation of insoluble metal compounds (with anions such as phosphate, and carbonate), and; reduction occurs which removes oxygen and changes the environmental conditions waters are in. The flow of water through the dike is relatively fast compared to the rate of reduction since the concentrations of sulfate are high relative to conservative mixing (this is shown as the positive Excess Sulfate in the Figures 1A-7 and 1A-8). If strongly reducing conditions existed all of the sulfate would be reduced and the sulfide produced would be significantly removed by sulfide mineral formation as in the North Cell.
- 3. *Movement through the dike walls*. The dike walls are made of clean sands, thus are relatively inert; however they act as a mechanical filter. As a filter, the dike retains the fine sediment placed in the dike, and removes the precipitates that form as the water reacts in the contained sediment. Eventually as with any filter, it would be expected that the filter (*i.e.* the dike walls) will become plugged as material is trapped along the flow lines. This is the area where the sampling wells are located. The groundwater sampled at this point reflects changes in the water chemistry resulting from transport through the three zones outlined above.
- 4. *Mixing with Bay water*. As the groundwater travels the dike as a result of the hydraulic gradient, it will encounter and mix with Bay water within the dike wall. The water from the dike is more dilute than Bay water so there will be some degree of floating, or riding over, of the less dense dike water on top of the more saline Bay water. The Bay water is aerated and slightly alkaline. This water will react with the dike water oxidizing the reduced water and precipitating iron oxy-hydroxides and other redox sensitive species. These precipitates are effective in scavenging trace metals and phosphate.

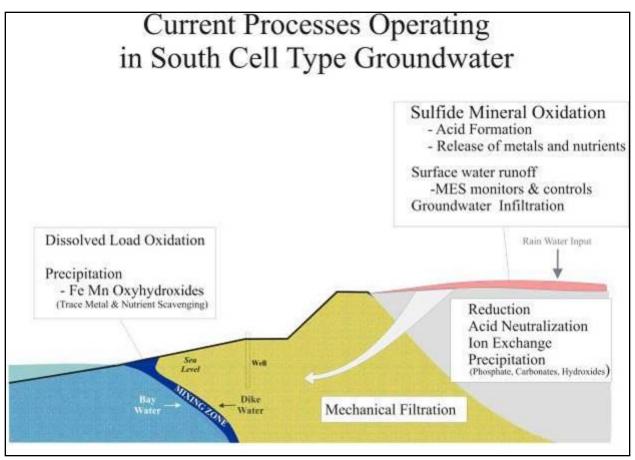


Figure 1A- 9: Schematic presentation of the processes which produce the groundwater similar to those found in the South Cell wells.

As noted the sampling wells are located in the sandy matrix of the dike walls which act as a filter for the groundwater. Except for March 2013 and March 2014 samplings, groundwater has been anaerobic for all of the sampling wells; all wells except for Well 2A, which has undergone an initial oxidation stage. The behavior of measured parameters in each well within the two cells is different reflecting a number of factors including: 1) the heterogeneous material contained in the dike; 2) source material that effected transport rates and chemistry of the groundwater, and 3) location of the well with respect to specific operation activities such as liming and surface water ponding.

Table 1A-2 is a summary of the trace metal data for the groundwater sampled during this monitoring year (four sampling periods), listing the number of samples, the number below detection, the mean, maximum and minimum concentration and the EPA Maximum Concentration Level in drinking water (MCL) (U.S. EPA, 2002). On average, metal concentrations in both the North and South Cell wells have shown a decreasing trend this monitoring year. Copper and lead remain below the detection limit in both cells. Fe and Mn are the only metals with concentration that exceed the EPA Secondary Maximum Concentration Levels (SMCL). These two metals are not considered a health risk but affect the taste and quality of the water. These metals precipitate from solution in aerobic conditions, so as the water

mixes with Bay water further down the flow path, these metals will precipitate out as metal oxyhydroxides. The metal-rich precipitate will cement the sands and make the dike more impermeable with time.

Table 1A-2: Monitoring wells trace metal analyses for 2013 and 2014 (four sampling								
periods). Values in mg/L, unless otherwise indicated. Detection limits ( <i>dl</i> ) for Fe and Mn								
were not reported (highlighted in yellow).								

	North Cell Type											
	n	<u>n&gt;dl</u>	<u>dl</u>	Mean	Min	Max	<u>MCL</u>					
Al	12	1	0.05	0.01	0.00	0.11	0.05 - 0.2*					
As	12	1	0.01	0.003	0.000	0.022	0.01					
Cd	12	0	0.001	<dl< td=""><td><dl< td=""><td><dl< td=""><td>0.005</td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td>0.005</td></dl<></td></dl<>	<dl< td=""><td>0.005</td></dl<>	0.005					
Cr (total)	12	0	0.005	<dl< td=""><td><dl< td=""><td><dl< td=""><td>0.1</td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td>0.1</td></dl<></td></dl<>	<dl< td=""><td>0.1</td></dl<>	0.1					
Cu	12	1	0.005	0.002	<dl< td=""><td>0.022</td><td>1.3</td></dl<>	0.022	1.3					
Fe	12			29.1	0.2	71.6	0.3*					
Pb	12	0	0.02	<dl< td=""><td><dl< td=""><td><dl< td=""><td>0</td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td>0</td></dl<></td></dl<>	<dl< td=""><td>0</td></dl<>	0					
Mn	12			3.1	0.1	7.1	0.05*					
Zn	12	8	0.005	0.181	<dl< td=""><td>0.650</td><td>5*</td></dl<>	0.650	5*					
Ag	12	0	0.001	<dl< td=""><td><dl< td=""><td><dl< td=""><td>0.1*</td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td>0.1*</td></dl<></td></dl<>	<dl< td=""><td>0.1*</td></dl<>	0.1*					
			5	South Cell T	<u>ype</u>							
	<u>n</u>	<u>n&gt;dl</u>	<u>dl</u>	<u>Mean</u>	<u>Min</u>	<u>Max</u>	<u>MCL</u>					
Al	12	0	0.05	<dl< td=""><td><dl< td=""><td><dl< td=""><td>0.05 - 0.2*</td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td>0.05 - 0.2*</td></dl<></td></dl<>	<dl< td=""><td>0.05 - 0.2*</td></dl<>	0.05 - 0.2*					
As	12	3	0.01	0.005	<dl< td=""><td>0.017</td><td>0.01</td></dl<>	0.017	0.01					
Cd	12	0	0.002	<dl< td=""><td><dl< td=""><td><dl< td=""><td>0.005</td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td>0.005</td></dl<></td></dl<>	<dl< td=""><td>0.005</td></dl<>	0.005					
Cr (total)	12	1	0.005	0.001	<dl< td=""><td>0.015</td><td>0.1</td></dl<>	0.015	0.1					
Cu	12	0	0.005	<dl< td=""><td><dl< td=""><td><dl< td=""><td>1.3</td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td>1.3</td></dl<></td></dl<>	<dl< td=""><td>1.3</td></dl<>	1.3					
Fe	12			57.3	4.1	170.0	0.3*					
Pb	12	0	0.02	<dl< td=""><td><dl< td=""><td><dl< td=""><td>0</td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td>0</td></dl<></td></dl<>	<dl< td=""><td>0</td></dl<>	0					
Mn	12			14.6	4.7	31.4	0.05*					
Zn	12	9	0.005	0.014	<dl< td=""><td>0.037</td><td>5*</td></dl<>	0.037	5*					
Ag	12	0	0.001	<dl< td=""><td><dl< td=""><td><dl< td=""><td>0.01*</td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td>0.01*</td></dl<></td></dl<>	<dl< td=""><td>0.01*</td></dl<>	0.01*					

Note:

MCL – EPA Maximum Concentration Levels for Inorganic in Drinking Water Values followed by \* are Secondary Maximum Concentration Levels (SMCL)

North Cell Type – Maintained Pore water behavior

South Cell Type – Oxidation at Surface followed by neutralization and partial reduction

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- U.S. EPA, 2002, National Primary Drinking Water Regulations, EPA 816-F-02-013 (July 2002), Table of contaminants and MCLs downloaded from U.S. EPA website: <u>http://permanent.access.gpo.gov/lps21800/www.epa.gov/safewater/mcl.html</u>

# APPENDIX II: BENTHIC COMMUNITY STUDIES (PROJECT III) Year 32

(September 2013 – August 2014)

## **Technical Report**

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July 2014

#### **EXECUTIVE SUMMARY**

The benthic macroinvertebrate community in the vicinity of the Hart-Miller Island Dredged Material Containment Facility (HMI DMCF) was studied for the thirty-second consecutive year under Project III of the HMI Exterior Monitoring Program. Benthic communities living close to the facility [Nearfield, South Cell Exterior Monitoring (formerly called South Cell Restoration Baseline), and Back River/Hawk Cove stations] were compared to communities located at some distance from the facility (Reference Stations). Water quality parameters, including dissolved oxygen concentrations, salinity, temperature, pH, conductivity, and Secchi depth were measured *in situ*. Twenty-two stations (12 Nearfield, 5 Reference, 2 Back River/Hawk Cove, and 3 South Cell Exterior Monitoring stations) were sampled on September 19, 2013. Unlike previous years, no spring cruise was conducted due to scaling back of monitoring efforts during the post closure era at HMI.

The salinity regime was in its historical average range. The Chesapeake Bay Benthic Index of Biotic Integrity (B-IBI), a multi-metric index of biotic condition that evaluates summer populations of benthic macro-invertebrates, was calculated for all stations. Metrics applicable to the low mesohaline classification (5 - 12 ppt) were used. The B-IBI's and derivative metrics (Total Infaunal Abundance, Pollution Indicative Taxa Abundance, Pollution Sensitive Taxa Abundance, and Shannon-Weiner Diversity Index) were compared to historical data and were analyzed both spacially and statistically.

The health of the benthic macroinvertebrate community around HMI in Year 32 was worse than historical averages. In Year 32, B-BIBI's around the island were at or near historical lows. Fourteen of the 22 stations failed to meet the benchmark criteria of 3.00. Nineteen of the 22 stations performed below their historic averages. Seven stations set new historic lows; four stations tied their historic lows; and no stations met their historic highs. Year 32 is the fourth consecutive year where B-IBI's have been trending downward.

The four year decline in B-IBI's can be attributed to fluctuations in the invertebrate community. They include decreases in the relative abundance of the pollution sensitive polychaete worm *M. viridis* (typically dominant) and the bivalves *R. cuneata* and *M. balthica*. Another fluctuation was a very high average abundance of the pollution indicative polychaete worm, *S. benedicti*. Lastly, the abundance of all organisms was especially high causing some decreases in the Total Infaunal Abundance metric scores and the relative Pollution Sensitive Taxa Abundance metric. The resultant dilution of pollution indicative species was not as influential on the Pollution Indicative Taxa Abundance metric scores.

The statistical analyses did not indicate that the stressed benthic invertebrate communities measured at stations in September 2013 were due to any adverse localized impacts from HMI operational discharges. Stressed benthic communities throughout the monitoring area were likely the result of large-scale Bay-wide and regional factors.

#### **INTRODUCTION**

Annual dredging of the shipping channels leading to the Port of Baltimore is necessary to maintain safe navigation. An average 4-5 million cubic yards of Bay sediments is dredged each year to maintain access to the Port. This requires the State of Maryland to develop environmentally responsible placement sites for dredged material. In 1981, the Hart-Miller Island Dredged Material Containment Facility (HMI DMCF) was constructed to accommodate the dredged material management needs for the Port of Baltimore and specifically the need to manage contaminated sediments dredged from Baltimore's Inner Harbor.

HMI is a 1,140-acre artificial island surrounded by a 29,000-foot long dike constructed along the historical footprints of Hart and Miller Islands at the mouth of the Back River. Over the years, a series of four spillways periodically discharged excess water released from on-site dredged material disposal operations.

An exterior monitoring program was developed to assess potential environmental impacts associated with HMI operations in support of the environmental permitting process for dredged material containment. Various agencies have worked together since the inception of this program to assess the environmental impacts resulting from facility construction and operation. Studies were completed prior to and during the early construction period to determine baseline environmental conditions in the HMI vicinity. Since Year 17, the Maryland Department of the Environment (MDE) has been responsible for all aspects of benthic community monitoring.

Midway through Year 28, on December 31, 2009, HMI stopped accepting dredged material. The fall of Year 28 represented the final monitoring data collected while HMI received dredged material. However, during the habitat development phase of this project HMI management will continue to move sediment and manage storm water run-off, resulting in periodic discharge into Chesapeake Bay. As the island gradually stabilizes over the next several years post closure exterior benthic monitoring will be necessary to document long-term trends. Discussions are continuing to determine how much post monitoring is necessary to eventually certify that the island has stabilized. Year 32 represents the fourth year of post closure data. However, during Year 32 samples were only collected during the fall. Fall only sampling will continue in 33 at a reduced (15) number of stations.

The goals of the Year 32 benthic community monitoring were:

- To monitor the benthic community condition; using, among other analytical tools, the Chesapeake Bay Benthic Index of Biological Integrity (B-IBI; Llanso 2002), and to compare the results at Nearfield stations to present local reference conditions;
- To monitor other potential sources of contamination to the HMI region by sampling stations near the mouth of Back River;
- To facilitate trend analysis by providing data of high quality for comparison with HMI monitoring studies over the operational phase of the project; and,

• To monitor benthic community conditions in areas near all functioning spillways, particularly South Cell Spillway 003. This will help the State to assess any environmental effects resulting from the South Cell closure and restoration.

#### **METHODS AND MATERIALS**

MDE staff collected all macroinvertebrate and water quality samples in Year 32. Field sampling cruises were conducted on board the Maryland Department of Natural Resources vessel *"R/V Kerhin"*. Twenty-two fixed benthic stations were monitored during a fall cruise (Table 2-1; Figure 2-1). Environmental parameters recorded at the time of sample collection are included in Tables 2-2 through 2-5.

Table 2-1: Sampling stations (latitudes and longitudes in degrees, decimal minutes), 7-digit
codes of stations used for Year 32 benthic community monitoring, and predominant
sediment type at each station for September.

				Maryland 7-Digit
Station #	Latitude	Longitude	Sediment Type	Station Designation
		Nearfield S		
MDE-01	39° 15.3948	$-76^{\circ} 20.5680$	Sand	XIF5505
MDE-03	39° 15.5436	-76° 19.9026	Silt/clay	XIG5699
MDE-07	39° 15.0618	-76° 20.3406	Silt/clay	XIF5302
MDE-09	39° 14.7618	-76° 20.5842	Silt/clay	XIF4806
MDE-11	39° 14.4432	-76° 20.104	Silt/clay	XIG4501
MDE-15	39° 14.5686	-76° 20.9526	Silt/clay	XIF4609
MDE-16	39° 14.5368	-76° 21.4494	Silt/clay	XIF4615
MDE-17	39° 14.1690	-76° 21.1860	Shell	XIF4285
MDE-19	39° 14.1732	-76° 22.1508	Silt/clay	XIF4221
MDE-33	39° 15.9702	-76° 20.8374	Sand	XIF6008
MDE-34	39° 15.7650	-76° 20.5392	Silt/clay	XIF5805
MDE-45	39° 14.7198	-76° 21.2538	Silt/clay	N/A
		<b>Reference</b> S	Stations	
MDE-13	39° 13.5102	-76° 20.6028	Silt/clay	XIG3506
MDE-22	39° 13.1934	-76° 22.4658	Silt/clay	XIF3224
MDE-36	39° 17.4768	$-76^{\circ}$ 18.9480	Silt/clay	XIG7589
MDE-50	39° 12.7488	-76° 18.3954	Sand	N/A
MDE-51	39° 12.1392	-76° 20.853	Silt/clay	N/A
	Ι	Back River/Hawk	<b>Cove Stations</b>	
MDE-27	39° 14.5770	-76° 24.2112	Silt/clay	XIF4642
MDE-30	39° 15.8502	-76° 22.5528	Silt/clay	XIF5925
	Sout	h Cell Exterior M	onitoring Stations	
MDE-42	39° 13.8232	-76° 22.1432	Silt/clay	XIF3879
MDE-43	39° 13.9385	-76° 21.4916	Silt/clay	XIF3985
MDE-44	39° 14.4229	-76° 21.8376	Silt/clay	XIF4482

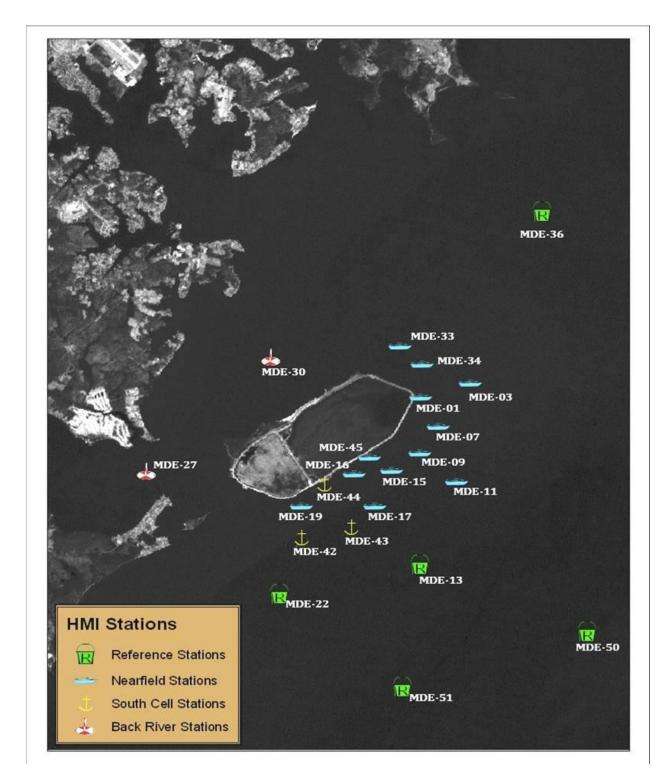


Figure 2-1: Year 32 benthic sampling stations for the HMI exterior monitoring program.

All stations sampled since Year 27 were again sampled for Year 32. Over the years, the list of stations sampled has changed several times. Occasionally old stations were deleted and new stations were added to suit monitoring needs. Year 32 is the sixth year without changes to the list of sampling stations<sup>1</sup>. Stations were classified by location and dominant sediment type (Table 2-1). Stations were divided into four location groups (Nearfield stations, Reference stations, Back River/Hawk Cove stations, and South Cell Exterior Monitoring stations) and five sediment types (silt/clay, shell, detritus, gravel, and sand). All benthic community stations coincided with stations sampled by the Maryland Geological Survey for sediment analysis.

Temperature, depth, salinity, pH, conductivity, and dissolved oxygen (DO) were measured *in situ* using a Yellow Springs Instruments (YSI) 6600 V2 multi-parameter water quality meter in September 2013. Water quality parameters were measured at approximately 0.5 m (1.6 feet) below the surface and 0.5 m above the bottom. The Secchi depth was measured at all stations.

All macroinvertebrate samples were collected using a Ponar grab sampler, which collects approximately 0.05 m<sup>2</sup> (0.56 ft<sup>2</sup>) of bottom substrate. Three replicate grab samples were collected at each station. A visual estimate of the substrate composition [percent contributions of detritus, gravel, shell, sand, and silt/clay (mud)] was made at each station (Table 2-2 and Table 2-4) and the dominant sediment type for each station was derived from these percentages. Each replicate was individually rinsed through a 0.5 mm sieve on board the vessel and preserved in a solution of 10 percent formalin and Bay water, with Rose Bengal dye added to stain the benthic organisms.

In the laboratory, each benthic macroinvertebrate replicate was placed into a 0.5 mm sieve and rinsed to remove field preservative and sediment. Organisms were sorted from the remaining debris, separated into vials by major taxonomic groups, and preserved in 70 percent ethanol. All laboratory staff were required to achieve a minimum baseline sorting efficiency of 95 percent and quality control checks were performed for every sample to ensure a minimum 90 percent recovery of all organisms in a replicate sample.

All organisms were identified to the lowest practical taxon (usually to species) using a stereo dissecting microscope. The number of specimens for each taxon collected in each replicate (raw data) is presented in the *Year 32 Data Report*. Members of the insect family Chironomidae (midges) were identified using methods similar to Llanso (2002). Where applicable, chironomids were slide mounted and identified to the lowest practical taxon using a binocular compound microscope. In cases where an animal was fragmented, only the head portion was counted as an individual taxon. All other body fragments were discarded. Individuals of the most common clam species (*Rangia cuneata*, *Macoma balthica*, and *Macoma mitchelli*) were measured to the nearest millimeter. An independent taxonomist verified 10 percent of all samples identified.

Six major measures of benthic community condition were examined, including: total infaunal abundance, relative abundance of pollution-indicative infaunal taxa, relative abundance

<sup>&</sup>lt;sup>1</sup> For a detailed explanation of the new sampling design see "Scientific Rationale for Relocating Hart-Miller Island Exterior Monitoring Stations in Advance of Facility Closure"

of pollution-sensitive infaunal taxa, the Shannon-Wiener diversity index, taxa richness, and total abundance of all taxa (excluding Bryozoa and Copepoda). Four of these measures (total infaunal abundance, relative abundance of pollution-indicative infaunal taxa, relative abundance of pollution-sensitive infaunal taxa, and the Shannon-Wiener diversity index) were used to calculate the B-IBI for September 2013. The B-IBI is a multi-metric index of biotic integrity used to determine if benthic populations in different areas of the Chesapeake Bay are stressed (Llanso 2002). In addition to the above metrics, the numerically dominant taxa and the length frequency distributions of the three most common clams (*R. cuneata*, *M. balthica*, and *M. mitchelli*) were examined.

Abundance measures were calculated based on the average abundance of each taxon from the three replicate samples collected at each station. Total abundance was calculated as the average abundance of epifaunal and infaunal organisms per square meter  $(\#/m^2)$ , excluding Bryozoa, which are colonial. Qualitative estimates (i.e., rare, common, or abundant) of the number of live bryozoan zooids are included in the *Year 32 Data Report*. Total infaunal abundance was calculated as the average abundance of infaunal organisms per square meter  $(\#/m^2)$ . These two different measures of abundance were calculated because epifaunal organisms are not included in the *B*-IBI (Ranasinghe et al. 1994).

For each station, data was converted to the base 2 logarithm in order to calculate the Shannon-Wiener diversity index (SWDI) (H') (Pielou 1966). Taxa richness (number of taxa) was calculated for each station as the total number of taxa (infaunal and epifaunal) found in all three replicates combined. Infaunal taxa richness was calculated as the number of infaunal taxa found in all three replicates combined. The most abundant taxa at reference and monitoring stations were also determined.

To evaluate the numerical similarity of the infaunal abundances among the 22 stations, a single-linkage cluster analysis was performed on a Euclidean distance matrix comprised of station infaunal abundance values for all 22 stations. This analysis was performed for September 2013 data. Friedman's nonparametric test was used to analyze the differences of the 10 most abundant infaunal species among the Nearfield, Reference, Back River/Hawk Cove, and South Cell Exterior Monitoring stations for September 2013. The statistical analyses were performed using SAS, Version 9.1 and SPSS, Version 11.5.

#### **RESULTS AND DISCUSSION**

#### Water Quality

Minimal variations between surface and bottom values for salinity, temperature, DO, conductivity, and pH values during the 2013 cruise (Table 2-5) indicated that water column stratification was not prevalent.

Secchi depths ranged from 0.30 m-1.0 m and averaged 0.65 m  $\pm$  0.18 m (Table 2-3). Water quality and Secchi depth measurements provide a snapshot of the conditions prevalent at the time of sampling, but do not necessarily reflect the dominant conditions for an extended period. The mean Secchi depth was 0.17 m less than the 16-year historic average of 0.82 m.

The following discussion will be limited to bottom values for the first three parameters (temperature, DO, Salinity) as bottom water quality measurements are most relevant to benthic macroinvertebrate health. In Year 32, bottom water temperatures showed little variation. The mean bottom water temperature ranged from  $20.31^{\circ}$ C –  $21.72^{\circ}$ C and averaged  $21.12^{\circ}$ C ±  $0.37^{\circ}$ C (Table 2-3). This mean was  $2.97^{\circ}$ C lower than the 27-year fall average of  $24.09^{\circ}$ C.

The mean bottom DO concentration exceeded the water quality standard (5.0 ppm) to protect aquatic life (Maryland Code of Regulations COMAR) during Year 32. The bottom DO ranged between 6.65 - 9.17 ppm and had a mean of 7.63 ppm  $\pm 0.63$  ppm (Table 2-3). This mean was 0.31 ppm higher than the 17-year fall average of 7.32 ppm.

In the early fall, this region of the Bay typically ranges between the oligohaline (0.5 ppt – 5 ppt) and mesohaline (>5 ppt – 18 ppt) salinity regimes (Lippson and Lippson 1997). The 28-year mean fall bottom salinity is 6.21 ppt,  $\pm$  2.86 ppt. Low Mesohaline conditions (5-12 ppt) were found during the fall 2013 sampling season.

In Year 32 salinity values varied slightly (Table 2-5, mean=7.37 ppt  $\pm$  1.19 ppt, range = 5.19 ppt – 8.94 ppt) and the mean fall salinity was 1.16 ppt higher than the historical average. This region of the Bay is subject to significant salinity fluctuations resulting from large interannual variation in rainfall in the watershed. In general, the Bay experiences relatively higher salinity values during the fall, because of dry summer conditions.

						Wind Speed (knots)		Speed			Wea	ther	Obs	erved B	ottom S	ediment	(%)
MDE			Water Depth	Wave Height	Wind			Air Temp.	Cloud Cover	Past 24							
Station	Time	Tide	( <b>m</b> )	( <b>m</b> )	Direction	Min.	Max	(°C)	(%)	hrs.	Today	silt/clay	sand	shell	gravel	detritus	
MDE-01	12:29	Flood	4.22	0.1	S	3	6	21.7	0	0	0	0	90	10	0	0	
MDE-03	12:14	Flood	5.04	0.1	S	3	6	21.1	0	0	0	70	0	30	0	0	
MDE-07	12:05	Flood	6.11	0.1	S	3	6	21.1	0	0	0	70	0	30	0	0	
MDE-09	11:51	Flood	5.53	0.1	S	3	6	20.6	0	0	0	70	0	30	0	0	
MDE-11	11:36	Flood	5.8	0.1	S	3	6	20.6	0	0	0	70	0	30	0	0	
MDE-13	10:39	Flood	4.83	0.1	S	3	6	17.8	0	0	0	95	0	5	0	0	
MDE-15	10:27	Flood	5.83	0.1	S	3	6	17.8	0	0	0	93	0	7	0	0	
MDE-16	10:03	Flood	4.74	0.1	S	3	6	16.7	0	0	0	95	0	5	0	0	
MDE-17	9:20	Flood	5.53	0.1	S	3	6	15.0	0	0	0	65	0	35	0	0	
MDE-19	9:39	Flood	4.59	0.1	S	3	6	15.0	0	0	0	65	0	35	0	0	
MDE-22	8:32	Flood	5.77	0.1	S	3	6	13.9	0	0	0	90	0	10	0	0	
MDE-27	13:53	Flood	3.67	0.1	S	3	6	23.9	0	0	0	75	0	15	0	10	
MDE-30	13:40	Flood	2.97	0.1	S	3	6	23.9	0	0	0	60	0	40	0	0	
MDE-33	12:55	Flood	2.3	0.1	S	3	6	23.3	0	0	0	0	90	10	0	0	
MDE-34	12:42	Flood	3.52	0.1	S	3	6	21.6	0	0	0	90	0	10	0	5	
MDE-36	13:15	Flood	2.85	0.1	S	3	6	23.3	0	0	0	70	0	30	0	0	
MDE-42	8:41	Flood	5.01	0.1	S	3	6	13.9	0	0	0	98	0	2	0	0	
MDE-43	9:05	Flood	4.95	0.1	S	3	6	14.4	0	0	0	95	0	5	0	0	
MDE-44	9:47	Flood	5.32	0.1	S	3	6	15.0	0	0	0	95	0	3	0	2	
MDE-45	10:18	Flood	4.8	0.1	S	3	6	16.7	0	0	0	70	0	30	0	0	
MDE-50	11:24	Flood	4.43	0.1	S	3	6	18.3	0	0	0	5	90	5	0	0	
MDE-51	10:58	Flood	4.74	0.1	S	3	6	18.3	0	0	0	90	0	10	0	0	

Table 2-2: Year 32 physical parameters measured *in situ* at all HMI stations on September 19, 2013.

Note: The Weather code 0 stands for "Clear".

									~
MDE	7-Digit		Depth	Salinity	Temp.	Dissolved Oxygen		Secchi Depth	Conductivity
Station	Code	Layer	(m)	(ppt)	(C)	(ppm)	pН	(m)	(µmos/cm)
				Nea	arfield Sta	tions			
MDE 01	VIESSOS	Surface	0.50	5.50	20.75	9.36	8.03	0.7	9,750
MDE-01	XIF5505	Bottom	3.72	5.59	20.63	9.17	8.06	0.7	9,900
MDE-03	XIG5699	Surface	0.50	6.36	21.33	8.44	7.87	0.8	11,110
MDE-03	AI03099	Bottom	4.54	6.88	21.15	7.94	7.82	0.8	12,000
MDE-07	XIF5302	Surface	0.50	6.22	20.98	8.15	7.83	0.7	10,920
MDL-07	XII 5502	Bottom	5.61	6.50	20.96	8.02	7.82	0.7	11,390
MDE-09	XIF4806	Surface	0.50	5.85	20.94	8.25	7.85	0.8	10,380
MIDE 05	711 4000	Bottom	5.03	7.31	21.13	7.47	7.76	0.0	12,710
MDE-11	XIG4501	Surface	0.50	6.94	21.11	7.84	7.79	0.9	12,080
	7110-301	Bottom	5.30	7.46	20.90	7.64	7.78	0.9	12,950
MDE-15	XIF4609	Surface	0.50	7.09	21.21	7.44	7.74	0.3	12,380
111111	1111 1007	Bottom	5.33	8.09	21.25	7.27	7.72	010	13,950
MDE-16	XIF4615	Surface	0.50	7.10	21.20	7.69	7.75	0.5	12,350
		Bottom	4.24	7.37	21.13	7.49	7.75	0.0	12,810
MDE-17	XIF4285	Surface	0.50	7.47	21.12	7.56	7.76	0.5	12,960
	1111 1200	Bottom	5.03	8.53	21.51	7.24	7.71	0.0	14,660
MDE-19	XIF4221	Surface	0.50	7.39	21.30	7.49	7.74	0.5	12,860
		Bottom	4.09	7.80	21.32	7.09	7.71		13,740
MDE-33	XIF6008	Surface	0.5	5.44	21.04	9.83	8.09	0.8	9,656
		Bottom	1.8	5.86	20.52	8.36	7.89	0.0	10,360
MDE-34	XIF5805	Surface	0.5	5.69	20.90	9.20	7.98	0.8	10,090
		Bottom	30.2	5.91	20.61	8.40	7.89		10,430
MDE-45	N/A	Surface	0.5	7.17	21.32	7.47	7.72	0.4	12,470
		Bottom	4.3	7.66	21.28	7.31	7.73		13,260
	1	a c	0.5		erence Sta		7.06		12.070
MDE-13	XIG3506	Surface	0.5	7.42	21.14	8.40	7.86	0.6	12,870
		Bottom	4.33	8.77	21.50	7.29	7.74		15,040
MDE-22	XIF3224	Surface	0.5	8.80 8.94	21.62 21.72	7.60 7.39	7.54	0.5	15,080 15,310
		Bottom					7.40		
MDE-36	XIG7589	Surface	0.5	4.95	21.01	8.75	7.97	0.7	8,847 9,267
		Bottom Surface	2.35 0.5	5.19 8.42	20.97 21.45	9.06 7.25	7.99		9,207
MDE-50	N/A	Bottom	3.93	8.42	21.43	7.14	7.70	1.0	14,480
		Surface	0.5	8.75	21.55	7.29	7.72		14,490
MDE-51	N/A	Bottom	4.24	8.85	21.32	7.17	7.72	0.9	14,990
		Dottoin	4.24			ove Stations	1.15		15,170
		Surface	0.5	5.47	21.87	10.29	8.46		9.687
MDE-27	XIF4642	Bottom	3.17	6.77	20.79	7.77	7.89	0.5	11,820
		Surface	0.5	5.28	21.29	9.34	8.05		9,385
MDE-30	XIF5925	Bottom	2.47	5.53	20.31	6.65	7.80	0.8	9,762
	1	Bottom				itoring Stations	,.00	1	>,,02
		Surface	0.5	7.75	21.35	7.22	7.62		13,400
MDE-42	XIF3879	Bottom	4.51	8.38	21.35	7.32	7.59	0.5	14,410
		Surface	0.5	7.36	20.94	7.79	7.76	-	12,780
MDE-43	XIF3985	Bottom	4.45	8.65	21.51	7.36	7.70	0.6	14,840
	WIE 4400	Surface	0.5	7.36	21.28	7.44	7.73	0.7	12,670
MDE-44	XIF4482	Bottom	4.82	7.58	21.26	7.41	7.74	0.5	13,130
					.=	1			-,

Table 2-3: Year 32 water quality parameters measured *in situ* at all HMI stations on September 19, 2013.

#### **BENTHIC MACROINVERTEBRATE COMMUNITY**

#### **Taxa Richness and Dominance**

A total of 36 taxa were found in Year 32. This is higher than the 11-year average of 31.18 taxa (fall only). The most common taxa groups were members of the phyla Arthropoda (joint-legged organisms), Annelida (segmented worms), and Mollusca/Bivalvia (shellfish having two separate shells joined by a muscular hinge). Sixteen taxa of Arthropoda were found in Year 32. The most common types of arthropods were the amphipods (including *Leptocheirus plumulosus*) and the isopods (including *Cyathura polita*). Seven taxa of annelid worms in the Class Polychaeta were found. Five species of bivalve mollusks were found. Overall, infaunal bivalve average abundance was lower in Year 32 than previous years (Table 2-4).

 Table 2-4: Average and total abundance (individuals per square meter) of each taxon found at HMI during the September 2013

 sampling; by substrate and station type. Because the mean bottom salinity regime was low mesohaline, taxa in bold are

 pollution sensitive while taxa highlighted in gray are pollution indicative.

Taxon	Average Abundance, All	Total Abundance, All	-	e Abunda nant Subs	-	Avera	Average Abundance by Station Type				
	stations	stations	Silt/Clay	Shell	Sand	Nearfield	Ref.	Back River	South Cell Exterior Monitoring		
Nemata	99.78	2195.20	119.47	6.40	12.80	33.07	119.04	534.40	44.80		
Carinoma tremophoros	4.95	108.80	5.69	0.00	2.13	5.33	5.12	0.00	6.40		
Bivalvia	54.40	1196.80	49.07	19.20	98.13	75.73	25.60	67.20	8.53		
Macoma sp.	24.15	531.20	9.96	32.00	106.67	10.67	62.72	38.40	4.27		
Macoma balthica	64.58	1420.80	65.07	12.80	78.93	4.27	234.24	51.20	32.00		
Macoma mitchelli	18.91	416.00	13.87	6.40	53.33	8.00	47.36	12.80	19.20		
Rangia cuneata	70.98	1561.60	70.40	6.40	96.00	93.33	74.24	28.80	4.27		
Ischadium recurvum	4.36	96.00	0.36	0.00	29.87	6.93	2.56	0.00	0.00		
Mytilopsis leucophaeata	497.45	10944.00	460.09	0.00	887.47	896.00	28.16	25.60	0.00		
Amphicteis floridus	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		
Capitellidae	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		
Heteromastus filiformis	38.98	857.60	42.67	76.80	4.27	26.13	75.52	3.20	53.33		
Spionidae	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		
Marenzelleria viridis	181.82	4000.00	212.62	6.40	55.47	205.87	103.68	416.00	59.73		
Streblospio benedicti	859.64	18912.00	706.49	518.40	1892.27	1121.07	382.72	643.20	753.07		
Polydora cornuta	401.75	8838.40	444.44	0.00	279.47	733.87	5.12	3.20	0.00		

Boccardiella ligerica	39.27	864.00	44.44	0.00	21.33	72.00	0.00	0.00	0.00
Nereidae	66.62	1465.60	24.53	0.00	341.33	108.80	32.00	0.00	0.00
Neanthes succinea	42.47	934.40	33.78	6.40	106.67	60.80	33.28	9.60	6.40

## Table 2-4- (continued)

Taxon	Average Abundance, All	Total Abundance,	•	e Abundar nant Subs		Average Abundance by Station Type				
Taxon	stations	All stations	Silt/Clay	Shell	Sand	Nearfield	Ref.	Back River	South Cell Exterior Monitoring	
Eteone heteropoda	25.31	556.80	23.47	12.80	40.53	26.13	28.16	38.40	8.53	
Naididae sp.	904.44	19897.60	998.76	550.40	456.53	822.40	593.92	1843.2 0	1124.27	
Amphipoda	215.27	4736.00	246.04	134.40	57.60	228.80	160.00	307.20	192.00	
Gammaridea	17.45	384.00	17.78	51.20	4.27	11.73	5.12	105.60	2.13	
Ameroculodes spp complex	6.11	134.40	6.76	12.80	0.00	2.13	21.76	0.00	0.00	
Leptocheirus plumulosus	1105.75	24326.40	1256.89	838.40	288.00	709.33	1397.76	2009.6 0	1602.13	
Gammarus sp.	1.16	25.60	1.07	6.40	0.00	1.07	0.00	0.00	4.27	
Melitadae	0.58	12.80	0.00	12.80	0.00	1.07	0.00	0.00	0.00	
Melita nitida	150.69	3315.20	169.24	89.60	59.73	112.53	143.36	80.00	362.67	
Corophiidae	27.64	608.00	21.33	0.00	74.67	50.67	0.00	0.00	0.00	
Apocorophium lacustre	1057.45	23264.00	1062.76	0.00	1378.13	1926.40	28.16	3.20	0.00	
Cyathura polita	102.98	2265.60	116.98	76.80	27.73	117.87	70.40	96.00	102.40	
Edotea triloba	34.91	768.00	42.31	0.00	2.13	48.00	6.40	80.00	0.00	
Chiridotea almyra	7.85	172.80	9.24	0.00	2.13	13.87	1.28	0.00	0.00	
Ciripedia	4.36	96.00	0.36	0.00	29.87	8.00	0.00	0.00	0.00	
Balanus improvisus	57.02	1254.40	8.53	0.00	366.93	96.53	19.20	0.00	0.00	
Balanus subalbidus	1.45	32.00	0.00	0.00	10.67	2.67	0.00	0.00	0.00	
Rhithropanopeus	35.20	774.40	7.11	0.00	215.47	64.53	0.00	0.00	0.00	

harrisii									
Membranipora sp	+	+	+	+	+	+	+	0.00	+
Chironomidae	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

### Table 2-4 – (continued)

Taxon	Average Abundance, All	Total Abundance, All	0	Abundar ant Subst	•	Average Abundance by Station Type				
	stations	stations	Silt/Clay	Shell	Sand	Nearfield	Ref.	Back River	South Cell Exterior Monitoring	
Coelotanypus sp.	9.31	204.80	11.02	6.40	0.00	5.87	0.00	32.00	23.47	
Procladius sp.	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
Cryptochironomus sp.	0.29	6.40	0.36	0.00	0.00	0.00	1.28	0.00	0.00	
Chironomus sp.	0.29	6.40	0.36	0.00	0.00	0.00	0.00	3.20	0.00	
Gobiosoma bosci	0.58	12.80	0.36	0.00	2.13	1.07	0.00	0.00	0.00	
Platyhelminthes	16.58	364.80	7.47	0.00	76.80	29.33	2.56	0.00	0.00	
Nudibranchia	0.29	6.40	0.00	0.00	2.13	0.53	0.00	0.00	0.00	
Mysidacea	2.62	57.60	2.13	0.00	6.40	1.60	3.84	9.60	0.00	
Cassidinea ovalis	5.53	121.60	0.00	0.00	40.53	10.13	0.00	0.00	0.00	
Hydrozoa	0.58	12.80	0.00	0.00	4.27	1.07	0.00	0.00	0.00	

Note: Presence of Membranipora sp. is indicated by +

Of the 36 taxa found in Year 32, fifteen were considered truly infaunal, fifteen were considered epifaunal, and the remaining six were considered too general to classify as either infaunal or epifaunal (see Ranasinghe et al. 1994). The most common infaunal species found during Year 32 were the amphipod *L. plumulosus*, the polychaete worms *M. viridis* and *S. benedicti*, the bivalve *R. cuneata*, worms from the family Naididae, and the isopod *C. polita*. The most common epifaunal species were the amphipod *A. lacustre* and the bivalve *M. leucopheata*.

Nearfield station MDE-01 had the highest number of taxa (22 taxa, Table 2-5). The station with the fewest number of taxa (11 taxa) was Back River/Hawk Cove station MDE-30 (Table 2-5). Overall, average taxa richness was highest at Reference stations but did not vary greatly between station types (average taxa richness: Reference=17.2 taxa, Nearfield=16.0 taxa, Back River/Hawk Cove=15.5 taxa, South Cell Exterior Monitoring=13.3 taxa). It is important to note that there are 12 Nearfield stations, 5 Reference stations, 3 South Cell Exterior Monitoring stations and 2 Back River/Hawk Cove stations. So, historic higher taxa abundances at Nearfield stations may simply be an artifact of sample size. No trend of increasing/decreasing taxa richness associated with distance from HMI could be discerned.

Station	Total Infauna	Total All	All Taxa	Infaunal Taxa	Shannon- Wiener	PSTA (%)	PITA (%)	Tolerance Score	% Carnivore/ Omnivore	Tanypodinae: Chironomidae	B-IBI
Nearfield Stations											
MDE-01	8697.60	17440.00	22	9	1.57	1.18	71.89	N/A	N/A	N/A	1.00
MDE-03	14969.60	41792.00	20	12	1.91	3.42	28.56	N/A	N/A	N/A	1.50
MDE-07	2483.20	2560.00	13	10	2.12	9.02	65.46	N/A	N/A	N/A	3.00
MDE-09	1766.40	1856.00	18	13	2.36	9.78	65.22	N/A	N/A	N/A	3.00
MDE-11	2624.00	3948.80	19	12	2.67	15.37	53.90	N/A	N/A	N/A	3.00
MDE-15	3270.40	3417.60	16	12	2.01	7.05	44.42	N/A	N/A	N/A	2.50
MDE-16	2368.00	2540.80	14	10	2.03	9.73	37.84	N/A	N/A	N/A	3.00
MDE-17	2310.40	2476.80	16	12	2.11	4.43	47.09	N/A	N/A	N/A	2.50
MDE-19	2816.00	3155.20	16	12	1.64	6.59	20.23	N/A	N/A	N/A	2.00
MDE-33	1388.80	1964.80	12	7	2.01	18.89	46.54	N/A	N/A	N/A	2.50
MDE-34	7942.40	9209.60	18	11	2.45	30.78	49.40	N/A	N/A	N/A	2.50
MDE-45	1657.60	1952.00	12	8	1.74	11.20	24.71	N/A	N/A	N/A	3.00
MEAN	4357.87	7692.80	16	11	2.05	10.62	46.27	N/A	N/A	N/A	2.46
Reference Stations											
MDE-13	2508.80	2700.80	16	11	2.28	3.06	60.46	N/A	N/A	N/A	2.00
MDE-22	3168.00	3398.40	14	11	2.18	20.61	15.96	N/A	N/A	N/A	3.00
MDE-36	5337.60	5625.60	21	13	1.77	12.47	21.34	N/A	N/A	N/A	2.50
MDE-50	1331.20	1964.80	19	11	2.65	30.77	20.19	N/A	N/A	N/A	3.50
MDE-51	4006.40	4275.20	16	13	2.51	15.18	39.78	N/A	N/A	N/A	3.00
MEAN	3270.40	3592.96	17.2	11.8	2.28	16.42	31.55	N/A	N/A	N/A	2.80
Back River/Hawk Cove Stations											
MDE-27	6489.60	7072.00	20	12	2.15	14.00	64.50	N/A	N/A	N/A	2.50
MDE-30	4646.40	4742.40	11	7	1.31	5.92	19.97	N/A	N/A	N/A	2.50
MEAN	5568.00	5907.20	15.5	9.5	1.73	9.96	42.23	N/A	N/A	N/A	2.50
South Cell Exterior Monitoring Stations											
MDE-42	4633.60	5158.40	15	11	1.96	4.83	48.34	N/A	N/A	N/A	2.00
MDE-43	3552.00	3705.60	12	10	1.98	3.96	56.04	N/A	N/A	N/A	2.00
MDE-44	3712.00	4243.20	13	10	1.81	6.21	40.34	N/A	N/A	N/A	2.50
MEAN	3965.87	4369.07	13.3	10.3	1.92	5.00	48.24	N/A	N/A	N/A	2.17

Table 2-5: Summary of metrics for each HMI benthic station surveyed during the Year 32 cruise. Total infaunal abundance and total abundance, excluding Polycladida, Nematoda, and Bryozoa, are individuals per square meter.

Since the first benthic survey studies of the HMI area in 1981, several taxa have been consistently dominant. Year 32 was no exception. Eight of the ten most dominant taxa in Year 32 have been consistently dominant through the years. Those are: the amphipods *L. plumulosus*, *A. lacustre*, and *M. nitida*, oligochaete worms of the family Naididae, the polychaete worms *M. viridis*, and *S. benedicti*, the isopod *C. polita*, and the bivalve, *R. cuneata*. Falling out of the most dominant taxa were the bivalve, *M. balthica* and the polycheate worm, *N. succinea*. *M. balthica* undergoes large swings in population density caused by low salinity die offs followed by recovery periods lasting several years. *N. succinea*, was the eleventh most dominant taxa and was found at about normal densities, throughout most stations. Two of the most dominant taxa in Year 32 were unusually abundant. Those were the polychaete worm *P. cornuta*, and the bivalve *M. leucophaeta*. The high average abundances of these taxa was driven by extremely high densities at just two stations (MDE-01 and MDE-03) where favorable habitat, clean shell substrate, allowed unusually high colonization and survival of the species. The average abundance of each taxon (individuals per square meter) found at each station during the cruise are provided in Table 2-6.

Table 2-6: Average number of individuals collected per square meter at each station during HMI Year 32 late summersampling, September 2013, stations MDE-1 to MDE-22. Because the mean bottom salinity regime was low mesohaline, taxa inbold are pollution sensitive while taxa highlighted in gray are pollution indicative.

Station											
Такор	MDE-	MDE-	MDE-	MDE-	MDE-	MDE-	MDE-	MDE-	MDE-	MDE-	MDE-
Taxon	01	03	07	09	11	13	15	16	17	19	22
Nemata	0	6.4	83.2	19.2	0	0	32	76.8	6.4	96	6.4
Carinoma tremaphoros	6.4	6.4	12.8	6.4	0	0	6.4	0	0	12.8	6.4
Bivalvia	51.2	480	0	0	6.4	0	0	38.4	19.2	6.4	0
<i>Macoma</i> sp.	0	0	0	0	0	0	12.8	0	32	6.4	0
Macoma balthica	0	0	0	6.4	6.4	6.4	0	6.4	12.8	19.2	486.4
Macoma mitchelli	0	6.4	6.4	25.6	0	6.4	6.4	0	6.4	12.8	19.2
Rangia cuneata	0	44.8	44.8	38.4	25.6	0	6.4	25.6	6.4	6.4	12.8
Ischadium recurvum	76.8	0	0	0	6.4	0	0	0	0	0	0
Mytilopsis leucophaeata	2233.6	7910.4	0	0	140.8	19.2	0	0	0	0	0
Amphicteis floridus	0	0	0	0	0	0	0	0	0	0	0
Capitellidae	0	0	0	0	0	0	0	0	0	0	0
Heteromastus filiformis	0	6.4	32	19.2	70.4	70.4	19.2	12.8	76.8	25.6	166.4
Spionidae	0	0	0	0	0	0	0	0	0	0	0
Marenzelleria viridis	25.6	153.6	64	83.2	102.4	32	70.4	108.8	6.4	12.8	38.4
Streblospio benedicti	4908.8	2585.6	582.4	550.4	851.2	582.4	544	339.2	518.4	288	192
Polydora cornuta	838.4	7635.2	0	6.4	326.4	19.2	0	0	0	0	0
Boccardiella ligerica	64	800	0	0	0	0	0	0	0	0	0
Nereidae	985.6	198.4	0	0	108.8	108.8	0	0	0	0	0
Neanthes succinea	307.2	192	6.4	32	108.8	83.2	6.4	19.2	6.4	12.8	6.4
Eteone heteropoda	25.6	102.4	0	6.4	57.6	70.4	6.4	0	12.8	0	0
Naididae sp.	1318.4	1587.2	1036.8	588.8	505.6	864	902.4	544	550.4	281.6	313.6
Amphipoda	140.8	1337.6	83.2	44.8	115.2	32	294.4	185.6	134.4	166.4	339.2
Gammaridea	0	0	0	0	0	12.8	0	0	51.2	89.6	0

Station											
	MDE-		MDE-	MDE-	MDE-	MDE-	MDE-	MDE-	MDE-	MDE-	MDE-
Taxon	01	MDE-03	07	09	11	13	15	16	17	19	22
Ameroculodes spp complex	0	0	0	0	0	0	6.4	0	12.8	6.4	0
Leptocheirus plumulosus	0	0	499.2	313.6	76.8	582.4	1248	1036.8	838.4	1734.4	1472
Gammarus sp.	0	0	0	0	0	0	0	0	6.4	6.4	0
Melitadae	0	0	0	0	0	0	0	0	12.8	0	0
Melita nitida	179.2	0	64	51.2	12.8	51.2	128	115.2	89.6	320	230.4
Corophiidae	224	345.6	0	0	38.4	0	0	0	0	0	0
Apocorophium lacustre	3961.6	17958.4	6.4	32	1043.2	25.6	0	6.4	0	0	0
Cyathura polita	76.8	313.6	115.2	44.8	262.4	38.4	153.6	83.2	76.8	147.2	115.2
Edotea triloba	0	0	0	0	6.4	0	0	0	0	0	0
Chiridotea almyra	0	0	0	0	0	0	0	0	0	0	0
Ciripedia	89.6	0	0	0	6.4	0	0	0	0	0	0
Balanus improvisus	1100.8	19.2	0	0	38.4	96	0	0	0	0	0
Balanus subalbidus	32	0	0	0	0	0	0	0	0	0	0
Rhithropanopeus harrisii	646.4	102.4	0	0	25.6	0	0	0	0	0	0
Membranipora sp	+	+	0	+	+	+	+	+	0	+	+
Chironomidae	0	0	0	0	0	0	0	0	0	0	0
Coelotanypus sp.	0	0	6.4	6.4	0	0	0	12.8	6.4	0	0
Procladius sp.	0	0	0	0	0	0	0	0	0	0	0
Cryptochironomus sp.	0	0	0	0	0	0	0	0	0	0	0
Chironomus sp.	0	0	0	0	0	0	0	0	0	0	0
Gobiosoma bosci	6.4	6.4	0	0	0	0	0	0	0	0	0
Platyhelminthes	224	128	0	0	0	0	0	0	0	0	0
Nudibranchia	6.4	0	0	0	0	0	0	0	0	0	0
Mysidacea	0	0	0	0	0	0	6.4	0	0	0	0
Cassidinea ovalis	121.6	0	0	0	0	0	0	0	0	0	0
Hydrozoa	12.8	0	0	0	0	0	0	0	0	0	0

Note: Presence of *Membranipora* sp. is indicated by +

Table 2-7: Average number of individuals collected per square meter at each station during the HMI Year 32 late summer sampling, September 2013, stations MDE-27 to MDE-51. Because the mean bottom salinity regime was low mesohaline, taxa in bold are pollution sensitive while taxa highlighted in gray are pollution indicative.

Station											
Taxon	MDE-	MDE-	MDE-	MDE-	MDE-	MDE-	MDE-	MDE-	MDE-	MDE-	MDE-
Τάχομ	27	30	33	34	36	42	43	44	45	50	51
Nemata	96	972.8	38.4	19.2	582.4	70.4	0	64	19.2	0	6.4
Carinoma tremaphoros	0	0	0	12.8	6.4	12.8	6.4	0	0	0	12.8
Bivalvia	134.4	0	115.2	192	0	6.4	0	19.2	0	128	0
Macoma sp.	76.8	0	51.2	25.6	44.8	0	12.8	0	0	268.8	0
Macoma balthica	102.4	0	0	0	6.4	76.8	0	19.2	0	236.8	435.2
Macoma mitchelli	25.6	0	0	19.2	19.2	6.4	0	51.2	12.8	160	32
Rangia cuneata	51.2	6.4	134.4	742.4	160	6.4	0	6.4	32	153.6	32
Ischadium recurvum	0	0	0	0	0	0	0	0	0	12.8	0
Mytilopsis leucophaeata	51.2	0	326.4	140.8	19.2	0	0	0	0	102.4	0
Amphicteis floridus	0	0	0	0	0	0	0	0	0	0	0
Capitellidae	0	0	0	0	0	0	0	0	0	0	0
Heteromastus filiformis	6.4	0	0	51.2	6.4	108.8	44.8	6.4	0	12.8	121.6
Spionidae	0	0	0	0	0	0	0	0	0	0	0
Marenzelleria viridis	665.6	166.4	128	1625.6	428.8	19.2	19.2	140.8	89.6	12.8	6.4
Streblospio benedicti	1184	102.4	576	1606.4	499.2	870.4	1036.8	352	102.4	192	448
Polydora cornuta	6.4	0	0	0	6.4	0	0	0	0	0	0
Boccardiella ligerica	0	0	0	0	0	0	0	0	0	0	0
Nereidae	0	0	0	12.8	0	0	0	0	0	38.4	12.8
Neanthes succinea	19.2	0	6.4	25.6	6.4	0	12.8	6.4	6.4	6.4	64
Eteone heteropoda	70.4	6.4	38.4	64	0	6.4	19.2	0	0	57.6	12.8
Naididae sp.	2918.4	768	32	2252.8	640	1356.8	934.4	1081.6	268.8	19.2	1132.8
Amphipoda	121.6	492.8	12.8	134.4	256	70.4	371.2	134.4	96	19.2	153.6
Gammaridea	0	211.2	0	0	0	6.4	0	0	0	12.8	0

 Table 2-7- (continued)

				Station							
Tower	MDE-	MDE-	MDE-	MDE-	MDE-	MDE-	MDE-	MDE-	MDE-	MDE-	MDE-
Taxon	27	30	33	34	36	42	43	44	45	50	51
Ameroculodes spp complex	0	0	0	0	12.8	0	0	0	0	0	96
Leptocheirus plumulosus	1228.8	2790.4	460.8	1318.4	3219.2	1971.2	985.6	1849.6	985.6	403.2	1312
Gammarus sp.	0	0	0	0	0	12.8	0	0	0	0	0
Melitadae	0	0	0	0	0	0	0	0	0	0	0
Melita nitida	121.6	38.4	0	140.8	172.8	499.2	140.8	448	249.6	0	262.4
Corophiidae	0	0	0	0	0	0	0	0	0	0	0
Apocorophium lacustre	0	6.4	70.4	32	12.8	0	0	0	6.4	102.4	0
Cyathura polita	89.6	102.4	0	76.8	57.6	121.6	121.6	64	64	6.4	134.4
Edotea triloba	160	0	0	569.6	25.6	0	0	0	0	6.4	0
Chiridotea almyra	0	0	0	166.4	0	0	0	0	0	6.4	0
Ciripedia	0	0	0	0	0	0	0	0	0	0	0
Balanus improvisus	0	0	0	0	0	0	0	0	0	0	0
Balanus subalbidus	0	0	0	0	0	0	0	0	0	0	0
Rhithropanopeus harrisii	0	0	0	0	0	0	0	0	0	0	0
Membranipora sp	+	0	0	+	0	0	+	0	0	+	0
Chironomidae	0	0	0	0	0	0	0	0	0	0	0
Coelotanypus sp.	12.8	51.2	0	0	0	6.4	0	64	38.4	0	0
Procladius sp.	0	0	0	0	0	0	0	0	0	0	0
Cryptochironomus sp.	0	0	0	0	6.4	0	0	0	0	0	0
Chironomus sp.	6.4	0	0	0	0	0	0	0	0	0	0
Gobiosoma bosci	0	0	0	0	0	0	0	0	0	0	0
Platyhelminthes	0	0	0	0	6.4	0	0	0	0	6.4	0
Nudibranchia	0	0	0	0	0	0	0	0	0	0	0
Mysidacea	19.2	0	12.8	0	6.4	0	0	0	0	6.4	6.4
Cassidinea ovalis	0	0	0	0	0	0	0	0	0	0	0
Hydrozoa	0	0	0	0	0	0	0	0	0	0	0

Note: Presence of Membranipora sp. is indicated by +

### Infaunal Taxa Abundance

In Year 32, total infaunal abundance at the various stations ranged from 1,331.20 to 14,969.60 organisms per square meter (individuals/m<sup>2</sup>) and averaged 4,167.27 individuals/m<sup>2</sup> (Table 2-5). In general, total infaunal abundances were above average for all stations. The highest abundance was found at the Nearfield station MDE-03, due primarily to large numbers of *P. cornuta*, the bilvave *M. leucophaeta*, and the amphipod *A. lacustre*. The lowest infaunal abundance was found at the Reference station MDE-50 (Table 2-5). The average total infaunal abundance was highest at Back River/Hawk Cove stations (5,568.00 individuals/m<sup>2</sup>) followed by Nearfield stations (4,357.87 individuals/m<sup>2</sup>), South Cell Exterior Monitoring stations (3,965.87 individuals/m<sup>2</sup>), and Reference stations (3,270.40 individuals/m<sup>2</sup>). While the relative differences between mean abundances at the various station types are historically typical, they are all above average. The 32-year mean (4,679.09 individuals/m<sup>2</sup>) of fall abundance for the Back River stations is much higher than the Reference (1,957.83 individuals/m<sup>2</sup>) and Nearfield (2,240.58 individuals/m<sup>2</sup>) means. It is also higher than the ten-year average for South Cell Exterior Monitoring stations (1,578.29 individuals/m<sup>2</sup>).

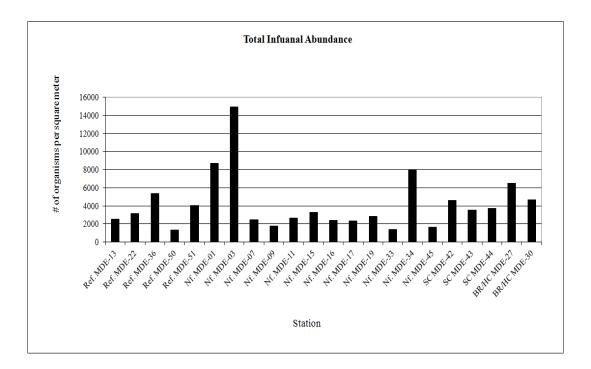


Figure 2-1: Total abundance of infaunal taxa collected at each HMI station in Year 32, September 2013 grouped by station type (Ref. = Reference; Nf. = Nearfield; SC = South Cell Exterior Monitoring; BR/HC = Back River Hawk Cove). Note: for Year 32 metrics, the ideal abundance range is between 1,500 and 2,500 individuals/ $m^2$ .

Total infaunal abundance and epifaunal abundance are subsets of total abundance. Infaunal abundance excludes certain organisms that have been omitted from the calculation of the B-IBI (see *Methods*). In Year 32, total infaunal abundance was similar to total abundance, typically accounting for  $\geq$ 85 percent of all organisms at all stations, except MDE-01 (51%) and MDE-03 (37%). This ratio is historically typical for this project.

# Diversity

Species diversity was examined using the Shannon-Wiener Diversity Index (SWDI), which measures diversity on a numerical scale from zero to four. A lower score indicates an unbalanced benthic community dominated by only one or two species whereas a higher score suggests a balanced, diverse benthic community. Diversity values for Year 32 are presented in Table 2-5.

SWDI values in Year 32 averaged  $2.05 \pm 0.35$  in September 2013. The fall average diversity was comparable to the 16-year mean fall diversity of 2.28. The lowest diversity value occurred at Back River/Hawk Cove station MDE-30 (1.31, Figure 2-3). This was due to the large percentage of Naididae worms and *L. plumulosus*, which accounted for 77 percent of total infaunal abundance at this station. The highest diversity value (2.67) occurred at Nearfield station MDE-11.

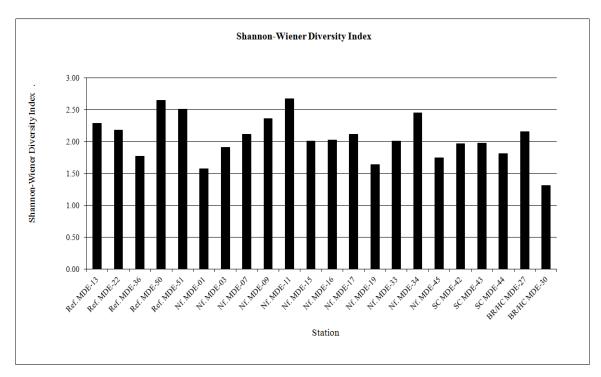


Figure 2-3: Shannon-Wiener Diversity Index (SWDI), HMI Year 33, September 2013 grouped by station type (Ref. = Reference; Nf. = Nearfield; SC = South Cell; BR/HC = Back River Hawk Cove).

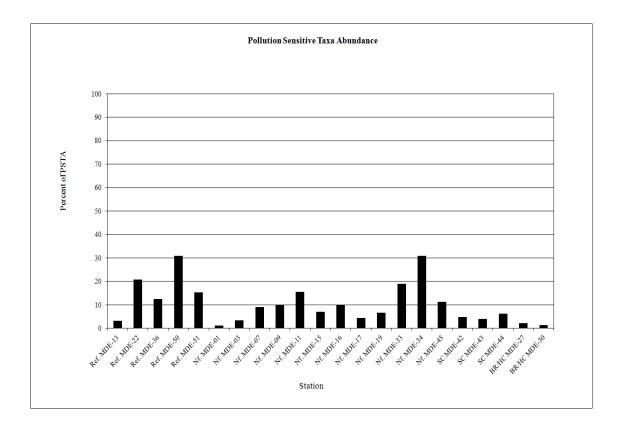
On average, Nearfield stations had diversity values similar to Reference stations. Comparing station types, the lowest average SWDI was 1.73 at the Back River/Hawk Cove stations followed by the South Cell Exterior Monitoring stations at 1.92, and Nearfield stations at 2.05. The highest average SWDI occurred at the Reference stations at 2.28 (Table 2-5). Historically, the 26-year mean SWDI values, ranked from lowest to highest, are associated with the following station types: Back River/Hawk Cove (2.13), Nearfield (2.34), Reference (2.41), and South Cell Exterior Monitoring (2.52, n=10 yrs).

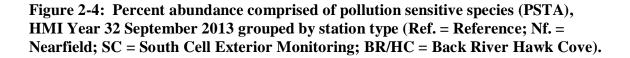
# **Pollution Sensitive Taxa Abundance (PSTA)**

Four taxa found during the September 2013 sampling cruise were designated as "pollution-sensitive" according to Alden et al. (2002). These were the polychaete worms *M. viridis*, the bivalves *R. cuneata* and *M. balthica*, and the isopod crustacean *C. polita*. The calculation of the PSTA is a ratio of the relative PSTA abundance to total infaunal abundance.

Small changes in salinity (causing conditions to be either above or below 5.0 ppt) can greatly affect the sensitivity/tolerance designation of several organisms, and correspondingly alter calculated abundances. Because this metric is, in part, salinity driven, and salinity varies from year to year, salinity must be accounted for prior to some historical analyses of PSTA fall data. In Year 32, the fall salinity regime was low mesohaline.

Pollution sensitive taxa occurred at all station types. PSTA ranged from 1.18 percent at MDE-01 (Nearfield station) to 30.78 percent at MDE-34 (Nearfield station – Table 2-5). The average PSTA for all stations was 11.11 percent. Comparing station types, the lowest average PSTA was 5.00 percent at the South Cell Exterior Monitoring stations, followed by the Back River/Hawk Cove stations at 9.96 percent, followed by the Nearfield stations at 10.62 percent. The highest average PSTA was 16.42 percent at Reference stations. Historically, the 32-year mean fall PSTA values, ranked from lowest to highest, are associated with the following station types: South Cell Exterior Monitoring (23.74 percent, n=9 years), Back River/Hawk Cove (29.27 percent), Nearfield (36.95 percent), and Reference (40.23 percent). PSTA values at all station types were near historic lows.





# **Pollution Indicative Taxa Abundance (PITA)**

Four taxa found during the Year 32 benthic monitoring were designated as "pollution-indicative" according to Alden et al. (2002): the Chironomid *Coelotanypus* sp., the polychaete worms *S. benedicti* and *E. heteropoda*, and oligochaete worms of the family Naididae. The calculation of the PITA is a ratio of the relative PITA abundance to total infaunal abundance.

Pollution indicative taxa occurred at all station types. The PITA ranged from 15.96 percent at MDE-22 (Reference station) to 71.89 percent at MDE-01 (Nearfield station) (Table 2-5). The average PITA for all stations was 42.83 percent. Comparing station types, the lowest average PITA was 31.55 percent at the Reference stations, followed by 42.23 percent at the Back River/Hawk Cove stations, and 46.27 percent at Nearfield stations. The highest average PITA occurred at the South Cell Exterior Monitoring stations at 48.24 percent. Historically, the 32-year mean fall PITA values, ranked lowest to highest, are associated with the following station types: Reference (22.38 percent), Nearfield (24.49 percent), Back River/Hawk Cove (38.53 percent), and

South Cell Exterior Monitoring (39.62 percent, n = 10 years). PITA values at all station types except Back River were poorer than the historic average.

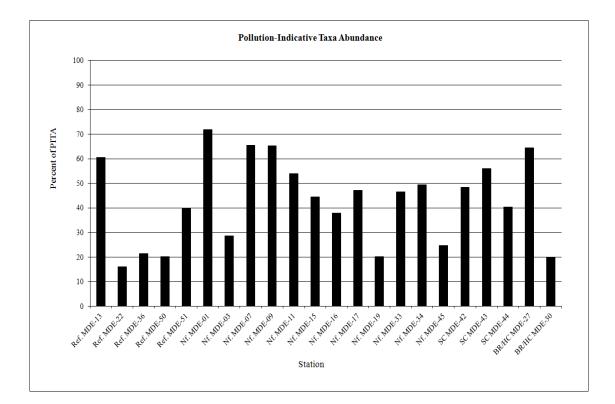


Figure 2-5: Percent abundance comprised of pollution indicative species (PITA), HMI Year 32 September 2013 grouped by station type (Ref.=Reference; Nf.=Nearfield; SC=South Cell Exterior Monitoring; BR/HC=Back River Hawk Cove).

# **Benthic Index of Biotic Integrity**

The B-IBI was calculated for all stations (see *Methods and Materials*). Four metrics were used to calculate the B-IBI for stations under the low mesohaline classification (5 - 12 ppt). These metrics were total infaunal abundance, relative abundance of pollution-indicative taxa, relative abundance of pollution-sensitive taxa, and Shannon-Wiener diversity index. The specific scoring criteria for the low mesohaline metrics are presented in Table 2-8. The B-IBI was developed as a benchmark to determine whether any given benthic sample taken from the Bay either approximates (B-IBI score = 5), deviates slightly (B-IBI score = 3), or deviates greatly (B-IBI score = 1) from conditions at the best Reference sites (Weisberg et al., 1997). A B-IBI score greater than or equal to 3.0 represents a benchmark to community that is not considered stressed

by *in situ* environmental conditions. The 22 benthic stations studied during Year 32 were compared to this benchmark.

Масяния	Score							
Measure	5	3	1					
Total Abundance (individuals per square meter)	≥ 1500-2500	500-1500 <b>or</b> ≥ 2500-6000	$< 500 \text{ or } \ge 6000$					
% Pollution-indicative Taxa	<u>&lt;</u> 10%	10-20%	> 20%					
% Pollution-sensitive Taxa	<u>&gt;</u> 25%	5-25%	<5%					
Shannon-Wiener Diversity Index	<u>&gt;</u> 2.5	1.7-2.5	< 1.7					

# Table 2-8: Low mesohaline scoring criteria for measures used in calculating the Chesapeake Bay B-IBI in September 2013 (Weisberg et al. 1997).

Compared to Year 31, individual station B-IBI Scores decreased at 11 stations, remained the same at 5, and increased at 6 stations. Eight of the twenty-two stations met or exceeded the benchmark criteria of 3.0 in Year 32. In Year 32, Back River/Hawk Cove stations MDE-27 (2.50) and MDE-30 (2.50), Reference stations MDE-13 (2.00) and MDE-36 (2.50), Nearfield Stations MDE-01 (1.00), MDE-03 (1.50), MDE-15 (2.50), MDE-17 (2.50), MDE-19 (2.00), MDE-33 (2.50), and MDE-34 (2.50), and South Cell Exterior Monitoring Stations MDE-42 (2.00), MDE-43 (2.00), and MDE-44 (2.50) failed to meet the benchmark criteria of 3.0 (Table 2-5). Nineteen stations were below their historic averages and three stations (Back River/Hawk Cove station MDE-27, Nearfield station MDE-45 and Reference station MDE-50, MDE-45 and MDE-50 were established in Year 27) were above the historic averages for B-IBI. In addition to nineteen stations being below their historic average four tied a historic low (Nearfield stations MDE-09, MDE-19, and MDE-34, and South Cell Exterior Monitoring station MDE-44). Seven stations (Nearfield stations MDE-01, MDE-03, MDE-11 and MDE-17, Reference station MDE-13, and South Cell Exterior Monitoring stations MDE-42, and MDE-43) set new historic lows. No stations set new historic highs.

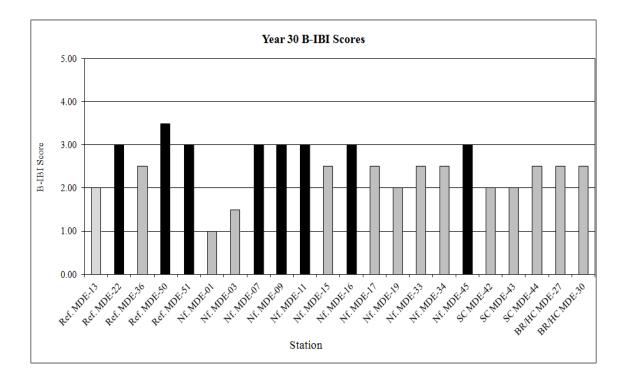
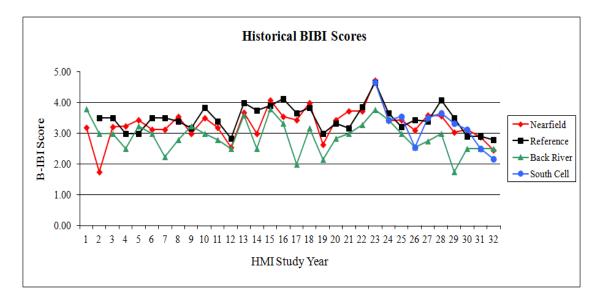


Figure 2-6: B-IBI Scores for all stations in September 2013 grouped by station type (Ref.=Reference; Nf.=Nearfield; SC=South Cell Exterior Monitoring; BR/HC=Back River Hawk Cove).

The mean B-IBI for Nearfield, South Cell Exterior Monitoring, Back River/Hawk Cove and Reference stations failed to meet the benchmark of 3.0. Average B-IBI scores by station type are shown in Figure 2-7. Compared to Year 31, the mean B-IBI decreased for Nearfield, South Cell Exterior Monitoring, and Reference station types and remained the same for Back River/Hawk Cove stations. The Year 32 mean B-IBI's for all station types were below their historic averages (ten year average for South Cell Exterior Monitoring Stations, Table 2-5).

The mean B-IBI for South Cell Exterior Monitoring and Reference stations set an all time low record (ten years of data for South Cell Exterior Monitoring stations). The mean B-IBI for Nearfield stations was the second lowest since Year 1. The mean B-IBI for Back River/Hawk Cove stations was the sixth lowest since Year 1 (six way tie).



# Figure 2-7: Average B-IBI Scores at HMI for Monitoring Years 1-32.

There was no trend of increasing or decreasing B-IBI scores associated with proximity to HMI in Year 32. Compared to other station types, South Cell Exterior Monitoring and Back River/Hawk Cove stations had the lowest mean B-IBI's in Year 32. Back River/Hawk Cove stations have had the lowest average 26 of 32 years.

The Year 32 low B-IBI's were attributable to several variations in the invertebrate community. Total infaunal abundances were exceptionally high for most organisms. These high abundances depressed the total infaunal abundance metric, depressed PSTA, but did not significantly improve PITA scores

As in most years with poor B-IBI's, the abundances of some pollution sensitive taxa were below average. Among these, the bivalves, *M. balthica* and *R. cuneata*, while rebounding from recent die-offs, were still below average in abundance. The abundances of pollution indicative taxa were also above historic averages. Worms in the family Naididae and the polychaete worm, *S. benedicti* were three times that of Year 31, another year with poor B-IBI's.

Based on B-IBI's, Year 32 was among the poorest years since HMI monitoring began. All station types except Back River/Hawk Cove stations have shown a three or four year steady decline in B-IBI. While the Nearfield and South Cell Exterior Monitoring station B-IBI's are at historic lows, so is the mean at Reference Stations, implying a regional decline is being recorded.

#### **Clam Length Frequency Distribution**

In September 2013, 233 *R. cuneata* were collected. The greatest average abundance of *R. cuneata* occurred at the Nearfield stations (13.83 clams/station), followed by the Reference stations (11.20 clams/station), the Back River/Hawk Cove stations (4.50 clams/station), and the South Cell Exterior Monitoring stations (0.67 clams/station). The greatest abundance of *R. cuneata* was found in the 1-5mm size class.

Historically, *R. cuneata* tends to be the most abundant bivalve mollusk found in this benthic monitoring project. It is classified as pollution sensitive during mesohaline years ( $\geq$ 5ppt). The population has historically been very dynamic in terms of overall abundance and distribution by size or station type. The main drivers of *R. cuneata* variability appear to be temperature and salinity. In the Chesapeake Bay, this species exists at the northern extent of its range. Because of this, it is subject to high winter mortality during cold winters (Hopkins, et al., 1973). Additionally, ideal salinity conditions for reproduction and recruitment do not occur regularly. The reduction in *Rangia* abundance from Year 30 (1,731 clams) to Year 31 (77 clams) (95.6 %) is greater than the typical winter die-off which usually ranges between 5 and 68%. In Year 32, the beginning of a recovery of the population (an increase to 233 clams in the smallest size class) was recorded. In Maryland, *R. cuneata* rarely if ever reaches its reported maximum age (15-20 years) or size (79 mm). Looking at 15 years of frequency distribution data around HMI, it is difficult to identify more than four age classes of clams at any time. This implies very few clams survive longer than five years.

In September 2013, 222 *M. balthica* were collected with 183 coming from Reference stations, 16 from Back River/Hawk Cove stations, 15 from South Cell Exterior Monitoring stations, and 8 from Nearfield stations. The greatest abundance of *M. balthica* was found in the 11-15 mm size class.

*M. balthica* has been commonly observed in low to moderate abundances throughout this benthic monitoring project. It is classified as pollution sensitive during mesohaline years ( $\geq$  5 ppt). The population has historically been somewhat dynamic in terms of overall abundance and size distribution. The main driver of *M. balthica* variability appears to be salinity. In the Chesapeake Bay, this species exists at salinities as low as about 5 ppt (Gosner, 1978), and is generally not found much more than 10-15 miles north of HMI. Seventeen years of monitoring data indicates that strong freshets are responsible for causing wide population fluctuations. After high mortality occurred during a strong freshet in Year 23 the population gradually recovered to previous densities only after the Upper Bay became more salty during Year 29. Another freshetinduced mortality was documented in 2011 (Year 30) as MDE confirmed a major die-off in the northern part of the Bay, in late June, as a result of low salinity Following that event, no M. balthica was found in the fall of Year 31. In Year 32, the beginning of a recovery of this population was also recorded. In September 2013, 65 *M. mitchelli* were collected, with 37 coming from Reference stations, 15 from Nearfield stations, 9 from South Cell Exterior Monitoring stations, and 4 from Back River/Hawk Cove stations. The greatest abundance of *M. mitchelli* was found in the 1-2 and 3-4 mm size classes. Similar to *M. balthica*, *M. mitchelli* populations declined in the spring of Year 22 and remained depressed for several years. Based on 16 years of historical HMI frequency distribution data, a strong freshet in Year 23 caused high mortality in this species; however, by Year 29 it appeared to have recovered to previous densities. The freshet of spring 2011 induced another mass mortality and the population has recovered. Populaion density of M. mitchelli is naturally lower than M. balthica in the HMI Region.

### **MULTIVARIATE AND FRIEDMAN'S ANALYSES**

### **Multivariate Analysis**

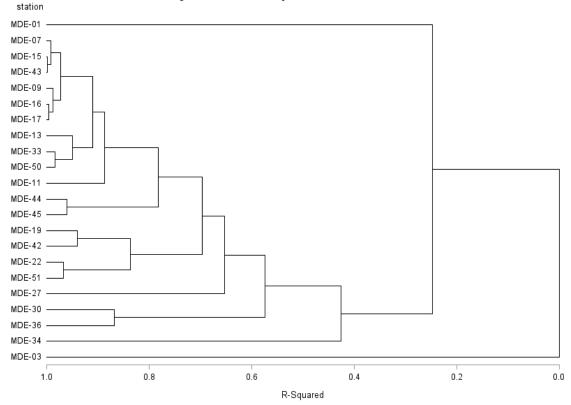
Multivariate cluster analysis was applied to Year 32 station invertebrate abundances to examine the patterns of variability among the HMI stations. Multivariate methods are used to make sense of large, complex data sets where several variables (for HMI, the invertebrate taxa abundances) are measured at each sampling location (22 HMI stations). In general, the purpose of multivariate methods is to simplify the complex data and identify patterns (Johnson, 1998a). Specifically, the cluster procedure was applied to the HMI data to identify groups of stations with similar benthic invertebrate assemblages.

The multivariate clustering procedure has been conducted twenty-seven times since Year 12. The formation of identifiable groups has been highly variable, but a number of station pairings have consistently reappeared. The most frequent station pairings that are found in identified cluster groups are: MDE-17 with MDE-30, MDE-19 with MDE-30, MDE-30 with MDE-44, MDE-03 with MDE-09, MDE-13 with MDE-17 and MDE-19 with MDE-22. Three stations have consistently been identified as outliers: MDE-27 (fifteen times since Year 19), MDE-01 (ten times since Year 19) and MDE-51 (four times since Year 27).

The cluster tree figure for September 2013 showed a clear articulation of several HMI station clusters (Figure 2-8).  $R^2$ , the coefficient of determination, was used to evaluate the strength of station clusters.  $R^2$  is the percentage of variation in the benthic assemblages that is "explained" by the cluster model. At an  $R^2 > 0.95$ , four station clusters were apparent, indicating very high similarity in their benthic assemblages. MDE-01, MDE-07, MDE-09, MDE-15, MDE-16, and MDE-17 formed one cluster; MDE-13, MDE-33, and MDE-50 formed a second cluster, MDE-44 and MDE-45 formed a third cluster, and MDE-22 and MDE-51 made up the fourth cluster. Another cluster was formed at an  $R^2 = 0.94$ , which was composed of the stations MDE-19 and MDE-42. At an  $R^2 = 0.91$ , the six and three station clusters combined into one group and at  $R^2 = 0.88$ , station MDE-11 joined this group. These 10 stations were identified as Cluster Group 1. Station clusters MDE-44 and MDE-45 (Cluster Group 2), MDE-22 and MDE-51 (Cluster Group 3) and MDE-19 with MDE-42 (Cluster Group 4) were kept as distinct, separate groups because of their lack of strong similarity of their benthic assemblages with other stations. The final identified group, Cluster Group 5, composed of stations MDE-30 and MDE-36, formed with an  $R^2 = 0.87$ . The cluster dendrogram indicated that three stations (MDE-01, MDE-03, and MDE-34) were strong outliers, with weak linkage to other stations ( $\mathbb{R}^2 < 0.45$ ), indicating that the benthic invertebrate assemblages at these stations were unique and dissimilar from other stations. The remaining station, MDE-27, linked to Cluster Groups 1 - 4 stations at  $R^2 = 0.66$ , indicating that the benthic invertebrate assemblage at this station were moderately to weakly similar to the benthic assemblages at these cluster groups. MDE-27 is an Intermediate Station that cannot be characterized as either an outlier or belonging to a cluster group.

The September 2013 cluster dendrogram results viewed in context with the B-IBI results presented earlier (see section "Benthic Index of Biotic Integrity"), indicate that stations of Cluster Group 3 (MDE-22 and MDE-51) had unstressed benthic invertebrate assemblages (B-IBI > 3.00), while the stations of Cluster Groups 4 (MDE-19 and MDE-42) and 5 (MDE-30 and MDE-36) all had in common stressed benthic invertebrate assemblages (B-IBI < 3.00). In contrast, Cluster Groups 1 and 2 were composed of stations with both "failing" and "passing" B-IBI scores, so neither of these cluster groups could be definitively characterized with respect to benthic community health. The three outlier stations (MDE-01, MDE-03, and MDE-34) were all identified by the B-IBI as having stressed benthic invertebrate assemblages. The identified strong similarities between the Cluster Group 3 benthic communities, verifies the assumption that these two reference stations (MDE-22 and MDE-51) are not influenced by HMI discharges. Likewise, the strong similarity in the benthic communities at Back River station MDE-30 and reference station MDE-36, supports the assumption (based on the repeated occurrence of MDE-27 as an outlier, marginal outlier, or intermediate station), that the Back River benthic community is distinct and not impacted by HMI discharges.

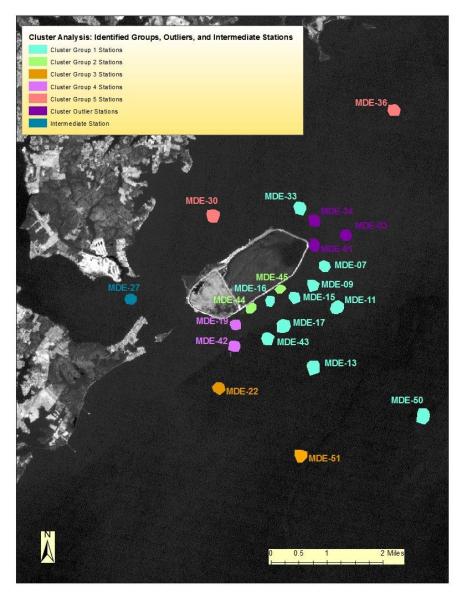
As in previous years, the relationship between identified cluster groups and station type (Nearfield, Reference, Back River and South Cell) was poor except for Cluster Group 2 (both South Cell stations) and Cluster Group 3 (both Reference stations). Likewise, bottom type correlated poorly with identified cluster groups because of the prevalence of silt/clay bottom in the HMI area.



Cluster Analysis Tree for September 19, 2013 Station Data

Figure 2-8: September 2013 Cluster Analysis tree.

Average distance between stations in Cluster Group 1 (8,203 ft) and distance between station pairs in Cluster Group 2 (3,291 ft), Cluster Group 3 (9,950 ft) and Cluster Group 4 (9,950 ft) were less than the overall average distance between all stations (12,141 ft), indicating that spatial proximity was an influencing factor in group formation. However, spatial proximity was less of an influencing factor in Cluster Group 5 formation, with distance between the two stations (19,666 feet) greater than the overall station to station average distance.



**Figure 2-9: Identified Cluster Groups, Strong Outiers and Intermediate Areas for September 2013** 

Color-coding of identified cluster groups, strong outliers, and the one intermediate station (neither strong grouping characteristics nor strong outlier characteristics) are shown in Figure 2.9. Cluster Group 3, the only identified group where healthy benthic communities predominate, is located to the south – southeast of the island.

# Friedman's Analysis

As in past years, Friedman's nonparametric ANOVA test was applied to Year 32 benthic macroinvertebrate data. The Friedman's nonparametric test determines if significant differences in the top ten most abundant invertebrate taxa occur between station types. For Year 32 the Friedman's test was run on the conventional four station

groups – Reference, Nearfield, South Cell Exterior Monitoring, and Back River. Modified station groups were tested with the Friedman's in Year 29 and Year 30 based on B-IBI result patterns in those years, which indicated unique conditions occurring at several stations near the North Cell and to a subset of Nearfield + South Cell stations. However, this was not evident with Year 32 B-IBI scores so no modified station groups were tested.

Friedman test results (Tables 2-9) indicated no significant differences in the ten most abundant infaunal taxa between the four station types in September 2013 (P = 0.516). Significant Friedman results occur infrequently (only 8 times in the 18 HMI monitoring years the statistical test has been utilized), usually because of high station to station variability of taxa abundances, both among and within station groups.

Table 2-9: Friedman Analysis of Variance for September 2013's 10 most abundant species among: Back River/Hawk Cove, Nearfield, South Cell Exterior Monitoring, and Reference stations. ANOVA Chi-Square. (N = 10, df = 3) = 2.28, p = 0.516.

Station Type	Average Rank	Mean	Std. Dev.
Nearfield	2.9	668	587
Reference	2.2	287	432
Back River	2.7	565	755
South Cell	2.2	405	568

### CONCLUSIONS

In Year 32, the benthic macroinvertebrate community was examined in the fall only (September 2013). The salinity regime remained in its historical average range after heavy freshwater inputs in early Year 30. As usual, little stratification of water quality was evident during either the fall or spring cruises. Dissolved oxygen at all stations exceeded the State Water Quality standard of 5.0 ppm deemed necessary to support healthy aquatic communities. Salinity, pH, Dissolved oxygen, and turbidity were slightly higher than normal in Year 32. Temperature was slightly lower than the historical mean. None of the differences from the mean were statistically significant. The B-IBI was calculated for all stations using four metrics applicable to the low mesohaline classification (5 - 12 ppt). The B-IBI's and derivative metrics were compared to historical data and analyzed both spacially and statistically.

The health of the benthic macroinvertebrate community around HMI in Year 32 was worse than historical averages. BIBI's around the island were at or near historical lows. Fourteen of the 22 stations failed to meet the benchmark criteria of 3.00. Nineteen of the 22 stations performed below their historic averages. Three stations tied their historic lows. Eight stations set new historic lows; and no stations met their historic highs. Year 32 is the fourth consecutive year where B-IBI's have been trending downward.

The mean B-IBI for all station types failed to meet the benchmark of 3.0 and were below historic averages. The mean B-IBI score for Nearfield stations (2.46) was 0.84 lower than the historic average and the second lowest in 32 years. The South Cell Exterior Monitoring stations mean (2.17) was 1.08 below average and at a historic low (ten years). The Reference stations mean (2.80) was 0.68 below average and the lowest in 32 years. The Back River/Hawk Cove stations mean (2.50) was 0.39 below average and tied for fifth lowest in 32 years. The reference stations were also at historic lows implying a regional decline.

In Year 30, MDE reported that there was a cluster of contiguous stations that performed poorly. The group of Nearfield stations MDE-15, MDE-16, MDE-19, and MDE-45 and South Cell Exterior Monitoring station MDE-44, is closer to the dike of the island and South Cell outfall/ barge offloading dock. Combined with Nearfield station MDE-17 and South Cell Exterior Monitoring stations MDE-42 and MDE-43, a group of eight stations exist in close proximity to the southwest corner of HMI. While six of these eight failed to meet the benchmark criteria of 3.00 in Year 31 and 32, poorly performing stations were widespread throughout the HMI region and in every station type. After three years of attention, it does not appear that this cluster consistently performs worse than other traditionally monitored station types.

The four year decline in B-IBI's and the Year 32 low B-IBI's were attributable to several variations in the invertebrate community. Total infaunal abundances were exceptionally high for most organisms (both pollution tolerant, pollution indicative, and non-designated species). These high abundances depressed the total infuanal abundance

metric slightly throughout the region. The greater effect of the increased abundances was on the PSTA. The three fold increase in pollution sensitive taxa was overwhelmed by the dilution by a nine fold increase in non-designated species, causing the PSTA to fall to only 11%. The dilution effect of non-designated species did not have a counteracting result on the PITA because the percentage of pollution indicative species was so high that increased dilution did not decrease the percentage of indicative species enough to improve the metric scores.

As in most years with poor B-IBI's, the abundances of some pollution sensitive taxa were below average. Among these, the bivalves, *M. balthica* and *R. cuneata*, while rebounding from recent die-offs, were still below average in abundance. The abundances of pollution indicative taxa were also above historic averages. Worms in the family Naididae and the polychaete worm, *S. benedicti* were three times that of Year 31, another year with poor B-IBI's.

The multivariate cluster analysis identified five station groups that had strongly similar benthic invertebrate assemblages ( $\mathbb{R}^2 > 0.87$ ). The ten station Cluster Group 1 (MDE-07, MDE-09, MDE-11, MDE-13, MDE-15, MDE-16, MDE-17, MDE-33, MDE-43, MDE-50) were generally located east of the island (except for MDE-33) and the group overall could not be characterized as having a healthy or stressed benthic invertebrate community, because it was composed of an equal number of stations with B-IBI < 3.00 and with B-IBI > 3.00. The other four identified clusters were composed of pairs of stations that exhibited lower than average spatial proximity (except for MDE-30 and MDE-36 of Cluster Group 5). Cluster Group 5 along with Cluster Group 4 (MDE-19 and MDE-42) had stressed benthic invertebrate communities, while Cluster Group 2 (MDE-44 and MDE-45) had both stressed and healthy benthic invertebrate communities. The strong outlier stations identified by the cluster dendrogram (MDE-01, MDE-03, and MDE-34) were all characterized as having stressed benthic invertebrate communities. The remaining station (MDE-27) was characterized as neither belonging to one of the identified groups nor being a strong outlier, indicating the benthic macroinvertebrate communities at this station was weakly similar to Cluster Groups 1 - 4.

The Friedman's nonparametric ANOVA test indicated no significant differences between the four station types. Hence, Friedman's results did not pinpoint any localized adverse impacts to the surrounding benthic community from HMI operational discharges, as a general pattern of stressed benthic invertebrate communities prevailed across the entire monitoring area. In future monitoring years the statistical analysis could be improved by modifying the sampling design to be more adaptive to changing conditions. To better focus on examining impacts to the benthic community from HMI operational discharges, the extent of discharge plumes should be identified to improve the validity of designated station types. The current station types could then be modified to include: Discharge Impacted stations, Nearfield stations, Reference stations and Back River stations.

Future monitoring plans: MDE proposed and MPA accepted the continuation of benthic monitoring at a reduced level until stabilization of the island is complete. This

will involve sampling fifteen select sites, every fall, starting in 2014 and continuing through 2019 at which time the monitoring frequency will be reevaluated.

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# APPENDIX 3: ANALYTICAL SERVICES YEAR 32 (PROJECT IV)

(September 2013 – August 2014)

# **Technical Report**

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> > August 2014

### **OBJECTIVES**

The Year 32, project goals were to continue to measure and evaluate the levels of contaminants in the sediment in the vicinity of HMI and to relate these, as far as possible, to historical data. Continued comparison and correlation of annual data with the historical HMI data, will indicate the extent of any contamination, biological exposure and if any trend in concentrations are developing at locations around the island.

Specific objectives for Year 32 were:

- To collect clams and associated sediment for analyses of trace elements, in the fall of 2013. A minimum of 10 sites were selected from the larger pool of Maryland Department of the Environment (MDE) biota stations for this work. Sediment and clams were collected at the same time. Both sediment and clams were analyzed for Hg, MeHg, Ag, Se, As, Pb and Cd;
- To determine the concentrations of target trace elements in surface sediments at the larger number of stations around HMI visited by the Maryland Geological Survey (MGS) in September 2013. Metal analysis focused on those metals not measured by MGS, specifically Hg, MeHg, Ag, Se and As; and
- To determine PCB and PAH concentrations sediment and clams collected in the fall of 2013 by Chesapeake Biological Laboratory (CBL).

The results of the quality assurance (QA/QC) procedures and the description of the analytical and field protocols are contained in the *Year 32 Data Report*. Overall, the QA/QC results were acceptable for a study of this nature. No evidence of bias or lack of precision or accuracy was indicated by the QA/QC results. Comparisons of duplicate analyses and comparison of measured values to certified values for the analyzed Standard Reference Materials are also discussed in the *Year 32 Data Report*. Again, the QA/QC objectives were met in this regard.

# METHODS AND MATERIALS

### **Sampling Procedures**

A large spatial survey of sediment was conducted by MGS in September 2013. Samples from this survey were collected by MGS personnel for CBL using a Ponar grab sampler. Samples were placed in acid washed plastic containers, frozen and delivered to CBL for trace element analysis. In September 2013 a subset of MDE biota stations was visited by MDE and CBL personnel to collect clams and sediment for trace element, PCB and PAH analyses. The simultaneous collection is required to make the best bioaccumulation calculations. Sediment for trace element and organic contaminants analyses were collected using plastic and stainless steel spatulas, respectively, integrating the top several centimeters and avoiding the sides of the sampler to minimize the possibility of contamination. Sediments for metals were placed in plastic sampling cups and were kept cooled in an ice chest or refrigerator until they could be processed in the laboratory. Sediments for organics were placed in glass jars with foil lined caps.

Sediment was sieved in the field for clams; the whole clams were placed in plastic bags with surface water and held on ice. The clams were depurated and then frozen to allow easy shucking the next day. Clams for trace metal analysis were removed whole from their shells with a Teflon-coated spatula and the spatula was acid rinsed between each site's samples, to avoid cross contamination. The clam tissues for analyses of organic contaminants were removed using a stainless steel spatula, which was rinsed with solvent between samples from different sites. The clam bodies from each site were homogenized in a plastic blender with a stainless steel blade for trace element analysis, and a glass blender with stainless steel blades, for organic contaminant analysis. Unused samples were returned to their respective bags and stored in the freezer until further analysis.

#### **Procedures for Trace Element Analyses**

For trace element analysis other than T-Hg and MeHg, EPA Method 3052 is generally followed. The Milestone EOTHO-EZ uses quartz reaction vessels placed inside Teflon cups, which are pressure sealed during digestion. For digestion, 1-2 grams of sediment is placed in the vessel with 9 ml of concentrated ultra pure Nitric Acid (HNO<sub>3</sub>) and 2 ml of concentrated ultrapure Hydrochloric Acid (HCl). The vessel is covered with a loose fitting quartz cap, and placed in the Teflon cup. 5 ml of 30% Hydrogen Peroxide (H<sub>2</sub>O<sub>2</sub>) is added to the Teflon cup and the cup sealed. The sample is heated to 180 °C and allowed to reflux for 15 minutes. The samples are then cooled and filtered through Whatman No. 41 filter paper by suction filtration and diluted to 100 ml with deionized water. Clams are digested in a similar fashion. These extracts are analyzed for Ag, As, Se, Pb and Cd using a Hewlett-Packard 4500 Inductively Coupled Plasma-Mass Spectrometer (ICP-MS).

Samples for the determination of T-Hg (1-3 g wet weight) were placed in Teflon vials along with a solution of 70% sulfuric/30% nitric acid. The Teflon vials are placed in

an oven and heated overnight at 60°C (Mason and Lawrence, 1999). The digestate was then diluted to 10 ml with distilled-deionized water. Prior to analysis, the samples were further oxidized for 30 minutes with 2 ml of bromine monochloride solution. The excess oxidant was neutralized with 10% hydroxylamine solution and the concentration of T-Hg in an aliquot of the solution was determined by tin chloride reduction cold vapor atomic fluorescence (CVAFS) detection after gold amalgamation in accordance with protocols outlined in USEPA Method 1631 (Mason et al. 1993).

For the determination of MeHg, clams and sediments were first extracted by subboiling distillation (Horvat et al. 1993). Clam or sediment tissue was weighed into Teflon vessels along with 1 ml of 50% sulfuric acid solution, 1 ml of a 20% potassium chloride solution and 18 ml of ultra pure water. The vessels were heated to approximately 90°C and volatiles and water distilled under a nitrogen stream for three hours. The distillate was reacted with a sodium tetraethylborate solution to convert the nonvolatile MeHg to gaseous MeHg (Bloom 1989). The volatile adduct was purged from solution and recollected on a graphitic carbon column at room temperature. The MeHg was then thermally desorbed from the column and analyzed by gas chromatography with CVAFS detection. Detection limits for T-Hg and MeHg are based on three standard deviations of the blank measurement.

A subsample of each trace metal sample (sediments) was used for dry weight determination. Weighed samples were placed in a VWR Scientific Forced Air Oven at 60°C overnight. Upon drying, samples were then reweighed and a dry/wet ratio was calculated.

### **Analytical Procedures for Organics**

The sediment and clam homogenates were extracted and purified using the method described by Kucklick et al. (1996). For this method, a subsample of clam homogenate, 5 g wet weight, is removed and ground with anhydrous sodium sulfate (~50 g). A perdeuterated PAH cocktail ( $d_8$ -napthalene,  $d_{10}$ -fluorene,  $d_{10}$ -fluoranthene,  $d_{12}$ perylene) and a noncommercial PCB solution (IUPAC #'s 14, 65, 166) are added as surrogates to each sample to track extraction efficiency. The mixture is then extracted in a Soxhlet apparatus with 250 mL of dichloromethane (DCM) for 24 hours. The extracts are then concentrated to 2 mL using a vacuum rotary evaporator and transferred into hexane. Each sample is transferred to a 4 ml Waters autosampler vial with sample and rinses amounting to approximately 4 mL. Gravimetric lipid analysis is performed on each sample with subsampled fractions determined gravimetrically (Kucklick et al. 1996). Samples are again concentrated in similar fashion as above, then solvent exchanged to hexane. To remove lipids the extracts are then eluted with 25 mL petroleum ether over 4 g deactivated Alumina [6% (w/w) water]. After concentrating, the extracts are spiked with a perdeuterated PAH mixture ( $d_{10}$ -acenapthene,  $d_{10}$ phenanthrene,  $d_{12}$ -benz[*a*]anthracene,  $d_{12}$ -benzo[*a*]pyrene,  $d_{12}$ -benzo[*g*,*h*,*I*]perylene) for quantification of PAH's. The samples are then analyzed using a Hewlett Packard 5890 gas chromatograph (GC) with a HP-5MS (cross linked 5% phenyl methyl siloxane)

capillary column (30m x 0.25mm x 0.25um film thickness) and a HP-5972 series mass spectrometer (MS) for PAH's (Ko and Baker 1995). Each sample is separated after GC/MS analysis into two fractions with 35 mL of petroleum ether and 50 mL of DCM/PET (1:1), respectively, over 8 g of deactivated Florisil [(2.5% (w/w) water (Kucklick et al.1996)]. The first fraction (F-1), contains PCBs and 1-100%, by weight of the less polar organochlorine pesticides [heptachlor (100%), 4,4-DDT (40%), 4,4-DDE (100%), t-nonachlor (24%), heptachlor (1%), 4,4-DDT(44%)]. The second extracted fraction, (F-2), contains 56-100% of the more polar organochlorine pesticides [a-HCH (100%), g-HCH (100%), c-chlordane (100%), t-chlordane (100%), t-nonachlor (76%), heptachlor (99%), heptachlor epoxide (100%), dieldrin (100%), 4,4-DDD (100%), 4,4-DDT (56%)]. Both fractions are solvent exchanged to hexane and concentrated to ~ 1 mL.

PCB congeners were analyzed by gas chromatography using a J&W Scientific DB-5 capillary column ( $60m \ge 0.32mm$ ,  $0.25\mu m$  film thickness) coupled to an Agilent HP-5972 detector. Individual PCB congeners are identified and quantified using the method of Mullins et al. (1985) using the noncommercial PCB congeners IUPAC 30 and 204 as internal standards.

### **RESULTS AND DISCUSSION**

### **Trace Elements in Sediment, September 2013**

Concentrations of As in the sediment collected around HMI in Year 32 (fall 2013) are generally close to the running mean and median calculated from historic values (Figure 3-1). Only 8 sites had As concentrations elevated above both the mean and median concentrations. Of these sites, only sediment collected from MDE 48 had concentrations above the standard deviation of the running mean. Concentrations of Se in sediment were above the historical running mean and median at sites MDE 13, MDE-14 and MDE 26. At no sites were Se concentrations outside the standard deviation around the mean (Figure 3-1).

Concentrations of Ag in the sediment collected from sites MDE-1 to MDE-41in the fall of 2013 were again lower than the median and average concentrations of previous years (Figure 3-2). This same condition, lower than average Ag concentrations in sediment has been observed for the past 4 years. Sites with a shorter history (sites numbered MDE-42 to MDE-51) had concentrations in 2013 that were close to the respective sites running means. As reported in the past, elevated Ag concentrations in 2000 and 2001 continue to bias the mean sediment concentration data and thus the median concentration (red line Figure 3-2) better reflects the general condition. Annual fluctuations in the concentration of Ag in sediment are system wide and appear unrelated to HMI operation.

Concentrations of mercury (T-Hg) in sediment were generally above the running mean calculated from previous years with concentrations at 23 of the 43 sites falling above the standard deviation of measurements made between 1998 and 2012 (Figure 3-2). The sites with elevated T-Hg concentrations are distributed all around the island and even the reference site, MDE-36, is elevated by almost a factor of 2.

Concentrations of MeHg in sediment collected in the fall of 2013 were generally comparable to previous years (Figure 3-3). Nine sites, MDE-25, MDE-38, MDE-44 through MDE-50 had concentrations of MeHg that were above the standard deviation of the sites running mean. Most of these sites have fewer years of record, which may explain this deviation, as the MeHg concentrations at these sites are similar to sites elsewhere around the island. The percent of mercury that occurred as MeHg was less than 1% at all sites except MDE-50 (Figure 3-3).

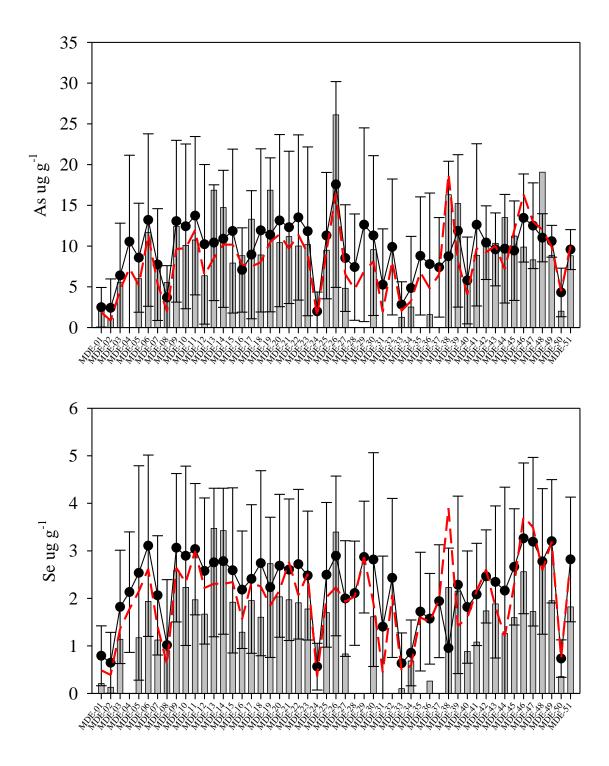


Figure 3-1: As and Se in sediment, expressed as dry weight concentration, collected by MGS in the fall of 2013 (bars) and the 1998-2012 mean (circles) with standard deviation (error bars) and the 1998-2012 median (dashed line). Sites 4, 24, 28, 29, 31, 32, 35, 37 are no longer sampled.

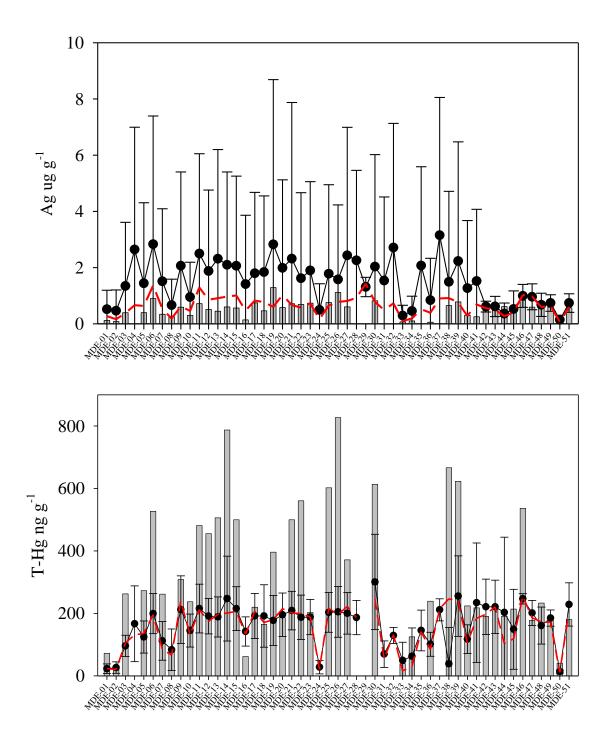


Figure 3-2: Ag and T-Hg concentrations in sediment, expressed as dry weight concentration, collected by MGS in the fall of 2013 (bars) and the 1998-2012 mean (circles) with standard deviation (error bars) and the 1998-2012 median (dashed line). Sites 4, 24, 28, 29, 31, 32, 35, 37 are no longer sampled.

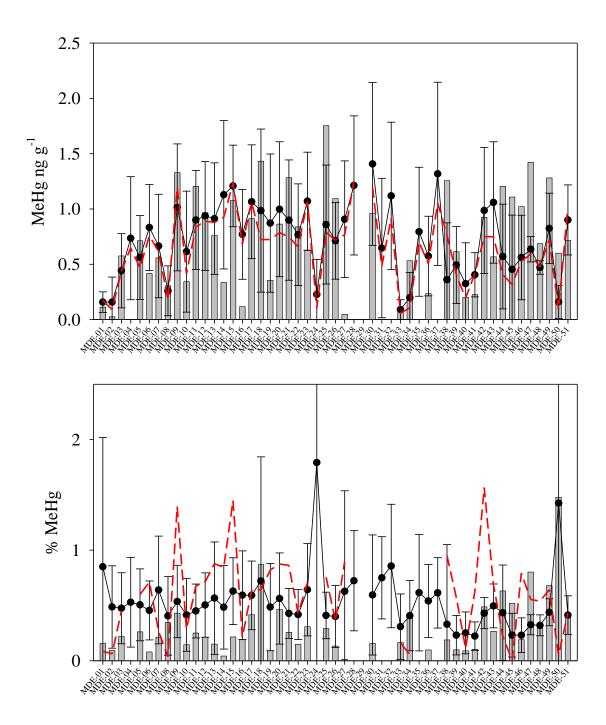


Figure 3-3: MeHg, expressed as dry weight concentrations, and percent of T-Hg as MeHg in sediment collected by MGS in the fall of 2013 (bars), and the 1998-2012 mean (circles), with standard deviation (error bars), and the 1998-2012 median (dashed line). Sites 4, 24, 28, 29, 31, 32, 35, 37 are no longer sampled.

# Relationships between trace elements (As, Se, Ag, Hg) in sediment among sites and years

If the sources of the trace elements to the sediment around HMI are similar, there would be an expectation forcorrelations to exist between some element concentrations in both time and space. Having a basic understanding of such trends allows anomalous stations and years to be identified especially if multiple elements can be used to confirm the existence of an anomaly. Stations located near the Back River and Baltimore Harbor need be treated with care because the potential for contaminants to migrate from sources within these water bodies to the vicinity around the HMI complex is great. MDE sites 1 to 44 have been monitored for greater than 10 years and provide the best data for which to perform such an analysis. In this section, temporal trends of elements across the individual sites and the relationships between elements among sites along with the influence of site characteristics on element concentrations are examined.

To examine the temporal trends at individual sites, the sites have been broken into regions based on proximity to one another and to reduce the number of figures. Such divisions are easy to see with sites from Back River, Harbor and Far Afield "reference" stations falling into obvious clusters, but for the rest of the sites, dividing the sites up is more arbitrary and the divisions chosen simply reflect geographical distribution around the island, and broken into near and far sites. The sites could have been dived based on other criteria such as sediment type, but the primary focus of the study is on identifying emerging hot spots, thus geographic location is the top priority.

# Arsenic in Sediment 1998-2013

In general concentrations of As in sediment are temporally coupled, meaning concentrations in an area around HMI increase and decrease together over time (Figures 3-4 and 3-5). Sites near Baltimore Harbor show the greatest variation in As concentrations, with concentrations ranging from less than 1 ug  $g^{-1}$  to nearly 50 ug  $g^{-1}$ . Between 1998 and 2001, variations were most extreme at all the sites including those classed together as the Far Afield sites (Figure 3-5). While year to year variability in sediment As concentrations was still present after 2001, changes were less severe. As reported in the Y31 report, a general upward trend in As concentration from 2005 to 2012 at a large number of sites was observed. While muted, and taking into account year to year variability, the trend does not appear to end in 2013, which is shown for the north Central Far stations in figure 3-6. Since this trend of increasing As concentration occurs in the reference stations (shown in the Far Afield plot), the patterns is not likely associated with HMI activities (Figure 3-5). This increasing trend in As concentration is not present in the sediment from the Back River side of the island. This lack of a difference is probably because variability at these sites has remained high over the entire study, but also many of the sites were not measured after 2009 when the trend was observed elsewhere.

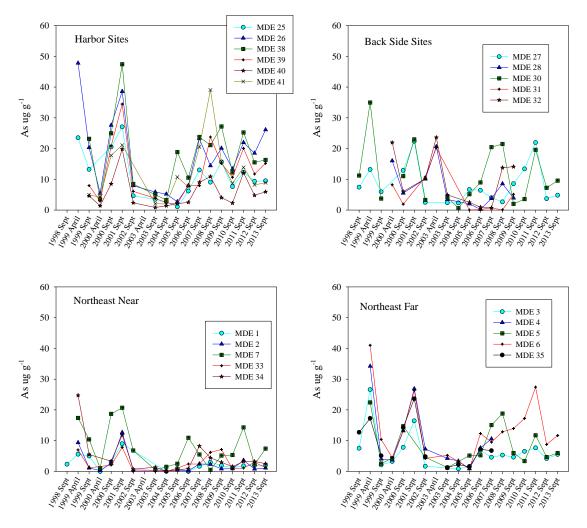


Figure 3-4: Arsenic (As) concentrations in sediment from 1998 to 2013 at the Harbor sites, Back River Sites, and sites of the Northeast side of the island.

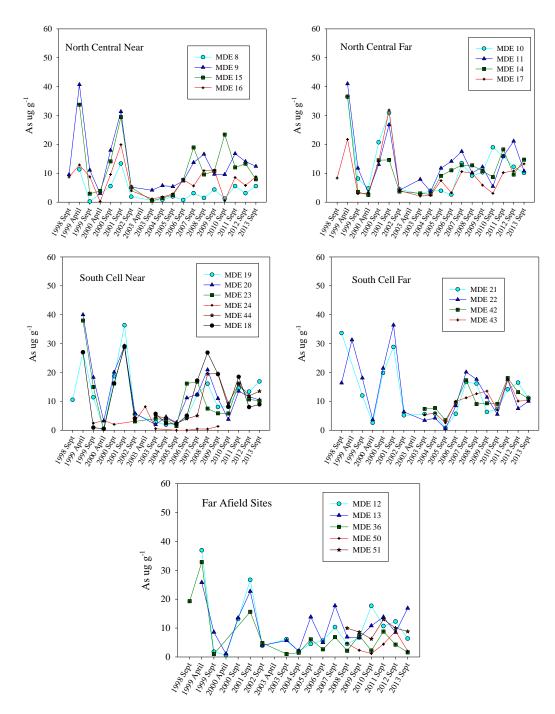


Figure 3- 5: Arsenic (As) concentrations in sediment from 1998 to 2013 sites located of the north east central side of the island, of the south cell and stations far afield from the island including reference stations.

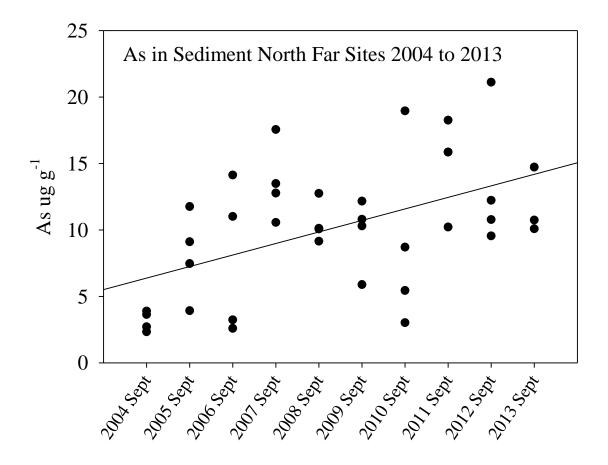


Figure 3-6: Arsenic (As) concentrations in sediment from 2004 to 2013 for North Far sites (R<sup>2</sup> is 0.26; P value 0.001).

# Selenium in Sediment 1998 to 2013

Concentrations of Se sediment concentrations have a "temporal synchronicity" across sites, meaning the concentration of Se largely rise and fall together in space and time (Figures 3-7, 3-8). Se concentrations range from undetectable to 8 ug g<sup>-1</sup>. There appears to be three time periods in the sediment concentration data; a period of elevated Se concentrations that extended from the onset of measurements up to 2002, followed by a period of lower concentrations from 2002 to 2006 and then a return to a period of elevated Se concentrations from 2006 to 2011. In 2012, lower Se concentrations prevailed and this trend continued in 2013. While more subdued than at many of the site groups, the Far Afield sites also followed the same temporal pattern of sediment Se concentrations (Figure 3-8). The spike in Se in 2000 to 2002 coincides with the rise in As (discussed above) and an increase in Ag (discussed below). In the past two years of study As and Se behavior diverge, with As trending up and Se trending down.

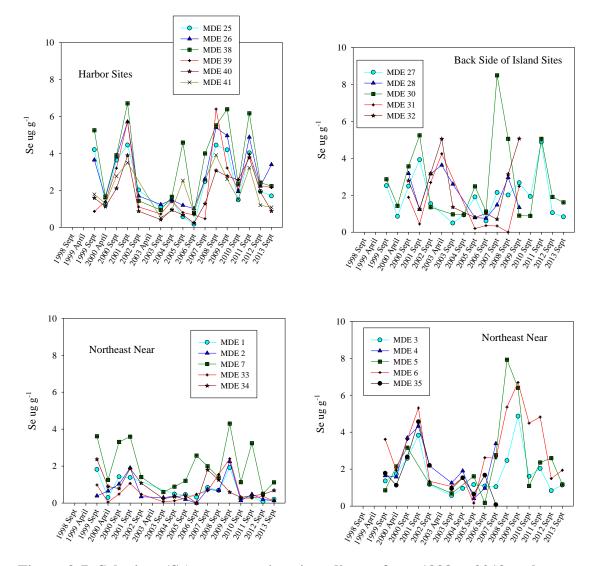


Figure 3-7: Selenium (Se) concentrations in sediment from 1998 to 2013 at the Harbor sites, Back River Sites, and sites of the Northeast side of the island.

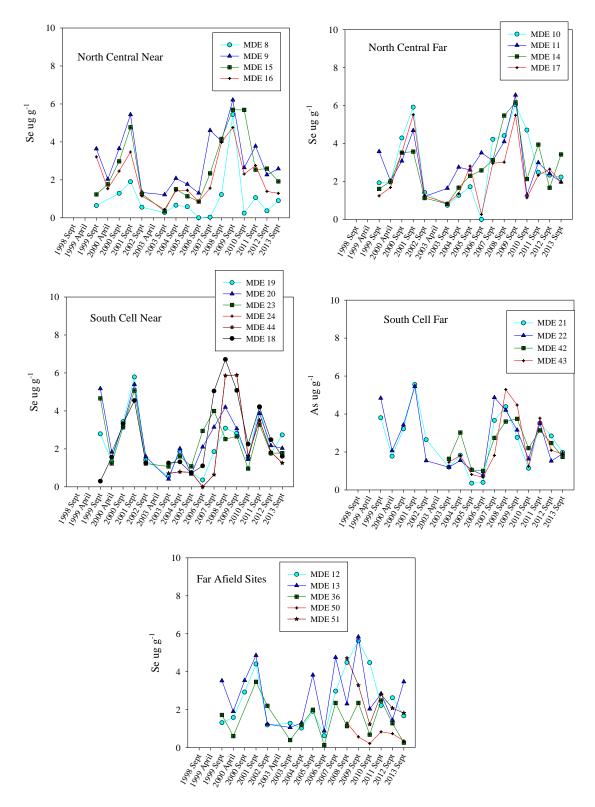


Figure 3- 8: Selenium (Se) concentrations in sediment from 1998 to 2013 sites located of the north east central side of the island, of the south cell and stations far afield from the island including reference stations.

#### Silver in Sediment 1998 to 2013

As reported for the other trace elements the concentrations of Ag in sediment vary in temporal synchrony and the concentrations of Ag in sediment around HMI can be divided into distinct periods (Figure 3-9, Figure 3-10). Following a period of low concentrations from 1998 and 1999, sediment concentrations of Ag were very high between 2000 and 2002 being almost a factor of 10 higher than in any other period studied. It has been difficult to provide an explanation for these high Ag concentrations in sediment, given elevated concentrations were observed at all sites including the reference site. From 2002 to 2006, Ag concentrations were low, generally being less than 1 ug g<sup>-1</sup>. In years after 2007, sediment Ag concentrations increased each year peaking in 2009 with concentrations as high as 3 ug g<sup>-1</sup> observed at some stations (e.g. MDE-6, MDE-11 and MDE-23). While the two peaks in Ag sediment concentration (2009 and 2000-2001) differ in magnitude, the pattern of a slow increase from 1998-2001 and 2006 to 2009 are followed by dramatic falls. From 2010 to 2012, Ag concentrations in sediment are low and generally less than 1 ug g<sup>-1</sup> as was seen from 2003-2006. This trend continued in 2013.

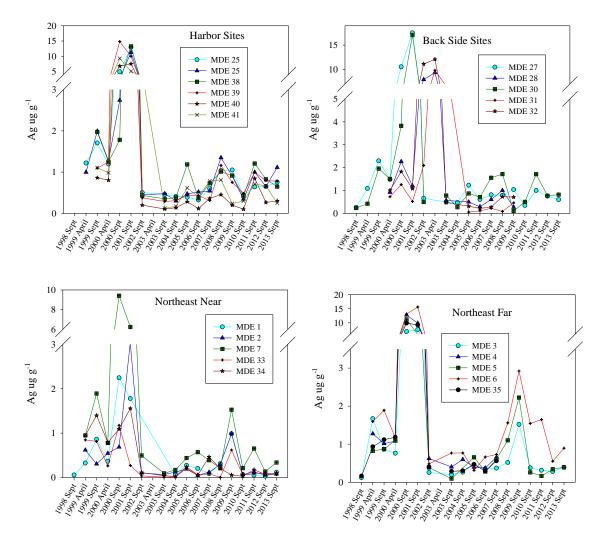


Figure 3-9: Silver (Ag) concentrations in sediment from 1998 to 2013 at the Harbor sites, Back River Sites, and sites of the Northeast side of the island. Note the broken scale.

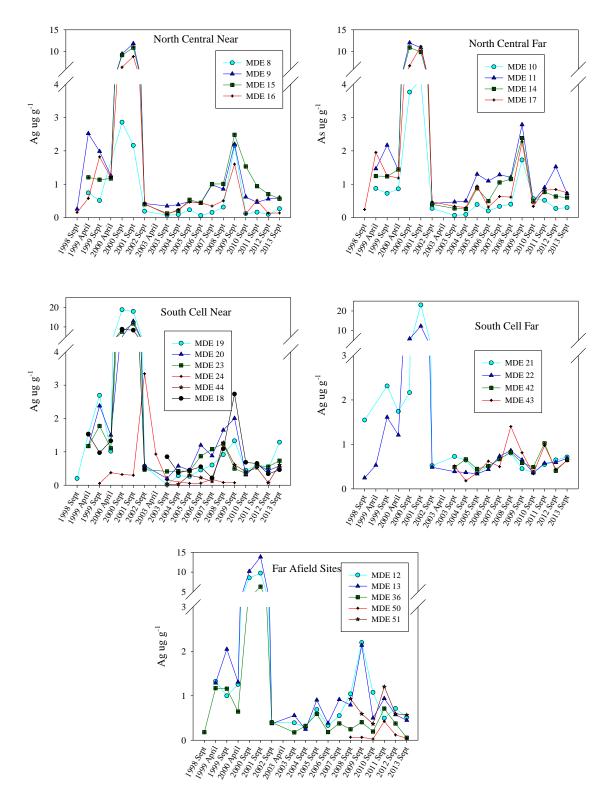


Figure 3- 10: Silver (Ag) concentrations in sediment from 1998 to 2013 sites located of the north east central side of the island, of the south cell and stations far afield from the island including reference stations. Note the broken scales.

### Mercury in Sediment 1998 to 2013

During the 1998-2013 period T-Hg concentrations in sediment fluctuated by as much as a factor of 5 at individual sites (e.g. MDE 4, MDE 32, MDE 41 and MDE 44) (Figure 3-11, 3-12). Even sediment from site MDE-36 has shown considerable variation. In 2013, high concentrations were observed at approximately half of the sites monitored. As described earlier, there is no spatial trend, sites from all nine groupings have record highs but also sites which have not changed from historic normal concentrations (Figures 3-11, 3-12). Many of the sites with unusually high T-Hg concentrations appear to be trending upward such as MDE-6, MDE-11, MDE-14, MDE-15, MDE-25 and MDE-39 but also including the reference site MDE-36. No changes in carbon or clay content have been observed at these sites (discussed below), so the increases in sediment concentrations are the result of an increase in T-Hg enrichment, not a change in sediment composition. The fact that the increase appears regional but does not occur at all sites is confounding and warrants close attention in future years.

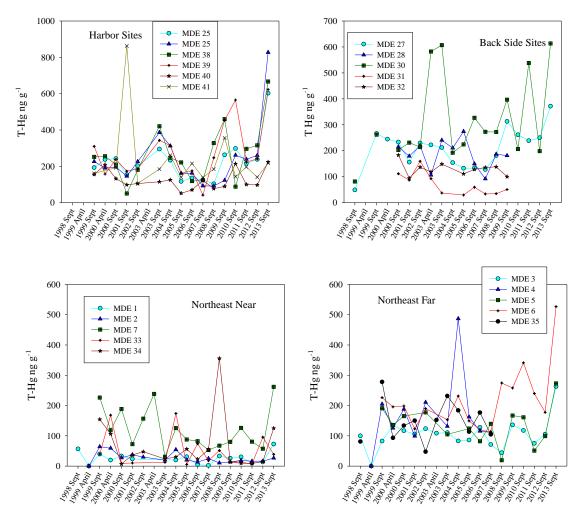


Figure 3-11: Total mercury (T-Hg) concentrations in sediment from 1998 to 2013 at the Harbor sites, Back River Sites, and sites of the Northeast side of the island.

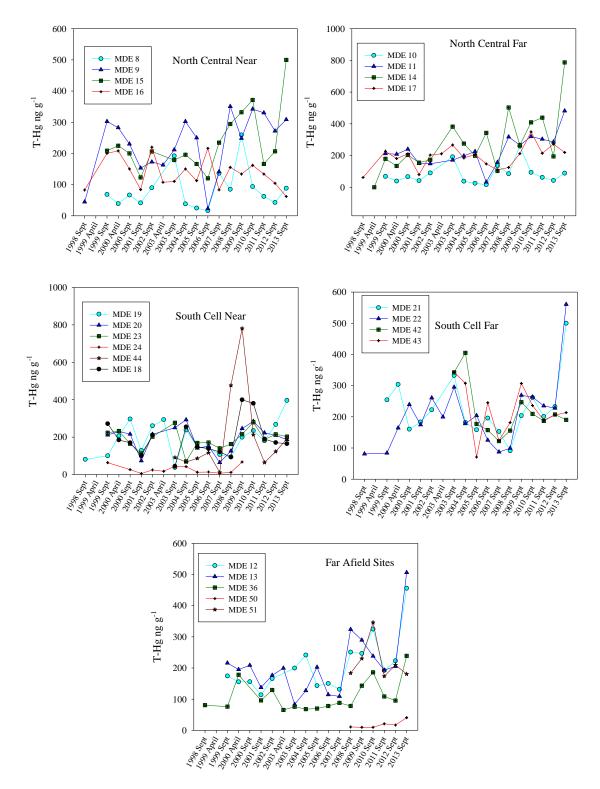


Figure 3- 12: Total mercury (Hg) concentrations in sediment from 1998 to 2013 sites located of the north east central side of the island, of the south cell and stations far afield from the island including reference stations.

## Methylmercury in Sediment 1998-2013

The concentrations of methylmercury (MeHg) were generally less than 2 ng  $g^{-1}$  at all sites over the study period. While MeHg concentrations at individual sites fluctuated over time, no strong temporal trend was apparent. Northeast Far sites maybe trending downward but the temporal variation was too great at other regions for any trend to be observed.

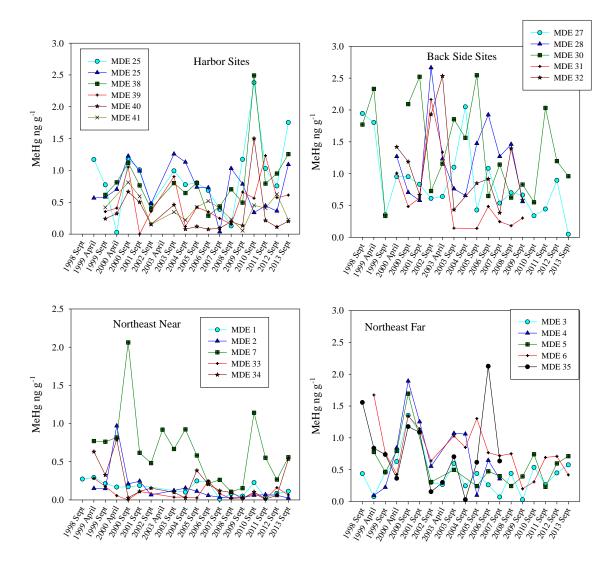


Figure 3-13: Methylmercury (MeHg) concentrations in sediment from 1998 to 2013 at the Harbor sites, Back River Sites, and sites of the Northeast side of the island.

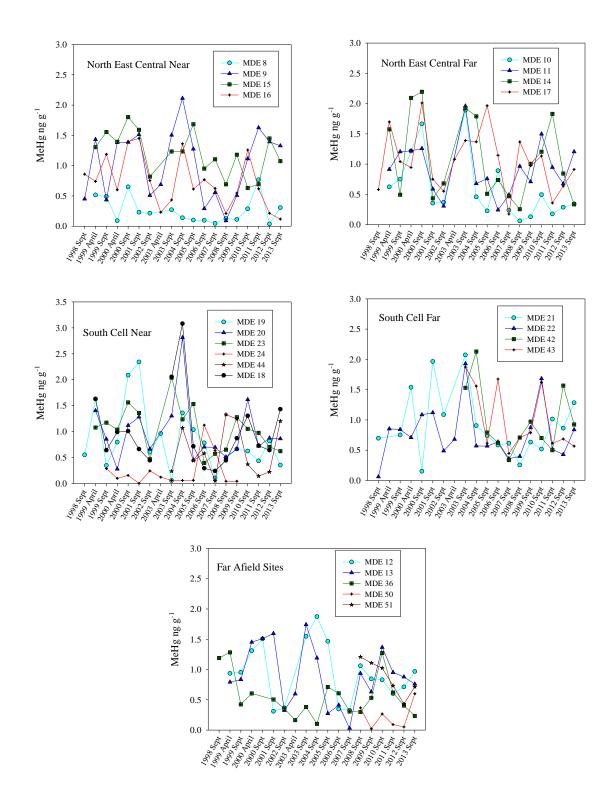


Figure 3- 14: Methylmercury (MeHg) concentrations in sediment from 1998 to 2013 sites located of the north east central side of the island, of the south cell and stations far afield from the island including reference stations.

## **Relationships among trace elements in Sediment**

Trace elements may be co-released from activities such as coal combustion and industrial activity, so relations and temporal deviations among the elements may help in determining sources. Such relationships between trace elements in sediment are seldom reported in the literature.

# Arsenic and Selenium

From the data collected around HMI,a generally strong correlation between As and Se concentrations in sediment is present when all the data from all years and all sites is compiled and examined independent of location and year (Figure 3-15a). There is some variability in the strength of the relationship between As and Se, when the data is broken out by years (not shown). The annual correlation  $r^2$ , have ranged from 0.22 to 0.84 between 1999 and 2012. In the fall of 2013 the relationship between As and Se was strong ( $r^2 = 0.78$ ) (Figure 3-15b). At the level of individual sites, the correlation between the two elements is generally not as strong, with the  $r^2$  ranging from 0.30 to 0.86 between 1999 and 2013. No relationship was found between As and Se at 4 sites (MDE-27, MDE-24 (no longer sampled), MDE-8 and MDE-2). In general As and Se concentrations are related and should increase and decrease together. Sustained departures from this relationship may suggest a change in element source.

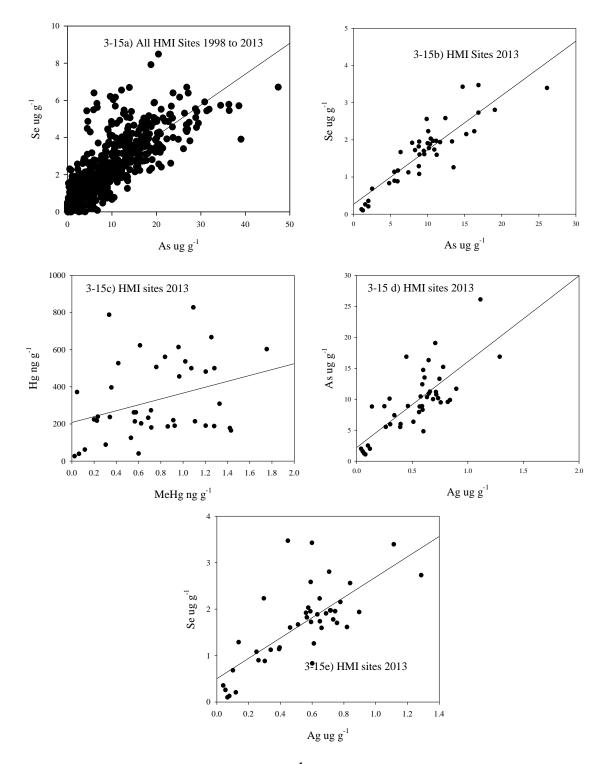


Figure 3- 11: Se vs As in sediment (ug g<sup>-1</sup> dry weight) for a) all HMI stations sampled from 1998 – 2013; b) sampled in the fall of 2013; c) correlation of T-Hg and MeHg concentration in September 2013, d) As vs Ag concentrations in September 2013 and e) Se vs Ag concentrations in September 2013.

# **Mercury and Methylmercury**

T-Hg is not well correlated with Se, As or Ag at the HMI stations either in time or space. Site MDE-44 remained the only site with a strong correlation between T-Hg and As, T-Hg and Se and T-Hg and Ag. When all sites are pooled, T-Hg is generally weakly correlated with MeHg over most of the years with  $r^2$  from linear regressions ranging for 0.11 to 0.48. In 2010, 2008 and 1998, no relationship was observed between T-Hg and MeHg. In 2013, the relationship between T-Hg and MeHg was weak when all sites are pooled ( $r^2 = 0.11$ ) (Figure 3-15c). The relationship between T-Hg and MeHg ranges from non-existent at about half the study sites to strong at sites MDE-21, MDE-31, MDE-37, MDE-41, MDE-43, MDE-44, and MDE-45. The small amount of data we have collected for sites MDE 45-51 makes this assessment much less robust. The dependence of MeHg on T-Hg is expected but in the Chesapeake Bay the relationship is often weakened by factors other than T-Hg concentration influencing MeHg production (Heyes et al. 2006). This appears to be the case in 2013, as T-Hg concentrations have increased at many sites but no increase in MeHg was observed suggesting little of the enriching Hg was bioavailable.

### Silver

As discussed in previous reports, Ag is poorly correlated with most other elements over the 1998 to 2013 study period. The high concentrations of Ag observed in 2000 and 2001 drastically skew the temporal results. When the data from these two years are removed, correlations between Ag and As and Ag and Se are generally strong. On an annual basis and independent of location, regressions between As and Ag concentrations in sediment generated  $r^2$  ranged from 0.32 to 0.71 between 2002 and 2012. The exception occurred in 2009 when no relationship between As and Ag was found. In 2013, concentrations of As in sediment was again well correlated with concentrations of Ag ( $r^2$ = 0.59) in sediment (Figure 3-15d).

Concentrations of Ag and Se in sediment were also well correlated across the years, with  $r^2$  ranging from 0.44 to 0.70 between 2002 and 2011. In 2013, the relationship was again strong ( $r^2$  of 0.54) (Figure 3.15e) but a continued decrease in the strength of the relationship would suggest a divergence of source or change in diagentic state, and is something to be monitored in the coming years.

When individual sites are examined over time, concentrations of Ag are not often well correlated with concentrations of the other elements. If the anomalous years of 2000 and 2001 are removed from the data set, correlations between Ag and other elements strengthen somewhat at most sites, but  $r^2$  are generally less than 0.5. Interestingly, the temporal correlations between Ag and As and Ag and Se are fewest in number from the sites on NE side of the island. The strongest relationships are at sites MDE-43 (Ag-Se  $r^2 = 0.70$ ) (Ag-As  $r^2 = 0.51$ ) and 44 (Ag-Se  $r^2 = 0.70$ ) (Ag-As  $r^2 = 0.58$ ) which lie off the south side of the island.

## **Relationships between trace element concentrations with other site characteristics**

The relationship between trace elements and other site variables such as organic carbon content, clay, silt and sand content was investigated. Some trace elements associate with clay sized particles, while others bind strongly with organic matter. A high sand content is indicative of an environment where trace elements are unlikely to accumulate.

As and Se concentrations in sediment seldom correlate with these other site variables over time at any one site. Thus changes in carbon or clay content do not influence As and Se concentrations at individual sites. This is also true when all sites are examined for any given year or over the entire study period.

When the data from all sites and times is combined and examined together, Hg is well correlated with carbon and clay content, unlike As and Se. (Figure 3-16). Furthermore, sediment T-Hg concentration is usually well correlated with carbon content and clay content among the sites in any one year; with the exception being1998. In 2013, the relationship between T-Hg and carbon was very weak as it was in 1998 (Figure 3-17).

When individual sites are examined over time T-Hg and carbon and T-Hg and clay content the relationship is not nearly as strong with Hg concentration correlated with sediment carbon content at only 8 sites and with clay content at only 6 sites. The reason for this is that the concentration of carbon and clay at a single site does not vary much over time thereby weakening the potential for temporal relationships. Hence, when the range in carbon and clay content are expanded by looking across sites within a year, the relationship between carbon and Hg strengthens greatly.

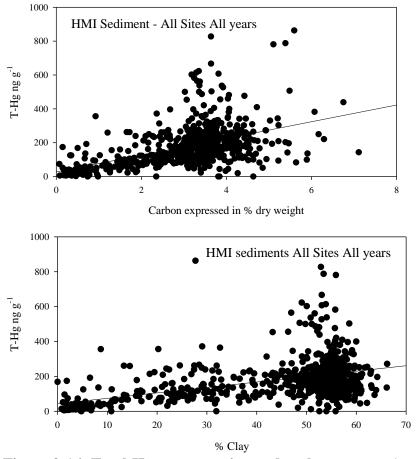


Figure 3-16: Total-Hg concentration and carbon content (upper) and clay (lower) in sediment for all sites and all years.

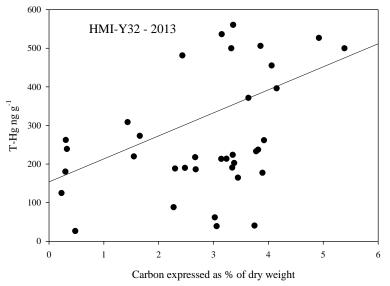


Figure 3-17: Sediment total mercury and carbon concentration in Y32 – September 2013 (r2 = .11).

## **General Conclusions Regarding Trace Element Concentrations**

In the past, stations have been observed to have enrichments of more than one trace element when compared to the sites running means. In 2013 only one site, MDE-48, had enrichment in multiple elements those being As, Hg and MeHg relative to past levels. Because of the general enrichment in Hg at many sites including the reference site MDE-36, we can only attribute the elevated concentrations to a regional event. T-Hg and MeHg enrichment occurred together at MDE-25, 26, 38, 46 and 48. Sites 46 and 48 are the only two sites not in the zone of influence of Baltimore Harbor and thus of interest with respect to operations at HMI. Site MDE-48 would warrant further monitoring.

Concentrations of As in sediment have been trending upward at a large number of sites since 2005 and this trend does not appear to end in 2013. The concentrations do not exceed concentrations seen in the early years of the study 1998-2001, thus the mean and median concentrations for the study period are not changing very quickly in response. The trend is worth watching and maybe simply be part of a normal oscillation, following a period of low concentrations between 2002 and 2005. Increases in As concentrations are not occurring at all sites, nor have they increased to pre 2002 levels.

Concentrations of Se appear to be trending downward, as concentrations in 2013 appear similar to 2012. Concentrations of Ag remain unchanged over the last few years where as Hg is trending upward at many sites. What is confusing about the increase Hg concentration is the increase can be seen at sites from all around the island but an equal number of sites also distributed around the island do not show increases in Hg concentration.

The relationships between As, Se and Ag concentrations in sediment suggest either that they have a similar origin or they had a similar diagenetic behavior once deposited in the sediments around HMI complex for most of the study period. The continued lack of a correlation between Ag and As at sites located NE of the island suggest a different mechanism of delivery or retention for these elements in this area compared to sites elsewhere around the complex. The weakening relationship between Ag and Se in 2011 and 2013 may indicate a divergence of the respective metal sources at some sites or a shift in the diagenetic behavior is becoming apparent. The behavior of T-Hg in HMI sediments is different from the other trace elements. T-Hg is seldom correlated with other trace elements, and is more dependent on organic matter and clay content of sediment than the other elements. This might imply a different source such as broad scale atmospheric deposition as being the main driver of Hg distribution but this does not explain the spikes in T-Hg concentration seen in some years at some sites.

Inter-annual variations in the relationships between trace elements, indicated by changing slopes of regression lines is sufficiently great that predicting one element concentration from another elements concentration is not possible. The strength of element to element relationships actually comes from the diversity of sites, not from temporal changes within a site. Spatial and temporal studies of multiple trace elements are rare. Concentrations of Ag, As and Se observed in sediments around HMI are

marginally higher than concentrations observed in a study by Moss Landing in 2007 (Sigala et al. 2007) for California Harbors. This is expected given the amount of current and past industrialization of the Baltimore Harbor area compared to these other sites.

#### **Trace Elements in Clams**

The clam *Rangia* was collected from 10 stations in the fall (September) of 2013. The stations visited included MDE-9, 11, 13, 17, 27, 33, 36, 42, 43 and 51. In general, concentrations of As, Se, Ag and Cd in these clams were similar to the running mean determined from the measurements made in previous years. At a few sites, trace element concentrations exceed the standard deviation around the running mean. Those were MDE-17 and 42 for Se, and MED-42 for Ag (Figure 3-18). Concentrations of Pb were extremely low at all sites compared to those measured in previous years. Concentrations of T-Hg in clams were close to the running mean of the station from which they were collected (Figure 3-19). Concentrations of MeHg were lower than the site means at all sites. The proportion of Hg that occurred as MeHg (%MeHg) was low when compared to previous years (Figure 3-19).

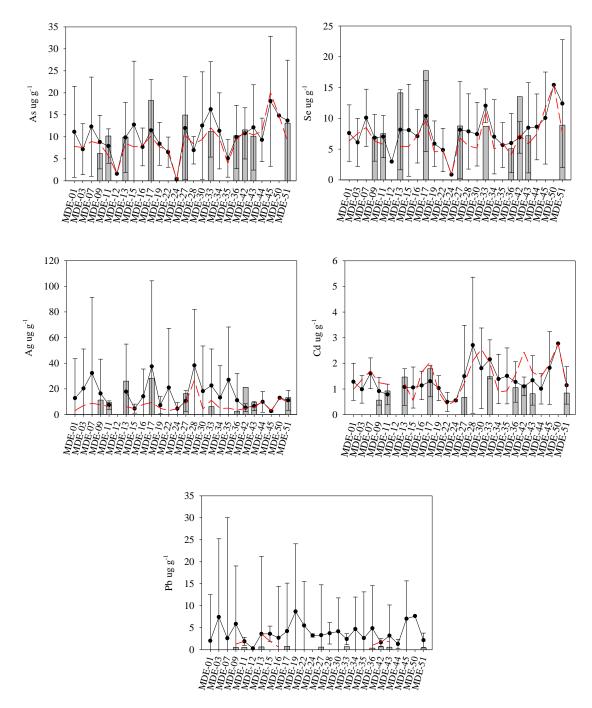


Figure 3- 18: Concentrations of Pb, Cd, As, Se, Ag in clams collected in September 2013. Concentrations (bars) are dry weight based and the 1998-2012 mean (circles) with standard deviation (error bars) for each site is presented along with the 1998-2012 median (dashed line).

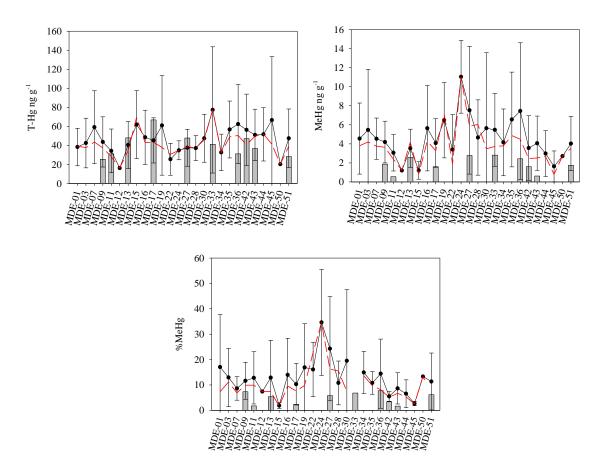


Figure 3- 19: Mercury (Hg) and methylmercury (MeHg) concentrations, expressed on a dry weight basis, and percent of Hg that is MeHg in clams, collected in September 2013 (bars) and the 1998-2012 mean (circles) with standard deviation (error bars) and the 1998-2012 median (dashed line).

## **Bioaccumulation Factors**

The bioaccumulation factors (BAFs) for the trace elements Cd, Pb, As, Ag, Se, T-Hg and MeHg (Figure 3-20) were calculated using clam concentrations in Figures 3-18, 3-19 and sediment concentrations presented in Table 3-1. While the station co-ordinates are the same as MGS, boat drifting might result in poor day to day sample co-ordination. Thus, to ensure the best sediment-clam matching, sediment was collected along with the clam collection and analyzed for Cd, Pb, As, Ag, Hg and MeHg.

In September 2013 the BAFs for Pb (not shown in Figures 3-22 and 3-23) were less than 1 for all sites, indicating no bioaccumulation of Pb from sediment to clams occurred. BAFs of less than 1 for Pb have been occurring for the duration of the study.

In September 2013 little bioaccumulation of As and T-Hg by the clams was observed (BAFs typically less than 10, Figure 3-22). Moderate bioaccumulation of Cd, Se and MeHg was observed, as BAFs were on the order of 10 or less. Of the 10 sites MDE-33 showed the greatest accumulation across the trace elements measured, being close to 100. The larger BAFs at MDE-33 were driven by concentrations in the sediment being low rather than clam concentrations being high (Table 3-1). Ag showed the greatest accumulation which was driven by the low sediment concentrations as the Ag concentrations in clams were typical of past years.

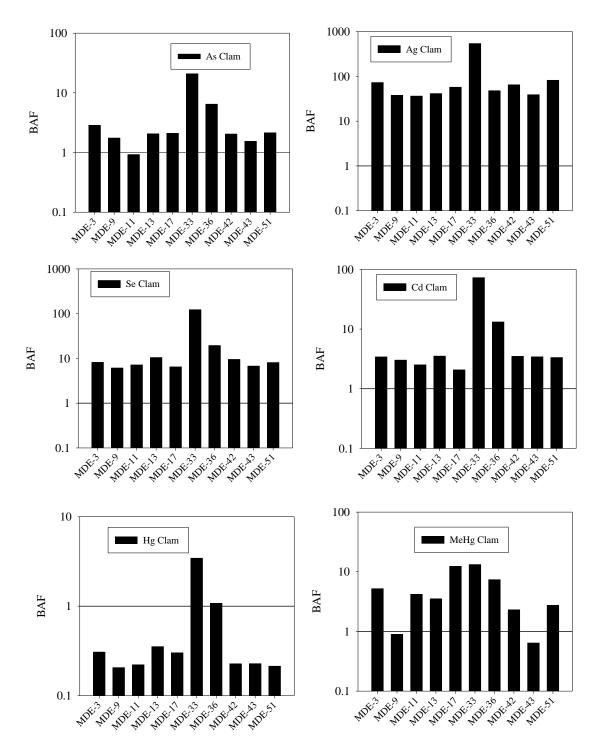


Figure 3- 20: Bioaccumulation factors for the metals As, Ag, Se, Cd, Hg and MeHg September 2013. Note BAF is presented on a log scale.

Table 3- 1: Trace element concentrations in sediment (dry weight) collected alongwith clams by CBL and MDE in September 2013. The sediment was taken from thesame sites but on different dates hence the data is different from what is shown infigures 3-20.

Sediment	As	Se	Ag	Cd	Pb	T-Hg	MeHg
Sept.	ug/g dry	ng/g dry	ng/g dry				
MDE-3	2.18	0.85	0.16	0.17	26.40	82.89	0.36
MDE-9	5.83	1.23	0.25	0.31	49.41	151.24	0.61
MDE-11	10.75	1.97	0.72	0.58	45.35	216.75	0.62
MDE-13	8.94	1.70	0.68	0.51	80.66	189.18	0.45
MDE-17	7.13	1.35	0.28	0.33	62.99	158.87	0.23
MDE-33	0.54	0.07	0.01	0.02	1.35	11.98	0.21
MDE-36	1.58	0.26	0.05	0.08	6.87	28.97	0.33
MDE-42	5.66	1.42	0.33	0.33	41.09	208.35	0.70
MDE-43	6.62	1.06	0.24	0.24	66.24	161.61	0.96
MDE-51	6.15	1.10	0.16	0.25	18.34	132.41	0.64

# **Investigating Potential Metal Toxicity**

For some trace metals, toxicological affects criteria or guidelines have been established by the National Oceanic and Atmospheric Agency (NOAA). These guidelines have been used as a frame of reference for the overall condition of the sediment around HMI for the elements available. The Probable Effects Levels (PEL) has been plotted along with the sediment trace element concentrations (Figures 3-21 and 3-22). For the metals As and Ag; sediment concentrations are below the PEL. In the case of T-Hg, two sites MDE-14 and MDE-26 are above the PEL. MDE 14 is located off the south side of the island whereas MDE 26 is along the line of sites close to Baltimore Harbor. While not above the PEL, sites 38 and 39 also have high T-Hg concentrations.

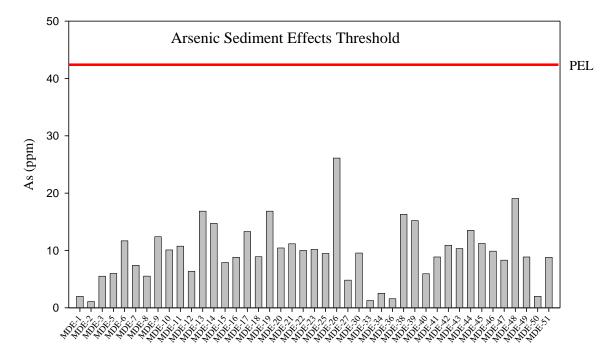


Figure 3- 21: Arsenic (As) concentrations in sediment (MGS collections) along with the Probable Effects Level (PEL) as identified by NOAA for marine sediment.

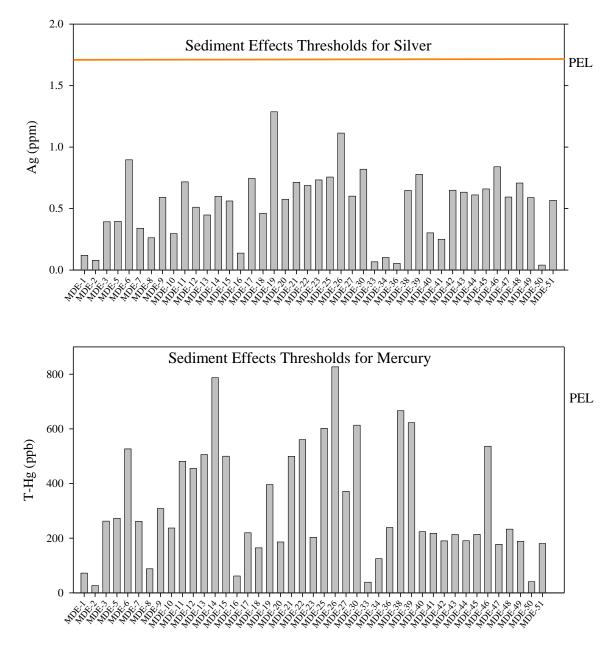
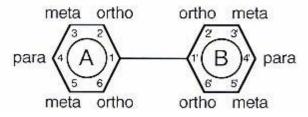


Figure 3- 22: Mercury (Hg) and Silver (Ag) concentrations in sediment (MGS collections) along with Probable Effects Level (PEL) as identified by NOAA for marine sediment.

## **PCBs in Sediment**

The PCB congeners analyzed in the sediments collected in September of 2013 are listed in Table 3-2. Each congener number indicates a different biphenyl molecule which has from 1 to 10 chlorine atoms attached at 10 possible sites as seen here.



The number of chlorine atoms attached and the placement around the biphenyl molecule is used in naming (Table 3-2). The degree of chlorination results in 10 groups: mono, tri, di, tetra, penta, hexa, hepta, octa, nona and decachlorobiphenyl. Within each group there exists the potential for a number of positional isomers and the sum of all the combinations is 209. More importantly, with increasing congener number the congeners become less soluble and bioavailable. Microorganisms have difficulty breaking down the more chlorinated molecules (5 or more chlorines). Because of continued refinement of analytical performance, more congeners were able to be measured in 2013 than in the years preceding 2010. The congeners were regrouped to match previous years in order to perform a historical comparison and the congeners listed in this table match those shown in Figures 3-23 a-j (Table 3-3).The PCB congeners in sediment measured around HMI in 2013 are summarized in Figure 3-23 a-j. These figures provide a "signature" from which to investigate trends within and among sites. Not all congeners can be differentiated during analysis, and some congeners must be combined. For example congeners 31 and 38 cannot be separated by the GC column and are said to co-elute and CBL designate the peak 31+28.

The sediments collected in 2013 contain high concentrations of the PCB congeners 31+28, 70+76, 66+95, 132+153+105, 208+195, 206 and 209. The concentrations of these congeners define the sediment sample signatures in 2013. High concentrations of these congeners occurred in sediment in most of the previous years, and this is very evident in the plots of the running means and medians for each of the sites. Sediment from station MDE-33 had few quantifiable congeners (Figure 3-23f). The organic matter content of the sediment was extremely low, less than 1% and since PCBs associate with organic matter, the low concentrations of PCBs found at the site are not surprising. In general, concentrations of many PCB congeners were consistent with station means of previous years. The congener concentrations are weighted toward the higher numbers which is to be expected, as with the increasing degree of chlorination PCBs are less soluble and more likely to stay bound to sediment (Table 3-4).

Table 3-2: Polychlorinated Biphenyl congeners measured by CBL in 2012. The congeners that can be detected vary slightly from year to year. In 2012 more congeners could be accurately measured than in 2010 (table 3-3). Most of the additional congeners that could be measured were not detected, hence they add little to the total PCB concentration.

1	Cong-1	Mono	38	Cong-63	Tetra	74	Cong-176	Hepta
2	Cong-2	Mono	39	Cong-74,61	Tetra	75	Cong-130,137	Hexa,Hexa
3	Cong-3	Mono	40	Cong-70,76	Tetra	76	Cong-164,163,138	Hexa,Hexa,Hexa
4	Cong-4,10	Di	41	Cong-93	Penta	77	Cong-158	Hexa
5	Cong-7,9	Di	42	Cong-66	Tetra	78	Cong-129	Hexa
6	Cong-6	Di	43	Cong-95	Penta	79	Cong-178	Hepta
7	Cong-8,5	Di	44	Cong-91	Penta	80	Cong-187	Hepta
8	Cong-19	Tri	45	Cong-56,60	Tetra	81	Cong-183	Hepta
9	Cong-12,13	Di	46	Cong-92	Penta	82	Cong-128,167	Hexa
10	Cong-18	Tri	47	Cong-84	Penta	83	Cong-185	Hepta
11	Cong-15	Di	48	Cong-101,90,89	Penta,Penta,Penta	84	Cong-174	Hepta
12	Cong-17	Tri	49	Cong-99	Penta	85	Cong-177	Hepta
13	Cong-24	Tri	50	Cong-119	Penta	86	Cong-156	Hexa
14	Cong-16,32	Tri	51	Cong-83	Penta	87	Cong-202	Octa
15	Cong-29	Tri	52	Cong-97	Penta	88	Cong-171	Hepta
16	Cong-26	Tri	53	Cong-81	Tetra	89	Cong-157	Hexa
17	Cong-25	Tri	54	Cong-87,115	Penta,Penta	90	Cong-200	Octa
18	Cong-28	Tri	55	Cong-85	Penta	91	Cong-172	Hepta
19	Cong-31	Tri	56	Cong-85	Penta	92	Cong-197	Hepta
20	Cong-20.33,41	Tri	57	Cong-136	Hexa	93	Cong-180	Hepta
21	Cong-51	Tetra	58	Cong-77	Tetra	94	Cong-193	Hepta
22	Cong-53	Tetra	59	Cong-110	Penta	95	Cong-191	Hepta
23	Cong-22	Tri	60	Cong-82	Penta	96	Cong-199	Octa
24	Cong-45	Tetra	61	Cong-151	Hexa	97	Cong-170,190	Hepta
25	Cong-46	Tetra	62	Cong-135,144	Hexa	98	Cong-198	Octa
26	Cong-52	Tetra	63	Cong-107,108	Penta	99	Cong-201	Octa
27	Cong-49	Tetra	64	Cong-149	Hexa	100	Cong-203,196	Octa
28	Cong-47,48	Tetra	65	Cong-118,106	Penta	101	Cong-189	Hepta
29	Cong-44	Tetra	66	Cong-134	Hexa	102	Cong-195	Octa
30	Cong-37	Tri	67	Cong-114	Penta	103	Cong-208	Nona, Octa
31	Cong-42	Tetra	68	Cong-146	Hexa	104	Cong-207	Nona
32	Cong-41,64,71	Tetra	69	Cong132,168	Hexa,Hexa,	105	Cong-194	Octa
33	Cong-103	Penta	70	Cong-105	Penta	106	Cong-205	Octa
35	Cong-40	Tetra	71	Cong-141	Hexa	107	Cong-206	Nona
36	Cong-100	Penta	72	Cong-179	Hepta	108	Cong-209	Deca
37	Cong-100	Penta	73	Cong-176	Hepta			

Table 3-3: The polychlorinated biphenyl congeners shown in Figures 3-26a-k and 3-27 a-k. For continuity in finger printing only the PCB congeners that have been detected over the life of the project are listed here. Thus, not all the PCB congeners measured (table 3-2), are shown in figures 3-26 and 3-27 a-k. This was done to allow inter year comparisons.

1	Cong-1	Mono	30	Cong-63	Tetra	59	Cong-187,182	Hepta
2	Cong-3	Mono	31	Cong-74	Tetra	60	Cong-183	Hepta
3	Cong-4,10	Di	32	Cong-70,76	Tetra	61	Cong-128,167	Hexa
4	Cong-7,9	Di	33	Cong-66,95	Tetra, Penta	62	Cong-185	Hepta
5	Cong-6	Di	34	Cong-91	Penta	63	Cong-174	Hepta
6	Cong-8,5	Di	35	Cong-56,60	Tetra	64	Cong-177	Hepta
7	Cong-19	Tri	36	Cong-89	Penta	65	Cong-202,171,156	Octa,Hepta, Hexa
8	Cong-12,13	Di	37	Cong-101	Penta	66	Cong-157	Hexa
9	Cong-18	Tri	38	Cong-99	Penta	67	Cong-172,197	Hepta
10	Cong-17	Tri	39	Cong-119	Penta	68	Cong-180	Hepta
11	Cong-24	Tri	40	Cong-83	Penta	69	Cong-193	Hepta
12	Cong-16,32	Tri	41	Cong-97	Penta	70	Cong-191	Hepta
13	Cong-29	Tri	42	Cong-81,87	Tetra, Penta	71	Cong-199	Octa
14	Cong-26	Tri	43	Cong-136	Hexa	72	Cong-170,190	Hepta
15	Cong-25	Tri	44	Cong-77,110	Tetra, Penta	73	Cong-198	Octa
16	Cong-31,28	Tri	45	Cong-151	Hexa	74	Cong-201	Octa
17	Cong-33,21,53	Tri	46	Cong-134,144	Hexa	75	Cong-203,196	Octa
18	Cong-51	Tetra	47	Cong-107	Penta	76	Cong-189	Hepta
19	Cong-22	Tri	48	Cong-123,149	Pent, Hexa	77	Cong-208,195	Nona, Octa
20	Cong-45	Tetra	49	Cong-118	Penta	78	Cong-207	Nona
21	Cong-46	tetra	50	Cong-134	Hexa	79	Cong-194	Octa
22	Cong-52	Tetra	51	Cong-114	Penta	80	Cong-205	Octa
23	Cong-49	Tetra	52	Cong-146	Hexa	81	Cong-206	Nona
24	Cong-48,47	Tetra	53	Cong132,153,105	Hexa,Hexa,Penta	82	Cong-209	Deca
25	Cong-44	Tetra	54	Cong-141	Hexa			
26	Cong-37,42	Tri, tetra	55	Cong-137,130,176	Hexa, Hexa, Hepta			
27	Cong-41,64,71	Tetra	56	Cong-163,138	Hexa			
28	Cong-40	Tetra	57	Cong-158	Hexa			
29	Cong-100	Penta	58	Cong-129,178	Hexa,Hepta			

Number of	Homolog	Molecular	Molecular	Number of	Solubility
Chlorines	Group	Formula	Weight	Isomers	(ug/L)
0	Biphenyl	$C_{12}H_{10}$	154.1	1	7000
1	Mono	C <sub>12</sub> H <sub>9</sub> Cl	188.0	3	1200-5500
2	Di	$C_{12}H_8Cl_2$	222.0	12	60-2000
3	Tri	$C_{12}H_7Cl_3$	256.0	24	15-100
4	Tetra	$C_{12}H_6Cl_4$	289.9	42	4.3-100
5	Penta	$C_{12}H_5Cl_5$	323.9	46	4-20
6	Hexa	$C_{12}H_4Cl_6$	357.8	42	0.4-1.0
7	Hepta	$C_{12}H_3Cl_7$	391.8	24	0.45-2.0
8	Octa	$C_{12}H_2Cl_8$	425.8	12	0.2-3.0
9	Nona	C <sub>12</sub> HCl <sub>9</sub>	459.7	3	0.018-0.11
10	Deca	$C_{12}Cl_{10}$	493.7	1	0.0012

 Table 3- 4: Polychlorinated biphenyl homologs and properties.

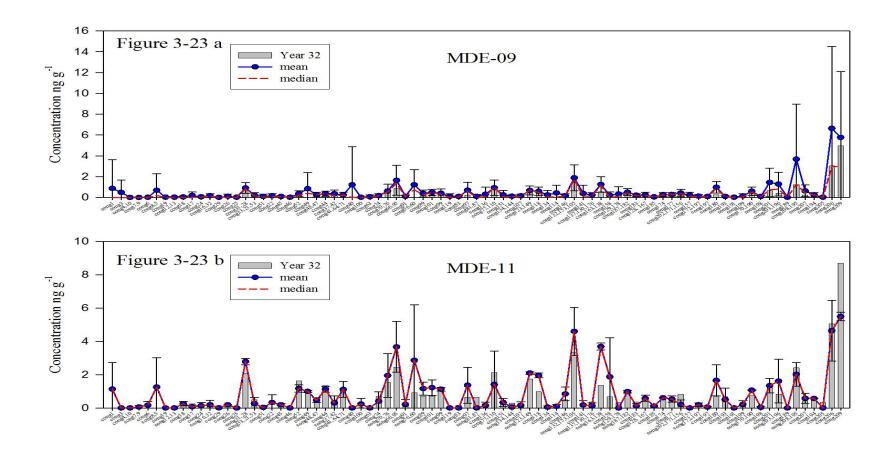


Figure 3- 23: Concentrations of PCB congeners in sediments from sites MDE-09 and MDE-11 from the fall of 2013 (bars), the 1998-2012 mean with standard deviation (blue circles and error bars) and the 1998-2012 median (dashed line) expressed in ng  $g^{-1}$  dry weight.

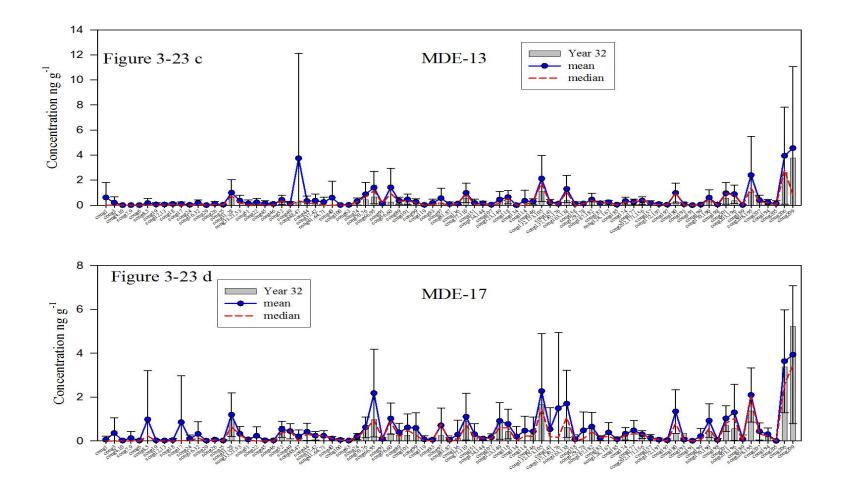


Figure 3-23 continued. Concentrations of PCB congeners in sediments from sites MDE-13 and MDE-17 from the fall of 2013 (bars), the 1998-2012 mean with standard deviation (blue circles and error bars) and the 1998-2012 median (dashed line) expressed in ng  $g^{-1}$  dry weight.

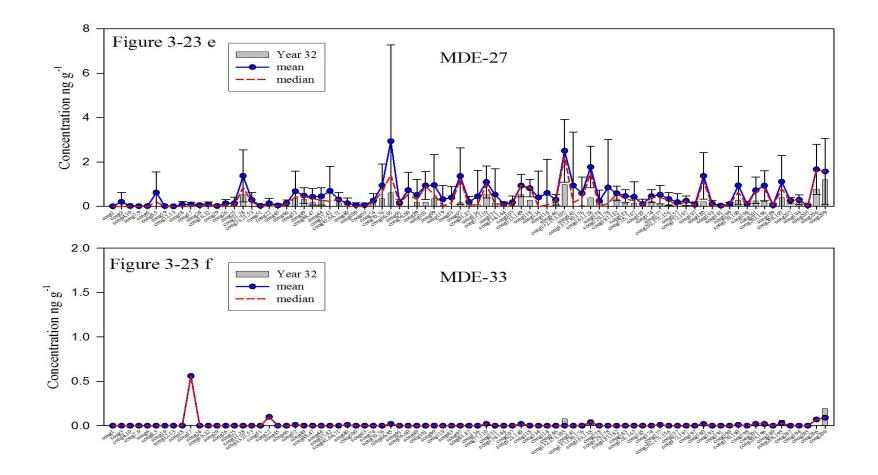


Figure 3-23 continued. Concentrations of PCB congeners in sediments from sites MDE-27 and MDE-33 from the fall of 2013 (bars), the 1998-2012 mean with standard deviation (blue circles and error bars) and the 1998-2012 median (dashed line) expressed in ng  $g^{-1}$  dry weight.

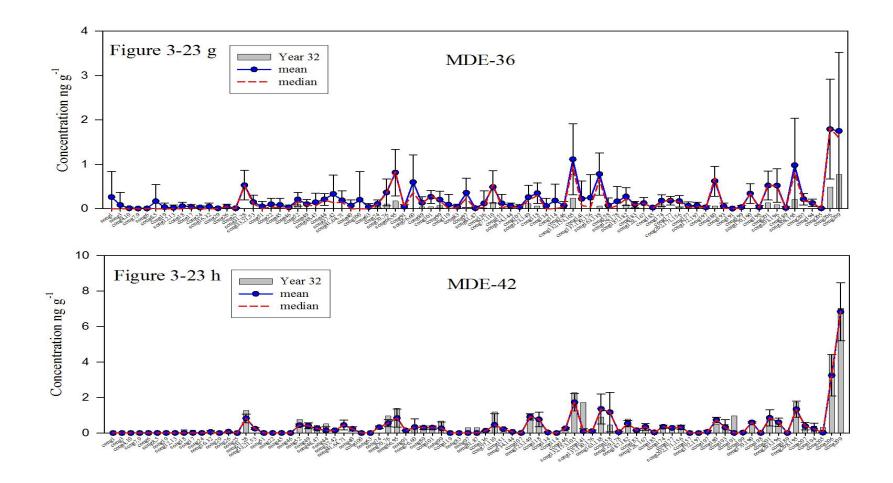


Figure 3-23 continued. Concentrations of PCB congeners in sediments from sites MDE-36 and MDE-42 from the fall of 2013 (bars), the 1998-2012 mean with standard deviation (blue circles and error bars) and the 1998-2012 median (dashed line) expressed in ng  $g^{-1}$  dry weight.

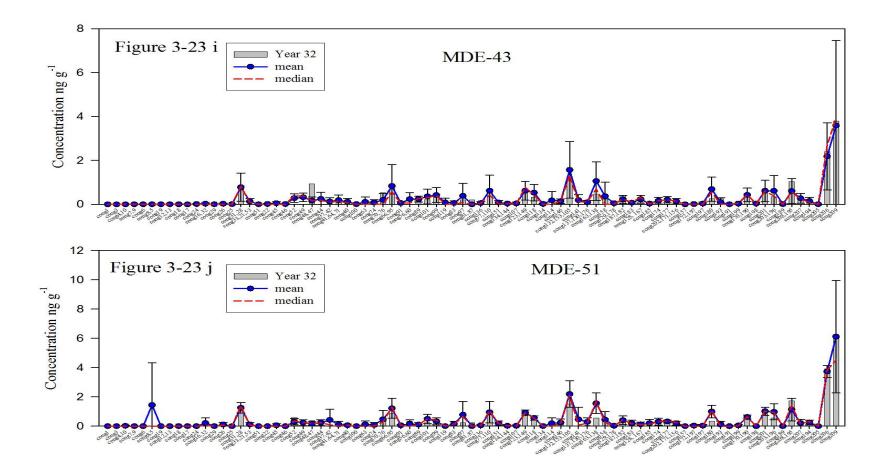


Figure 3-23 continued. Concentrations of PCB congeners in sediments from sites MDE-43 and MDE-51 from the fall of 2013, the 1998-2012 mean with standard deviation (blue circles and error bars) and the 1998-2012 median (dashed line) expressed in ng  $g^{-1}$  dry weight.

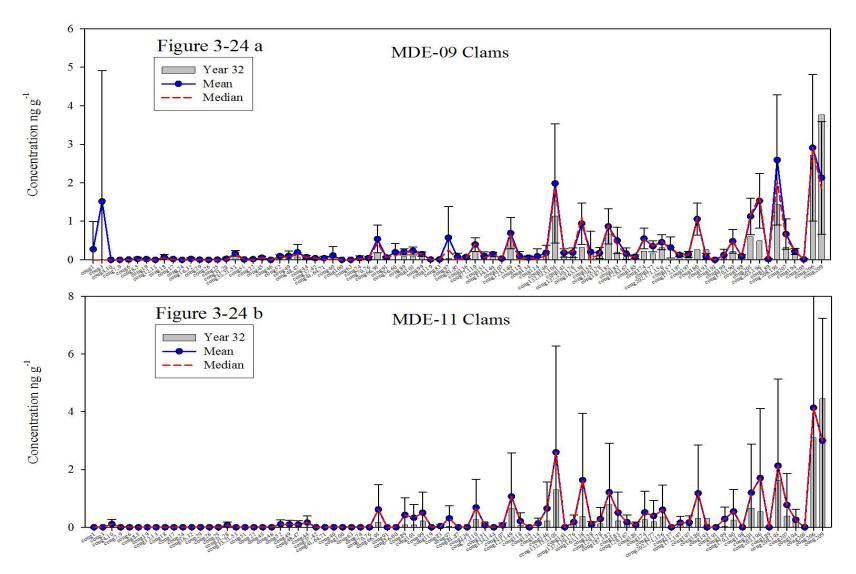


Figure 3- 24: Concentrations of PCB congeners in clams from sites MDE-09 and MDE-11 obtained in the fall of 2013 (bars), the 1998-2012 mean with standard deviation (blue circles and error bars) and the 1998-2012 median (dashed line) expressed in ng  $g^{-1}$  wet weight.

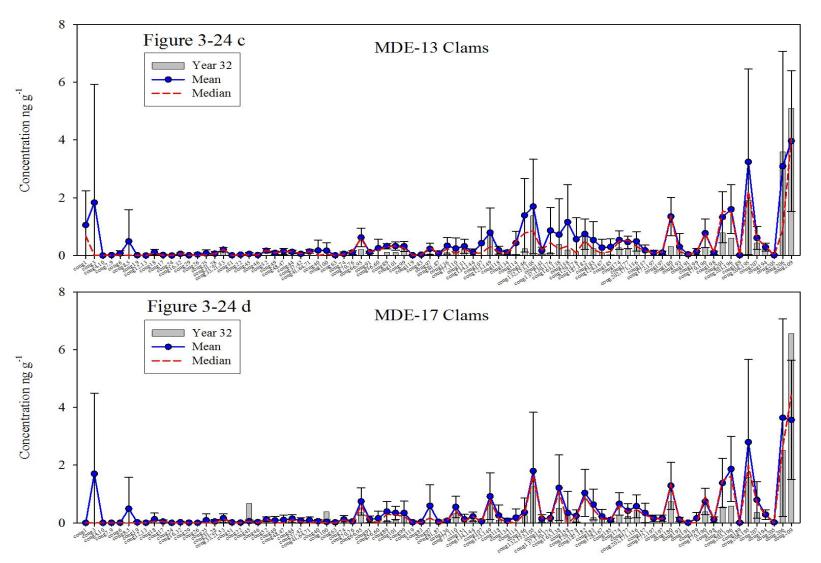


Figure 3-24 continued. Concentrations of PCB congeners in clams from sites MDE-13 and MDE-17 obtained in the fall of 2013 (bars), the 1998-2012 mean with standard deviation (blue circles and error bars) and the 1998-2012 median (dashed line) expressed in ng g<sup>-1</sup> wet weight.

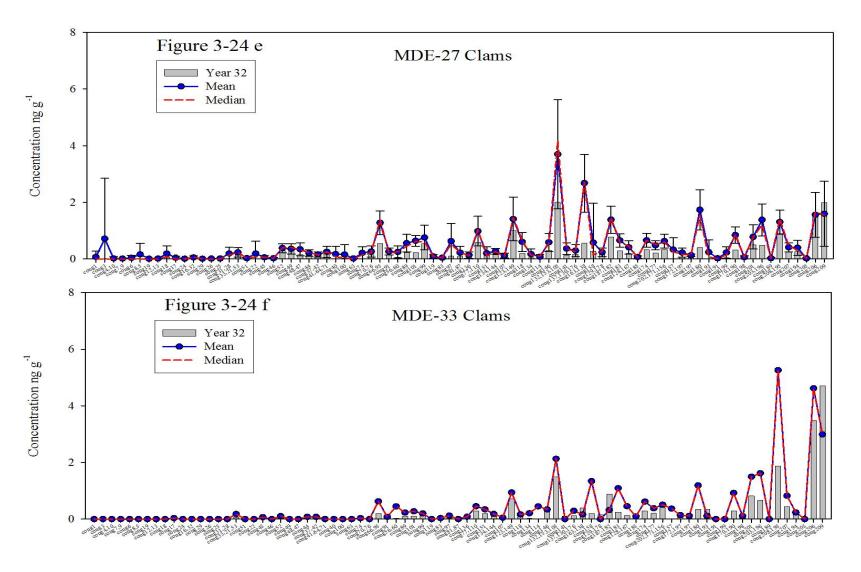


Figure 3-24 continued. Concentrations of PCB congeners in clams from sites MDE-27 and MDE-33 obtained in the fall of 2013(bars), the 1998-2012 mean with standard deviation (blue circles and error bars) and the 1998-2012 median (dashed line) expressed in ng g<sup>-1</sup> wet weight.

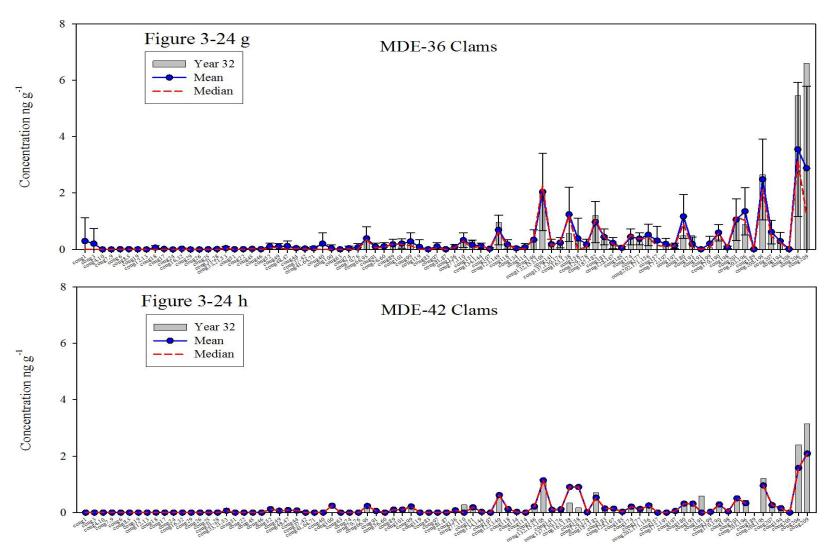


Figure 3-24 continued. Concentrations of PCB congeners in clams from sites MDE-36 and MDE-42 obtained in the fall of 2013 (bars), the 1998-2012 mean with standard deviation (blue circles and error bars) and the 1998-2012 median (dashed line) expressed in ng  $g^{-1}$  wet weight.

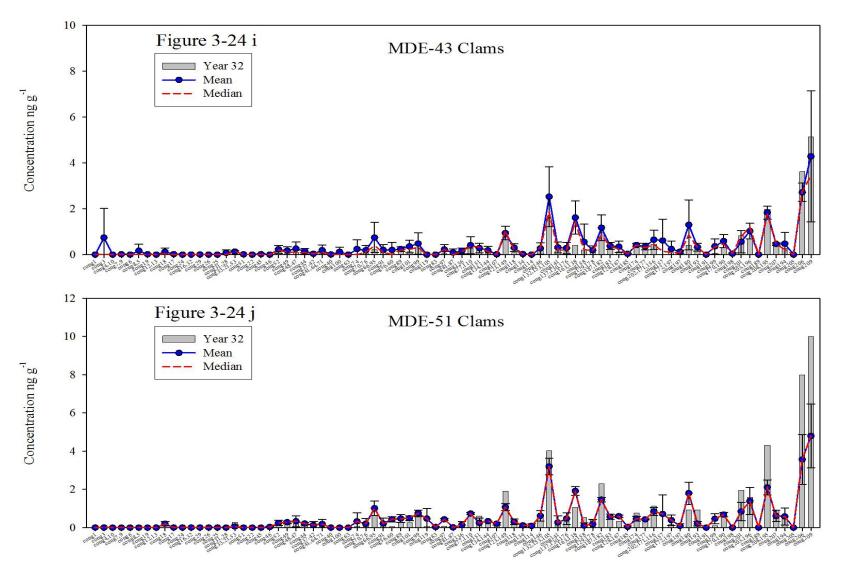


Figure 3-24 continued. Concentrations of PCB congeners in clams from sites MDE-43 and MDE-51 obtained in the fall of 2013 (bars), the 1998-2012 mean with standard deviation (blue circles and error bars) and the 1998-2012 median (dashed line) expressed in ng  $g^{-1}$  wet weight.

#### **PCB congener profiles in Clams**

The PCBs congeners determined in the clams collected in September of 2013 are listed in Table 3-3. As was the case for sediments, for continuity of examining change over time, only the PCBs listed in Table 3-4 are plotted in Figure 3-24a-j. As in the case of the sediment, these figures provide a "signature" from which to investigate trends in the types and amounts of PCBs within and among the sites. The clams traditionally have contained significant amounts of some congener and congener groups. In 2013 these include 66+95, 123 + 149, 132+153+105, 187+182, 201, 180, 208+195, 206 and 209; and while some sites have other congener and congener groups present in significant amounts these congener groups largely define the pattern across the sites. The major components of the congener patterns observed in clams are similar to those seen in the sediments.

# **Total PCB concentrations in sediments and clams**

The total concentration of PCBs in sediments and clams at each site were calculated by summing the individual PCB congener concentrations and these totals were compared to previous years for the same stations (Figure 3-25). The total PCB concentrations in sediment collected in September 2013 were generally similar to or below the historical site averages, being within the standard deviation of the mean. Total PCB concentrations at site MDE-42 were above and outside the standard deviation around the mean. However, with only 3 measurements, this should not be considered anomalous. Total PCB concentrations in clams were also similar to or below the running mean for all sites.

Many older studies have relied on grouping PCBs of similar structure into classes or homologs. The homolog distributions for sediment and clams for each site are plotted as percentage of the total PCB concentration in Figures 3-26 and 3-27. Data from station MDE-36 is plotted along with each station to act as a guide. The assumption being that MDE-36 represents the Bay as a whole.

The homolog distributions of homologs in sediments follow the same pattern as MDE-36, even if concentrations of homolog groups are higher at all the other sites. The exception is MDE-33, where concentrations of PCBs are very low.

The distribution of homologs measured in clams track the control site (MDE-36) very well all sites except for MDE-27 (Figure 3-27). At MDE-27 the homologs are weighted toward the lighter masses as opposed to the typical distribution of homologs being weighted toward the higher masses

To compare sediments with clams, PCB homologs concentrations (Figure 3-28) and percentages (Figure 3-29) for each site were overlaid. The sediment and clams are very similar with perhaps a little bias to the lower molecular weight complexes in the sediment. This same relationship was observed in 2011 and 2012.

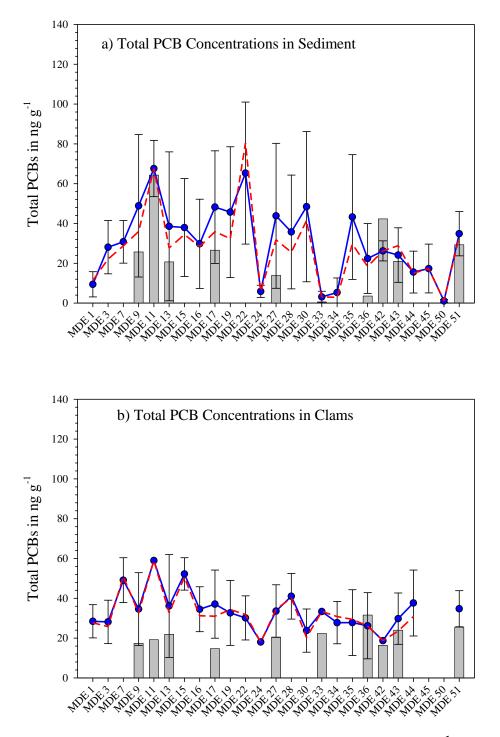


Figure 3- 25: Total PCB concentrations in sediments (a) (ng g<sup>-1</sup> dry weight) and total PCB concentrations in clams (ng g<sup>-1</sup> wet weight) collected in September 2013 (bars), the 1998-2012 mean with standard deviation (blue circles and error bars) and the 1998-2012 median (dashed line).

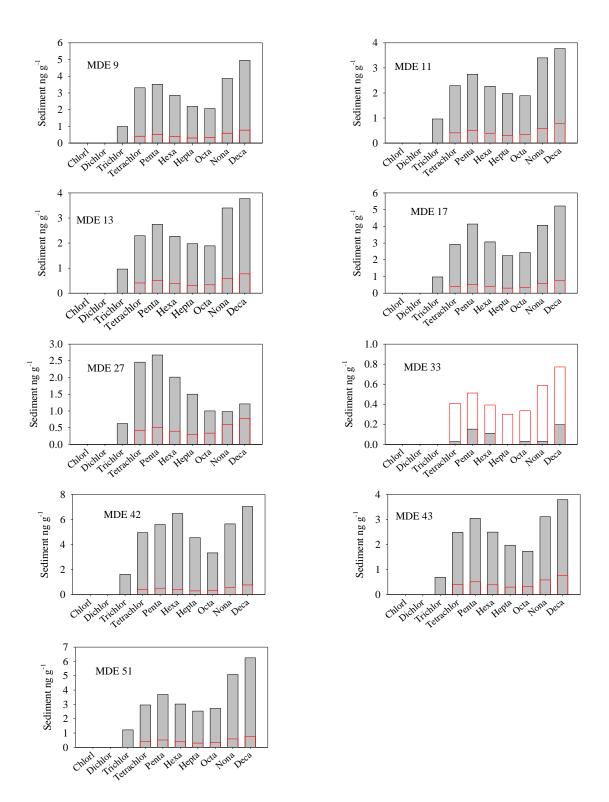


Figure 3- 26: PCB homolog distributions in sediment. The reference site MDE-36 is plotted in red on all plots as guide.

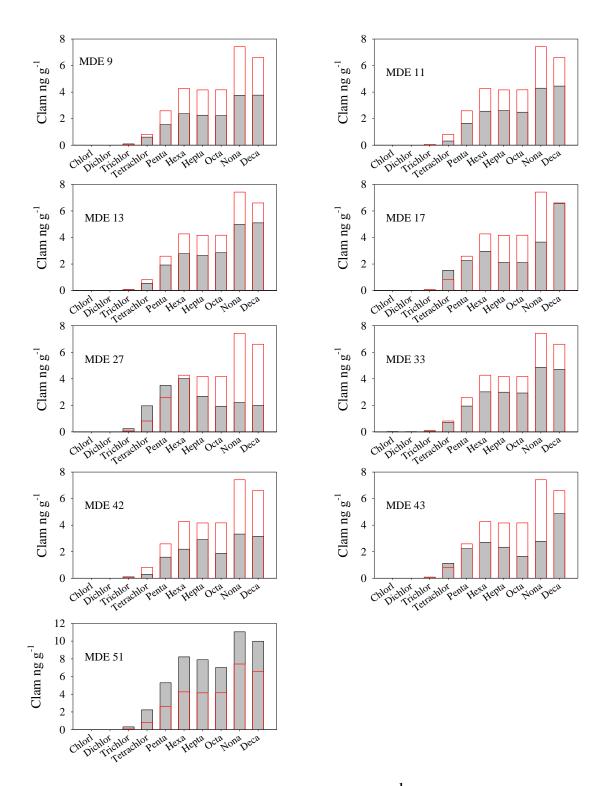


Figure 3-27: PCB homolog distributions in clams (ng g<sup>-1</sup>) wet weight. The reference site MDE-36 is plotted in red on all plots as guide.

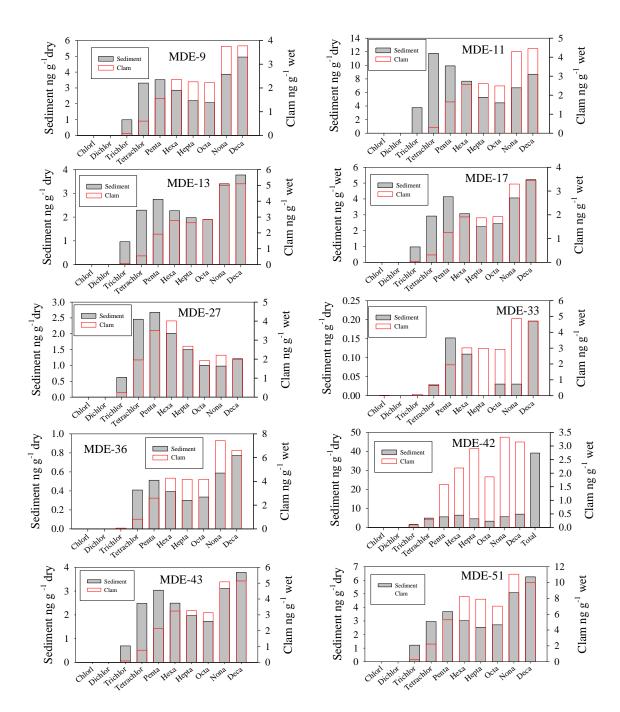


Figure 3-28: PCB homolog distributions in sediment and clams of each HMI site.

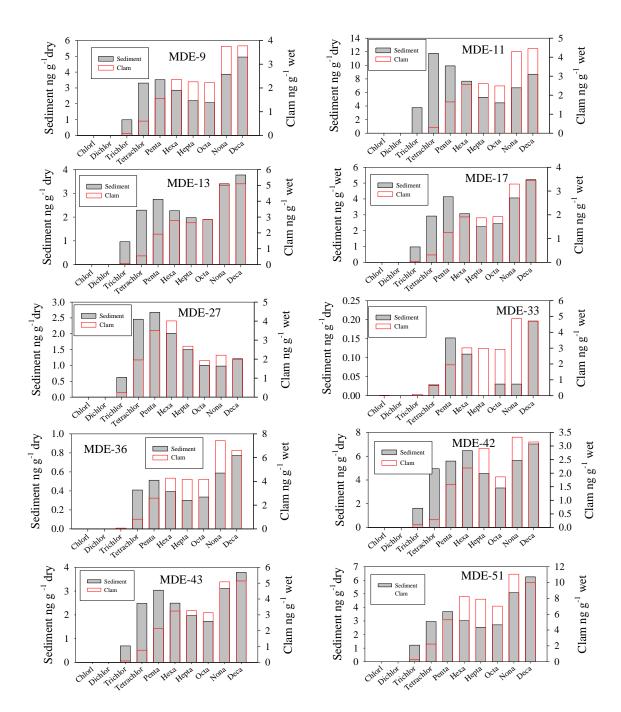


Figure 3-29: PCB homolog distribution in sediment and clams as a % of total.

# PCB Concentrations from 1998-2013

To assess if sediment PCB concentrations in sediment have changed since the onset of the project, sites were selected having the longest continuous record. The total-PCB concentrations from those sites are shown in Figure 3-30. From these records it appears that PCB concentrations in sediments have decreased since the first few years of the project. Prior to 2002, concentrations nearly 2-3 times that of today were regularly

observed. Since that time concentrations have fluctuated around a more consistent site mean. PCB concentrations at site MDE-36 were on the order of 60 ng g<sup>-1</sup> in 1998 but are now less than 20 ng g<sup>-1</sup>. This finding is consistent with PCB concentrations in fish generally decreasing in the Chesapeake Bay

(http://www.mde.state.md.us/programs/PressRoom/Pages/041311.aspx).

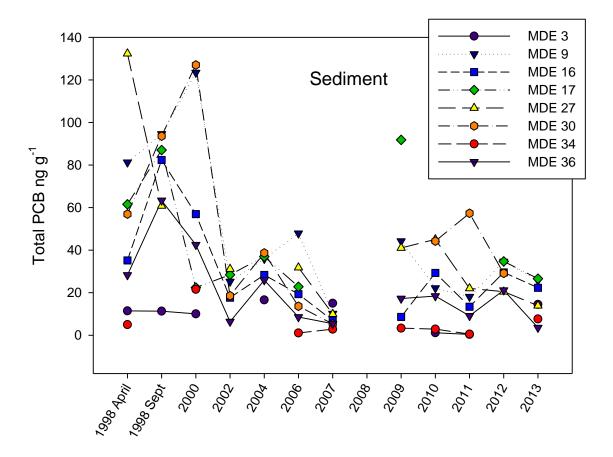


Figure 3 -30: Total PCB concentrations at sites MDE-3, MDE-9, MDE-16, MDE-17, MDE-27, MDE-30, MDE-34 and MDE-36 in ng g<sup>-1</sup> dry weight.

## **Polycyclic Aromatic Hydrocarbons in Sediments**

The concentrations of a series of polycyclic aromatic hydrocarbons (PAHs) (Table 3-5) from sites in the vicinity of HMI are shown in Figure 3-31a-j. As described for PCBs, when examined as a group the PAHs provide a fingerprint with which to look for differences among stations and if any trends among locations are apparent in time and space. The most common compounds found were: 2-methylnaphthalene, phenanthrene, fluoranthene, pyrene, benzo[b]fluoranthene and perylene. The relative proportions of these compounds together form the pattern that is found at almost all the HMI stations sampled in 2013. These compounds are combustion products of gasoline, diesel and municipal waste, mostly delivered via particles or soot. This pattern was similar to that observed in 2011 and 2012. As can be seen by the deviation from the mean and median in Figure 3-31, the concentrations of PAHs at sites MDE-36 was lower than has been observed in past samplings whereas the other stations were close to the historic averages. Sediment at stations MDE-33 was also lower but we have only sampled that site on 2 occasions as clams largely because of the inability to collect clams.

# Table 3-5: Polycyclic aromatic hydrocarbons given in the same order as in Figure 3-31 a-j (left to right). Note: 1,4 + 1,5 + 2,3-Dimethylnaphthalene was split into 4-Dimethylnaphthalene and 1,5-Dimethylnaphthalene to enable a historical comparison.

1 Naphthalene	18	Phenanthrene	36	Benzo[a]fluorene
2 2-Methylnaphthalene	19	Anthracene	37	Benzo[b]fluorene
3 1-Methylnaphthalene	20	2-Methyldibenzothiophene	38	Benz[a]anthracene
4 Biphenyl	21	4-Methyldibenzothiophene	39	Chrysene+triphenylene
5 2,6-dimethylnaphthalene	22	2-Methylphenanthrene	40	Naphthacene
6 1,3-Dimethylnaphthalene	23	2-Methylanthracene	41	4+6 methylchrysene
7 1,6-Dimethylnaphthalene	24	4H-Cyclopenta[def]phenanthrene	42	Benzo(b)fluoranthene
8 1,4-Dimethylnaphthalene	25	1-Methylanthracene	43	Benzo(k)fluoranthene
9 1,5-Dimethylnaphthalene	26	1-Methylphenanthrene	44	Benzo(e)pyrene
10 Acenaphthylene	27	9-Methylanthracene	45	Benzo(a)pyrene
11 1,2-Dimethylnaphthalene	28	3,6-dimethylphenanthrene	46	Perylene
12 1,8-Dimethylnaphthalene	30	Fluoranthene	47	3-Methylcholanthrene
13 Acenaphthene	31	Pyrene	48	Indeno(1,2,3-cd)pyrene
14 2,3,5-trimethylnaphthalene	32	2,3-dimethylanthracene	49	Dibenz(a,c+a,h)anthracene
15 Fluorene	33	9,10-dimethylanthracene	50	Benzo(g,h,i)perylene
16 1-Methylfluorene	34	1-methylpyrene	51	Anthanthrene
17 Dibenzothiophene	35	2-methylfluoranthene	52	Coronene

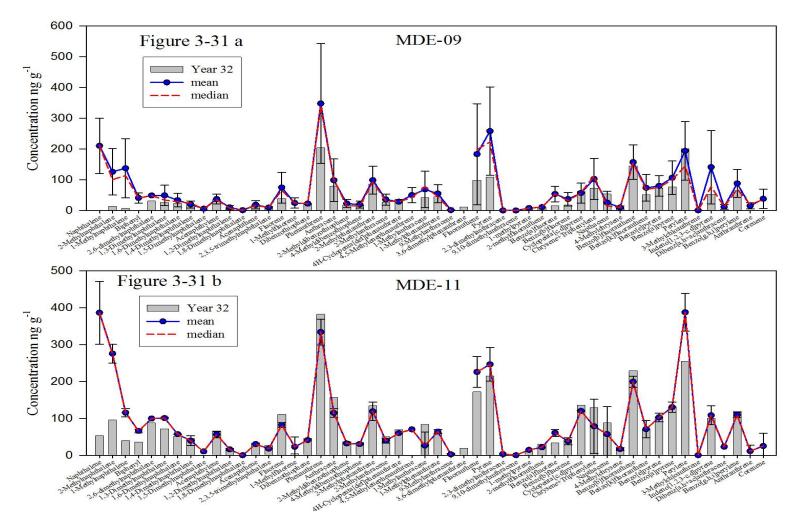


Figure 3- 31: Concentrations of PAHs in sediments from site MDE-09 and MDE-11 obtained in the fall of 2013 (bars), the 1998-2012 mean with standard deviation (blue circles and error bars) and the 1998-2012 median (dashed line), expressed in ng  $g^{-1}$  dry weight.

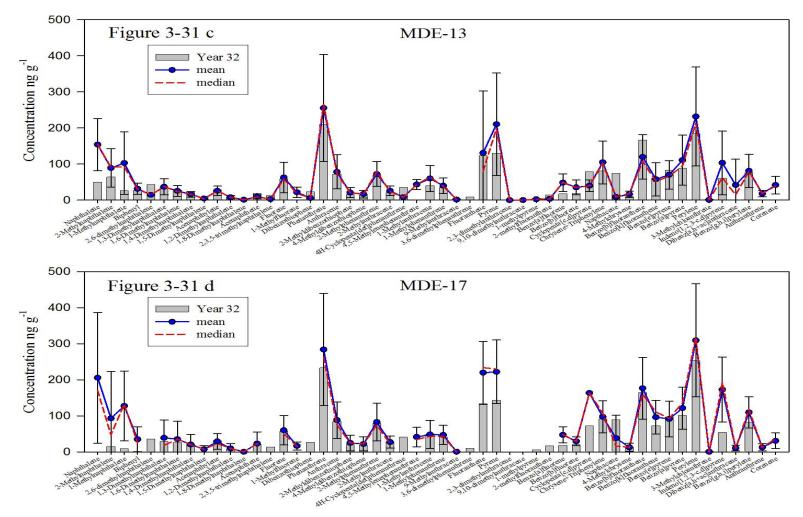


Figure 3-31 continued. Concentrations of PAHs in sediments from site MDE-13 and MDE-17 obtained in the fall of 2013 (bars), the 1998-2012 mean with standard deviation (blue circles and error bars) and the 1998-2012 median (dashed line), expressed in ng  $g^{-1}$  dry weight.

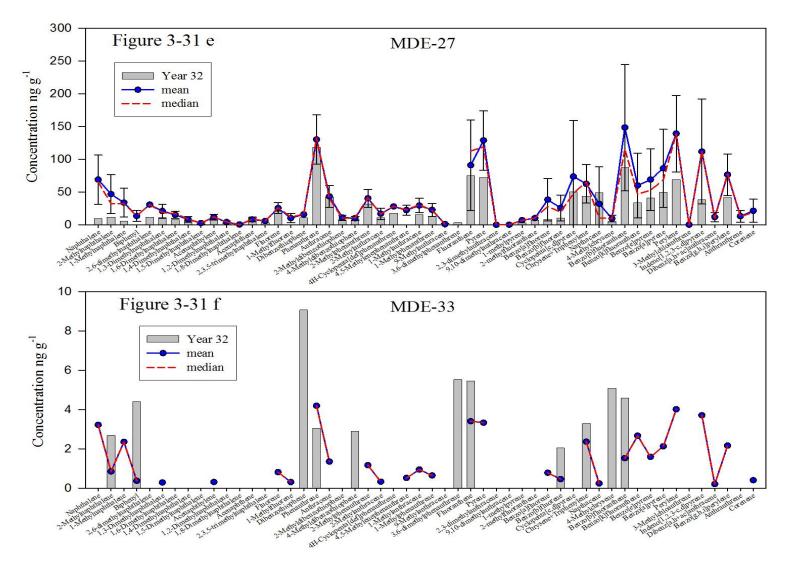


Figure 3-31 continued. Concentrations of PAHs in sediments from site MDE-27 and MDE-33 obtained in the fall of 2013 (bars), the 1998-2012 mean with standard deviation (blue circles and error bars) and the 1998-2012 median (dashed line), expressed in ng g<sup>-1</sup> dry weight.

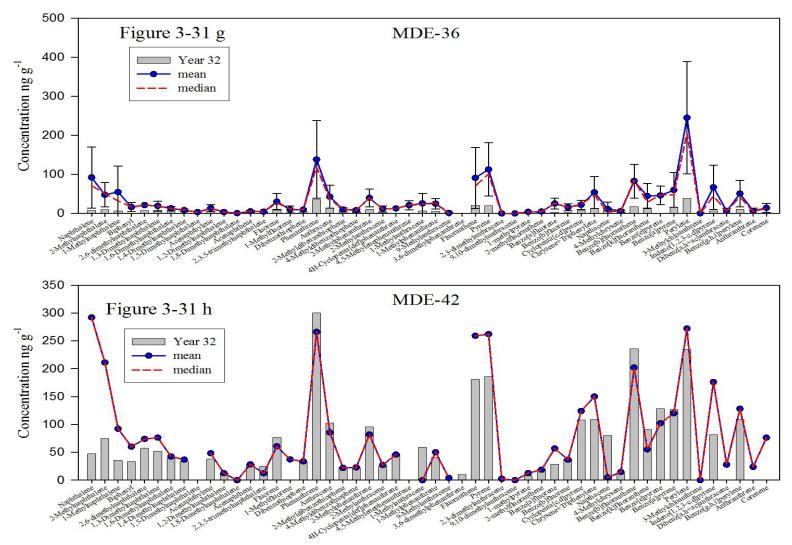


Figure 3-31 continued. Concentrations of PAHs in sediments from site MDE-36 and MDE-42 obtained in the fall of 2013 (bars), the 1998-2012 mean with standard deviation (blue circles and error bars) and the 1998-2012 median (dashed line), expressed in ng  $g^{-1}$  dry weight.

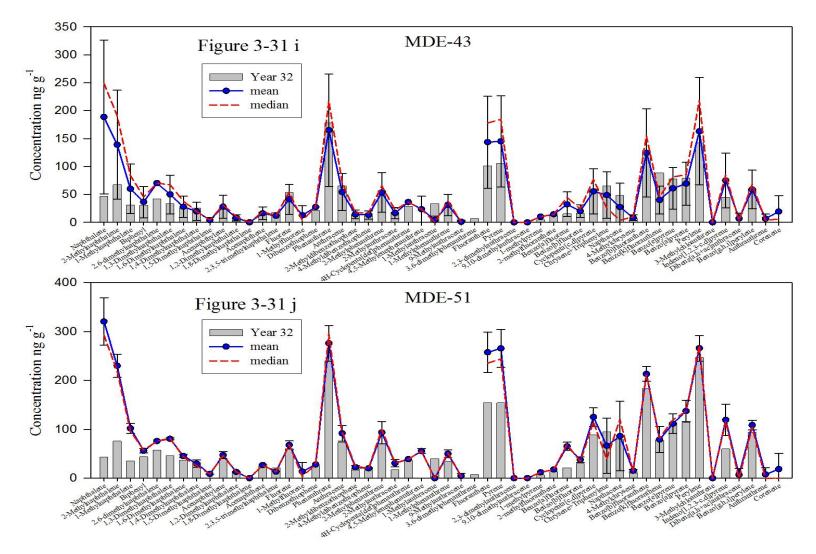


Figure 3-31 continued. Concentrations of PAHs in sediments from site MDE-43 and MDE-51 obtained in the fall of 2013 (bars), the 1998-2012 mean with standard deviation (blue circles and error bars) and the 1998-2012 median (dashed line), expressed in ng  $g^{-1}$  dry weight.

## **Polycyclic Aromatic Hydrocarbons in Clams**

The concentrations of PAHs found in clams collected in the vicinity of HMI are shown in Figure 3-32 a-j and order listed in Table 3-6. Few compounds were above the detection limits therefore little information can be gleaned from the data. Metabolism of PAHs by clams could be partially responsible for the low values as could be low accumulation over the weeks leading up to collection.

Table 3-6: Polycyclic aromatic hydrocarbons given in the same order as in Figure3-32 a-j (left to right). Note: 1,4 + 1,5 + 2,3-Dimethylnaphthalene was split into 4-Dimethylnaphthalene and 1,5-Dimethylnaphthalene to enable a historicalcomparison

1 Naphthalene	18 Phenanthrene	36 Benzo[a]fluorene
2 2-Methylnaphthalene	19 Anthracene	37 Benzo[b]fluorene
3 1-Methylnaphthalene	20 2-Methyldibenzothiophene	38 Benz[a]anthracene
4 Biphenyl	21 4-Methyldibenzothiophene	39 Chrysene
5 2,6-dimethylnaphthalene	22 2-Methylphenanthrene	40 Naphthacene
6 1,3-Dimethylnaphthalene	23 2-Methylanthracene	41 4-Methylchrysene
7 1,6-Dimethylnaphthalene	24 4H-Cyclopenta[def]phenanthrene	42 Benzo(b)fluoranthene
8 1,4-DimethyInaphthalene	25 1-Methylanthracene	43 Benzo(k)fluoranthene
9 1,5-DimethyInaphthalene	26 1-Methylphenanthrene	44 Benzo(e)pyrene
10 Acenaphthylene	27 9-Methylanthracene	45 Benzo(a)pyrene
11 1,2-Dimethylnaphthalene	28 3,6-dimethylphenanthrene	46 Perylene
12 1,8-Dimethylnaphthalene	30 Fluoranthene	47 3-Methylcholanthrene
13 Acenaphthene	31 Pyrene	48 Indeno(1,2,3-cd)pyrene
14 2,3,5-trimethylnaphthalene	32 2,3-dimethylanthracene	49 Dibenz(a,c+a,h)anthracene
15 Fluorene	33 9,10-dimethylanthracene	50 Benzo(g,h,i)perylene
16 1-Methylfluorene	34 1-methylpyrene	51 Anthanthrene
17 Dibenzothiophene	35 2-methylfluoranthene	52 Coronene

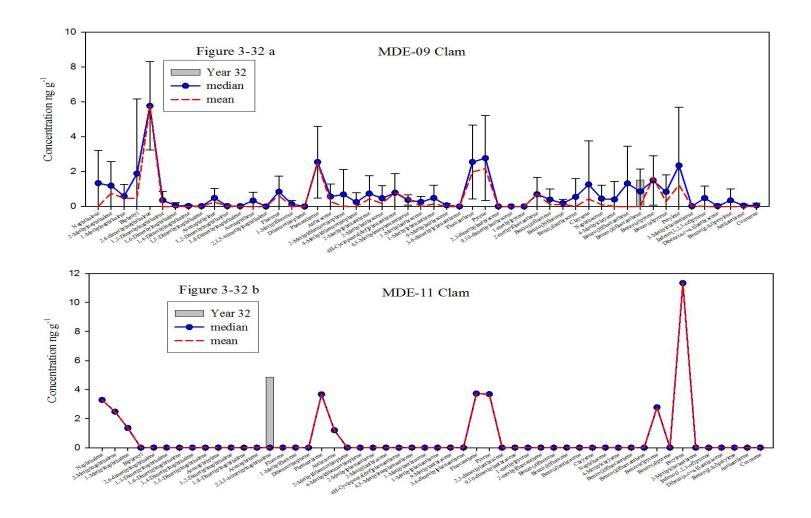


Figure 3- 32: Concentrations of PAHs in clams from site MDE-03 and MDE-09 obtained in the fall of 2012 (bars), the 1998-2011 mean with standard deviation (blue circles and error bars) and the 1998-2011 median (dashed line), expressed in ng g<sup>-1</sup> wet weight.

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Figure 3-32 continued. Concentrations of PAHs in clams from site MDE-13 and MDE-17 obtained in the fall of 2013 (bars), the 1998-2012 mean with standard deviation (blue circles and error bars) and the 1998-2012 median (dashed line), expressed in ng g<sup>-1</sup> wet weight.

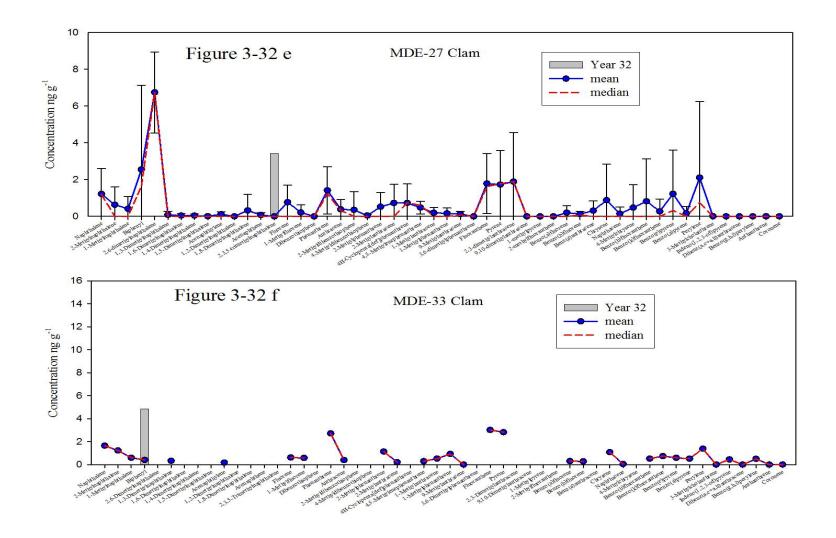


Figure 3-32 continued. Concentrations of PAHs in clams from site MDE-27 and MDE-33 obtained in the fall of 2013 (bars), the 1998-2012 mean with standard deviation (blue circles and error bars) and the 1998-2012 median (dashed line), expressed in ng  $g^{-1}$  wet weight.

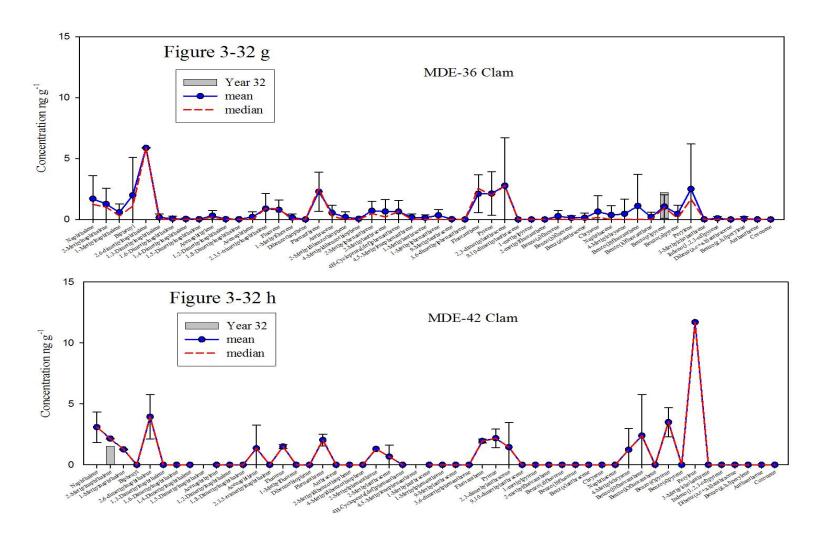


Figure 3-32 continued. Concentrations of PAHs in clams from site MDE-36 and MDE-42 obtained in the fall of 2013 (bars), the 1998-2012 mean with standard deviation (blue circles and error bars) and the 1998-2012 median (dashed line), expressed in ng g<sup>-1</sup> wet weight.

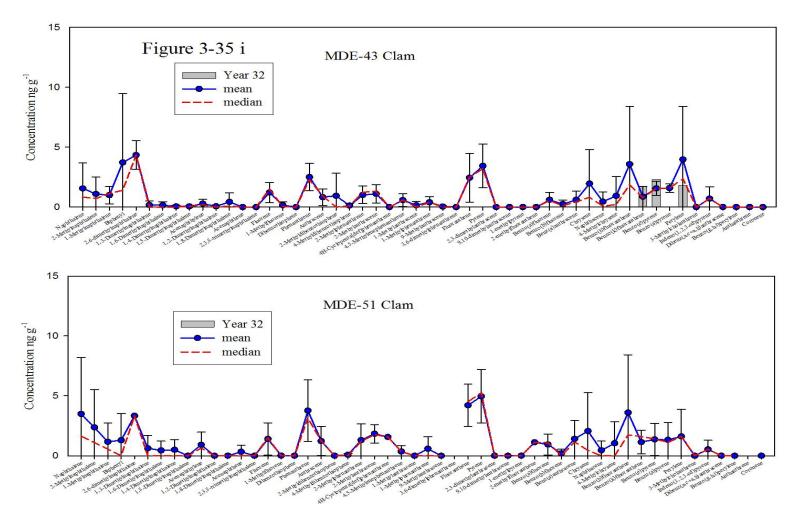


Figure 3-32 continued. Concentrations of PAHs in clams from site MDE-43 and MDE-51 obtained in the fall of 2013 (bars), the 1998-2012 mean with standard deviation (blue circles and error bars) and the 1998-2012 median (dashed line), expressed in ng  $g^{-1}$  wet weight.

## **Total PAH concentrations in sediments and clams**

The total concentrations of PAHs in sediment collected in 2013 from sites around the HMI complex were similar to or below historical levels (Figure 3-33a). PAH concentrations at site MDE-34 were above the standard deviation of the average of historic concentrations, although concentrations at this site are typically very low. The total concentrations of PAHs at the reference site MDE 36 were very low compared to past measurements.

Concentrations of PAHs in clams were well below historic levels at all sites, including the reference sites MDE-36 (Figure 3-33b). The very low PAH concentrations in clams appears to be unusual, although this phenomena has been observed in the past, in 2006 (Year 25) and in 2003 (Year 22). A number of explanations are possible from low accumulation, metabolism of PAHs to loss of lipid from stress or low food intake.

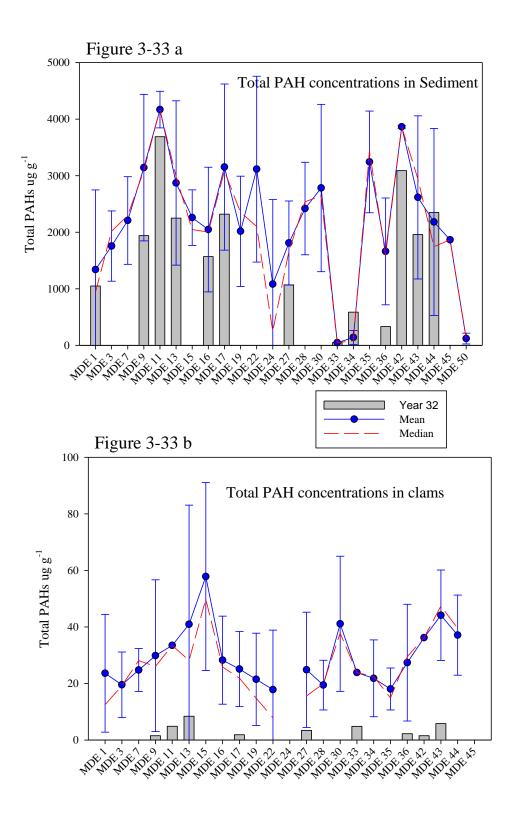


Figure 3- 33: Total PAH concentrations in sediments (a) (ng g<sup>-1</sup> dry weight) and total PAH concentrations in clams (b) (ng g<sup>-1</sup> wet weight) collected in September 2013 (bars), the 1998-2012 mean with standard deviation (blue circles and error bars) and the 1998-2012 median (dashed line).

#### **Bioaccumulation Factors for PCBs and PAHs**

PAHs are typically not accumulated in organisms to the same degree as PCBs. Organisms have varying abilities to metabolize and depurate PAHs although this ability in shellfish and clams is thought to be more limited. Exposure to PAHs has a metabolic cost stems from the need to repair DNA damage. Concentrations do not reflect the overall exposure in the life of the clam but do give an indication of recent exposure. Because they do not accumulate particularly well PAHs are not transferred up the food web to the same degree of PCBs. PAH concentrations in clams are orders of magnitude below the sediment concentrations, hence no bioconcentration from sediment is observed in 2013 as has been the case in previous years. PCBs accumulate in organisms because they are metabolized at a rate slower than the rate of accumulation; hence Bioaccumulation Factors (BAFs) can be calculated as a means of assessing the relative bioavailability in a given area. PCB BAFs calculated on a wet weight basis are less than 2 for most of the sites studied in 2013 with the exception of MDE-33 and MDE 36 (Figure 3-34); the high factors being driven by low concentrations of PCBs in sediment.

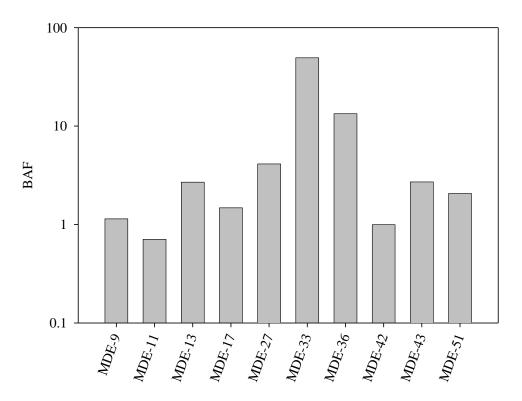


Figure 3- 34: 2013 PCB bioaccumulation factors between sediment and clams.

# The Potential Sediment Toxicity from Organic Contaminants

The potential toxicity of the PAH and PCB concentrations in sediments around HMI was assessed by comparing the total concentrations to the Threshold Effects Level (TEL) and Probable Effects Level (PEL) as developed by NOAA for marine sediments. The TEL is surpassed at a number of the sites, which is not surprising given Baltimore's industrial and urban influence on sediments (Figure 3-35). The PEL was not surpassed by any of the sites for either PCBs or PAHs (Figure 3-35). Concentrations of individual compounds, for which criteria have been established, fall below the established PELs.

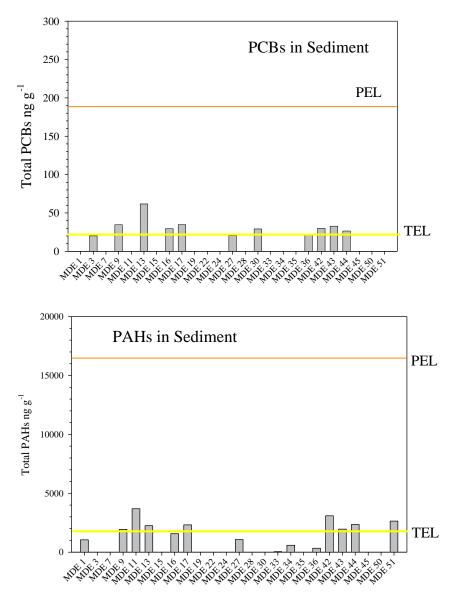


Figure 3-35: Total PCB and total PAH concentrations in relation to the Threshold Effects Level (TEL) and the Probable Effects Level (PEL) for samples collected in September 2013.

#### SECTION SUMMARY

In past years, sediments of a few sites have been observed as being enriched in more than one trace element to a degree well above the historic means. This was not the case in 2013. In general, concentrations were very close the sites running median for 1998-2012 with exception of T-Hg, which was elevated in concentration at more than half of the sites. Concentrations of As have been trending upward in recent years, but this may simply be part of an oscillation as we have seen in previous years for it and other trace elements. Some deviations in the relationships between trace elements in sediment suggest changes in source or are the result of differences in diagenetic behavior. Concentrations of trace elements in clams were similar to or below concentrations observed in previous years. Bioaccumulation of some trace elements such as MeHg occurred as expected. The pattern in metal bioaccumulation was very similar in both seasons and no sites appeared to stand out as being different than the rest.

In the case of the organic contaminants, concentrations of PCBs in sediment were similar to historic values and the concentration in clams was below historic levels. The sediments contained high concentrations of the PCB congeners 31+28, 66+95, 70+76, 132+153+105, 208+195, 206 and 209 which were found in most of the previous years. In the case of clams, congeners 66+95, 123 + 149, 132+153+105, 187+182, 180, 201, 208+195, 206 and 209 dominated. The sediment and clams display similar distributions of congeners and bioaccumulation from sediment top clams was low in 2013.

As in past years 2-methylnaphthalene, phenanthrene, fluoranthene, pyrene, benzo[b]fluoranthene, and perylene make up the majority of PAHs in sediment. Most of these compounds are combustion products of coal, wood and oil. Naphthalene was present but in concentrations lower than past years. Sites MDE-13, 16, 43 and 44 had PAH concentrations above the upper level of the historic standard deviation around the mean, but reference site MDE-36 also displayed this trend. PAHs were seldom detected in the clams. This has been the case in the past; concentrations of PAHs being very low in clams collected in 2003 and 2006.

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