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Cox Creek Dredge Material Containment Facility Exterior Monitoring: Sedimentary Environment 2008

by
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EXECUTIVE SUMMARY

The Cox Creek site is a dredged material containment facility (DMCF) located in Baltimore Harbor. The Cox Creek DMCF is a site which was in operation in the 1960's through 1984, which has been reactivated. A limited amount of material was accepted in 2005 – 2008. The site is an upland disposal site anchored to land, with a diked containment area projecting into the Harbor. Dredged material from Baltimore Harbor is the primary material designated for placement at the site. Use of the site will prevent overboard disposal of dredged sediment and accept material that would in the past be sent to the Hart-Miller Island Dredge Material Containment Facility (HMI DMCF). HMI DMCF is to be closed at the end of 2009.

A total of 10 sites were sampled to monitor the effects of reactivation and operation of the containment facility. Nine (9) monitoring sites adjacent to the area with 1 site designated as reference site. EA Engineering, Science and Technology (EA) collected the samples and the Maryland Geological Survey (MGS) was responsible for analyses and interpretation of the data. The samples were collected September 23 & 24, 2008. Samples consisted of undisturbed sediments collected at the sediment-water interface.

The data showed:

1. Sediments are generally fine grained with a gradient of higher sand content close to the dike, sand content diminishing away from the dike toward the channel.
2. Based on the total nitrogen (N) content of the sediment, the Cox Creek DMCF study area has a greater terrigenous carbon (C) input compared to input from primary production.
3. The sulfur to carbon (S:C) ratio is lower than further into the harbor indicating that the area is slightly more disturbed or has a higher sedimentation rate than further into the Harbor.
4. In monitoring years 2006 and 2007 cadmium (Cd), manganese (Mn), nickel (Ni) and 25% of the zinc (Zn) sites were within background levels found for the Northern Chesapeake Bay. The number of samples and the number of elements within background levels increased in year 2008: Cd, Mn, and Ni, remained at background; the number of sites for Zn increased from 25% to 70%, and chromium (Cr) and copper (Cu) had samples within background.
5. Target metals in the study areas follow the general pattern seen in the 1994 - 1997 Baltimore Harbor study. Site specific variations at the Cox Creek DMCF appear to be a strong source of iron (Fe) and lead (Pb), and a lesser source of Cr, Cu and Zn to the external sedimentary environment.
6. The levels from the dike are comparable to enrichment levels found in that part of the Harbor.
7. The reference site is not representative of the area. Both physically and chemically the site is not representative of the DMCF. This monitoring year the greatest variation occurred at the reference site; for example the % sand dropped more than 50% (>60% in 2007 to < 10% in 2008) and the clay to mud ration (CMR) increased more than 20%
8. General distribution patterns and concentrations are comparable for all three monitoring years indicating effects from the operations of the DMCF are not significantly altering the exterior environment.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

PURPOSE

The Cox Creek DMCF is located in Baltimore Harbor. The Cox Creek facility is currently accepting material. The site is an upland disposal site anchored on land, with a diked containment area projecting into the Harbor. The site is designed to accept dredged material from Baltimore Harbor, and prevent overboard disposal of dredged sediment. The site is similar in design to the HMI DMCF. Based on the monitoring history of HMI DMCF, if the containment areas are maintained in a similar manner no adverse environmental effects are anticipated. However, it is crucial to assure that the placement of dredged material does not have any unanticipated adverse effects to the environment. A scheduled routine monitoring program has been put in place to track any changes to the exterior environment in the area. This study is the third year of sampling prior to full operational acceptance of dredged material to establish a baseline to assess the results for future studies.

OBJECTIVES

The objectives of the sediment quality baseline project are:

1. To measure physical parameters and the concentration of metals and other chemicals in the sediment that could be indicators of accompanying effects to the benthic infauna and potential bioaccumulation through the food chain, and;
2. To provide a baseline for operational input on the operations of the site. This information can be used to prevent deleterious effects to the exterior sedimentary environment. These effects commonly arise from sediment oxidation that results in acid formation that can produce nutrient, trace metal and trace organic mobilization from the sediments.

Effective future monitoring and operational input requires:

1. Documentation of the changes in the exterior physical sedimentary environment due to the construction at and operation of the site. The changes are to be placed into a regional context so that the changes can be properly interpreted.
2. A framework of the physical/geochemical sedimentary environment for the benthic infaunal studies.
3. The ability to recognize the onset of potential problems that may develop so modifications in monitoring and operations can be implemented *prior* to the manifestation of major problems within the living resources.

BACKGROUND

Cox Creek DMCF is located approximately 1 mile south of the Francis Scott Key Bridge, on the western shore of the Patapsco River in the upper Chesapeake Bay (Figure 1). The U.S. Army Corps of Engineers Baltimore District originally constructed Cox Creek DMCF in the mid 1960s. This site was used periodically from the mid 1960s through 1984. The Maryland Port Administration (MPA) purchased half of the site in 1993 and the other half in 1997. The remaining capacity was reserved for future dredging needs of the Baltimore Harbor.

Cox Creek DMCF was renovated to accept dredged material and has 102 acres for dredged material placement with an average annual capacity of 500,000 cubic yards (cy). The plan for renovating the DMCF had been developed through cooperative efforts of Federal and State agencies. Cox Creek DMCF is roughly 10% of the size of the Hart HMI DMCF or Poplar Island Environmental Restoration Site; two dredged material placement sites that serve the approach channels leading to the Port of Baltimore. At the final elevation of 36 feet above mean lower low water (+36 ft MLLW), Cox Creek DMCF will hold approximately 6 million cubic yards (mcy) of material dredged from Baltimore shipping channels and port facilities. The expected site life is 12 years based on inflow of dredged material from maintenance and new work dredging in the Harbor. Innovative reuse of the dredged material could possibly extend the operating life of this DMCF.

Operational Goals:

- Optimize site capacity for dredged material through the use of crust management techniques and site modifications.
- Protect the environment by removing sediments from the Harbor while maintaining water quality standards regulated under a discharge permit from Maryland Department of the Environment.
- Enhance the Swan Creek Watershed by creating a tidal marsh environment adjacent to the DMCF.

Design Features

The DMCF dikes were constructed to +36 ft MLLW. (the same height as adjacent land), to create a 133-acre facility (102 useable acres) with two cells that provide storage capacity for current and future Harbor dredging needs. The DMCF capacity is approximately 6 mcy to accept material dredged from Baltimore shipping channels and port facilities. The DMCF has a municipal water supply, is easily accessible by roadway, close to US 695 and is water accessible with an unloading pier.

The Cox Creek DMCF unloading pier is a modified L-Shaped 300-foot long by 50-ft. wide concrete pier, with a 32-ft. wide trestle, located approximately 160 ft. offshore and parallel to the dike shoreline (Kotulak and Headland, 2007). The pier is designed for one-way traffic flow for the dredged material offloading operation and can accommodate a barge having a length of 296 ft., width of 54 ft., and loaded draft of 16 ft. The pier is designed to support a Manitowoc 4100 track-mounted crane with a 22-ft. width using a 10 cy bucket - the maximum reach for a loaded bucket is 75 ft. The crane will off-load into a hopper to feed articulated dump trucks.

The design dredge depth of the unloading pier is –16 ft. MLLW with the ability to accommodate a 2-ft. overdredge depth to –18 ft. MLLW. The pier deck elevation is 10 ft. MLLW.

Operations

The DMCF will contain dredged material from the Baltimore Harbor. Dredged material is planned to be inflowed using a hydraulic unloader, although mechanical placement may also be considered. Placement at the DMCF is planned to be seasonal. Normally, inflow/placement is planned for the period between October and April; crust management is planned for May through September. Inflow periods will be determined by the quantity of dredging performed each year and the urgency of the project. A discharge permit from the Maryland Department of the Environment sets limits for water discharge quality, monitoring and reporting requirements. Discharge occurs during inflow and crust management activities, with much lower volumes of discharge during crust management.

PREVIOUS STUDIES

Baltimore and the surrounding area in the main Chesapeake Bay has been the subject of studies since the early 1970's. However, the most pertinent studies to this project are the on-going monitoring efforts around HMI DMCF (see Hill and Van Ryswick, 2006) and the *Spatial Mapping of Sedimentary Contaminants in the Baltimore Harbor* (Baker et al., 1997). The Spatial Mapping study was the most thorough and comprehensive study of the Harbor to date. The study incorporated; physical characteristics, sedimentation rates, metals, and organic compounds, as well as a range of benthic community studies including toxicology testing. Samples included surficial sediments and a range of coring techniques (box cores, gravity cores, and vibracores). This study was carried out during the period of 1994 - 1997, and was a cooperative study with the University of Maryland and the Maryland Geological Survey funded by the Maryland Department of the Environment. Although there were only a few samples that fell within the study areas for this report, the Spatial Mapping study provides a broader context for the sites of interest.

The HMI DMCF is a diked containment area in the main stem of the Chesapeake Bay north of the mouth of Baltimore Harbor. It has been monitored continuously, prior to its construction (starting in 1981) up to the present. HMI DMCF is similar in construction, and presumably in operation, to Cox Creek DMCF and the proposed Masonville DMCF. Therefore, if the facilities' operations impact the exterior sedimentary environment, decisions based on the HMI DMCF model should be directly applicable. Additionally, HMI DMCF is in the same geochemical regime as Baltimore Harbor (Hill, 1984 and 1988) and the baseline levels determined at HMI DMCF are directly applicable. The HMI DMCF baseline was used in evaluating the metals data in the Spatial Mapping study.

The results of both of these studies will be referred to in the following discussion and were used in the first year monitoring study at the Cox Creek DMCF. The results of the last two years' studies showed:

1. Sediments are generally fine grained with a gradient of higher sand content close to the dike diminishing out toward the channel.

2. Based on the total N content of the sediment the Cox Creek DMCF study area has a greater terrigenous C input compared to input from primary production.
3. The S:C ratio is lower than further into the harbor indicating that the area is slightly more disturbed or has a higher sedimentation rate than further into the Harbor.
4. Cd, Mn, Ni and 60% of the Zn sites are within background levels found for the Northern Chesapeake Bay.
5. Target metals in the study areas follow the general pattern seen in the 1994 - 1997 Baltimore Harbor study. Site specific variations are; - The Cox Creek DMCF appears to be a strong source of Fe and Pb, and a lesser source of Cr, Cu and Zn to the external sedimentary environment.
6. The enrichment levels attributed to the facility's operation are comparable to enrichment levels found in that part of the Harbor.
7. The reference site is not representative of the area. The site is physically different with a sand content of 70%; the next highest sand content is ~40% with the average sand content less than 20%. The reference site helps provide spatial coverage to define the external source of the metals, but may not be a good gauge to measure changes due to construction and operation of the DMCF.

METHODOLOGY

Field

EA Engineering, Science and Technology (EA) collected the samples and the Maryland Geological Survey (MGS) was responsible for analyses and interpretation of the data. The samples were collected September 23 & 24, 2008. Samples consisted of undisturbed sediments collected at the sediment-water interface using a Ponar grab sampler. From each of these samples, two sub-samples were taken and packaged in Whirl-pak plastic bags. One sub-sample was designated for textural analysis, the other for metals and total C, N, S and phosphorus (P). After collection, the samples were stored at 4^0C until analysis and were analyzed less than 6 months after delivery to MGS. The location of the samples is shown in Figure 1. A total of 10 sites were sampled; 9 monitoring sites and 1 site designated as a reference site (REF). The locations of the sampling sites are given in Appendix I.

Laboratory Procedures

Physical Parameters

Two physical properties of the sediment samples were analyzed: water content and grain size composition (% sand-silt-clay). Water content is calculated as the percentage of water weight to the total weight of the wet sediment. Bulk density and porosity can also be determined from water content measurements. The relative proportions of sand, silt, and clay were determined by standardized sedimentological procedures described by Kerhin et al. (1988). Briefly described,

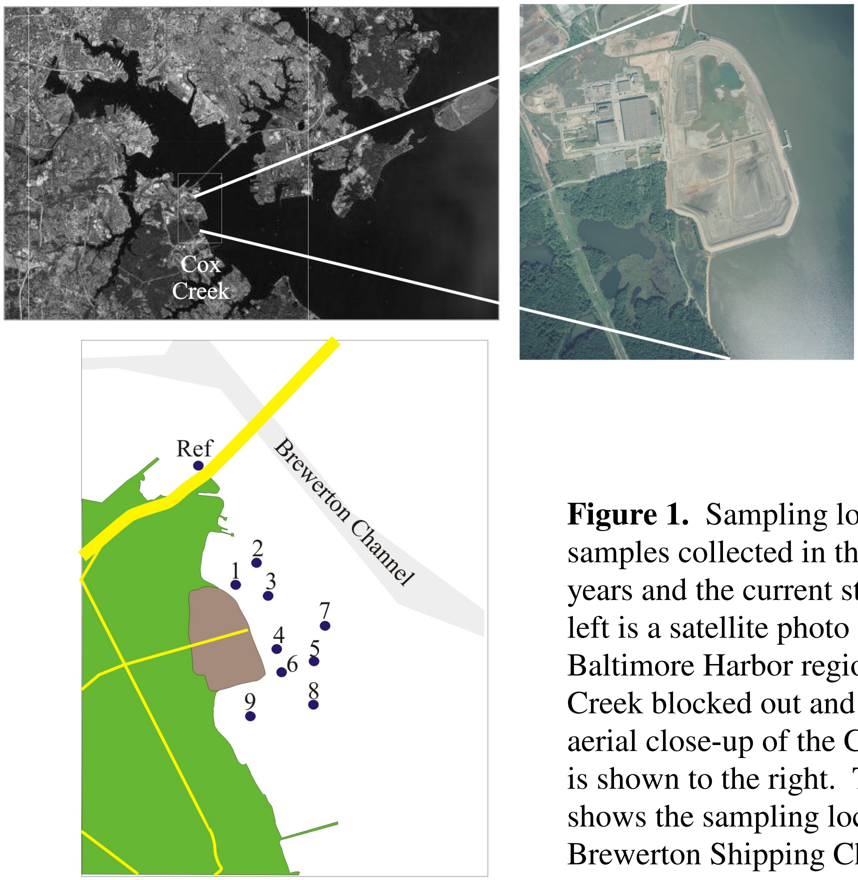


Figure 1. Sampling locations for samples collected in the previous two years and the current study. The upper left is a satellite photo showing the Baltimore Harbor region with Cox Creek blocked out and labeled. An aerial close-up of the Cox Creek DMCF is shown to the right. The lower figure shows the sampling locations; the Brewerton Shipping Channel marked for reference.

the sediment samples were pre-treated with hydrochloric acid and hydrogen peroxide to remove carbonate and organic matter, respectively. The samples were then wet sieved through a 62-um 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 was determined; and the sediments categorized according to Shepard's Nomenclature (1954) and Pejrup's (1988) classification. The results of these analyses are given in Appendix II.

Elemental Analyses

Concentrations of 51 elements were measured in the sediments. This included a suite of 47 metals along with total C, N, S, and P. The primary metals of interest (target metals) are: Fe, Mn, Zn, Cu, Cr, Ni, Cd and Pb. The metals chosen are particularly useful in interpreting geochemical trends and as measures of priority pollutants (Helz et al., 1982, Sinex and Helz, 1981; Kerhin et al., 1982a&b; Hennessee et. al., 1995). The metals in this subset of analytes (except Fe) are indicators that reflect, and track, the behavior of other metals in different geochemical partitions in the sediment; additionally, they are elements whose concentrations can be influenced by anthropogenic activity. If changes occur in these metals, more detailed analyses may be warranted. Additionally, all of the "Metals of Concern" (United States Environmental Protection Agency (USEPA) Chesapeake Bay Program Implementation Committee) for the Chesapeake Bay are in this subset. The only metal of concern not in the subset is mercury (Hg); it was measured as an ancillary metal and the concentrations were all below detection. This year, total Hg was measured using a cold vapor technique to determine measurable concentrations of Hg in the area.

Fe is analyzed as a metal not readily influenced by anthropogenic activity. Thus, it can be used to normalize the data. Although grain size correlation techniques for interpretation are the best normalization method to use (see the following sections), comparison of the analyses to larger national sediment databases can be accomplished with Fe when grain size data is not available. However, normalization using Fe is problematic in the Cox Creek DMCF area due to its proximity to Sparrow's Point, the historical location of Bethlehem Steel. This will be discussed later.

All of the elemental analyses were determined using methods that conform to the specifications of the Environmental Protection Agency Environmental Monitoring and Assessment Program (EPA-EMAP) and the National Oceanographic and Atmospheric Administation (NOAA) Status and Trends program. Metals and total P were determined by Activation Laboratories LTD. (Actlabs) using one or both of the following methods: 1) a four acid "total" digestion, followed by Inductively Coupled Plasma - Mass Spectrometry (ICP-MS) and 2) Neutron Activation Analysis (NAA). The method for C, N, and S analysis is discussed in the next section. Table I shows the recoveries of the metals of interest for the three standard reference materials (SRMs) used for quality control and quality assurance (QA/QC). The precision, accuracy and comparability of the data are excellent, with most analytes within two standard deviations of the certified values.

Quality control entailed the routine inclusion of blanks, replicates and SRMs in the analysis; one in five samples analyzed was either a blank, replicate, or an SRM. The analytical results are given in Appendix II. In addition to the target metals of concern and P, an additional 40 elements were analyzed and reported. The additional elements did not undergo the rigorous scrutiny of the MGS QA/QC procedure, though they were subject to Actlabs' QA/QC procedure using a series of SRM in house; these elements will be included in the report for informational purposes as ancillary element data in Appendix II.

Table I. Results of metal and P analyses of SRMs from the National Institute of Standards and Technology (NIST: SRM 2702 - Inorganics in Marine Sediment and SRM 8704 - Buffalo River Sediment) and the Canadian Research Council (CRC) (SRM PACS-2) compared to the certified or known values. MGS values were obtained by averaging the results of all SRM analyses run with the unknowns.

	P (%)	Cd	Cr	Cu	Fe (%)	Mn	Ni	Pb	Zn	Hg (ng/g)
Detection Limit	0.001	0.3	2	1	0.01	1	1	3	1	5
NISTSRM 8704 - Buffalo River										
Ave.	0.089	3.5	136.7	80.7	3.96	541	46.7	134.3	345.0	947
Std	0.002	0.3	11.6	4.2	0.11	25	4.9	13.6	15.4	39
Cert	nc	2.9	121.9	nc	3.97	544	42.9	150.0	408.0	985
Std	nc	0.3	3.8	nc	0.10	21	3.7	17.0	15.0	54
Recovery	nc	119	112	nc	100	99	109	90	85	96
NISTSRM 270 2- Inorganics in Marine Sediment										
Ave.	0.134	1.4	372.0	109.5	7.59	1720	84.5	110.5	428.5	379
Std	0.001	0.1	8.5	3.5	0.11	57	3.5	4.9	14.8	3
Cert	0.155	0.8	352.0	117.7	7.91	1757	75.4	132.8	485.3	438
Std	0.006	0.0	22.0	5.6	0.24	58	1.5	1.1	4.2	24
Recovery	86	165	106	93	96	98	112	83	88	87
CRCSRM - PACS-2										
Ave.	0.089	2.8	106.5	283.5	4.19	418	45.0	151.5	325.0	2680
Std	0.004	0.1	2.1	9.2	0.04	17	0.0	4.9	4.2	57
Cert	0.096	2.1	90.7	310.0	4.09	440	39.5	183.0	364.0	3040
Std	0.004	0.2	4.6	12.0	0.06	19	2.3	8.0	23.0	200
Recovery	93	130	117	91	102	95	114	83	89	88

Note: ***bdl - below detection limit; nc - no certified value***

Carbon, Nitrogen, and Sulfur

C, N and S are important environmental factors. Concentrations of these species influence the fate of toxic chemicals, through sorption, ion exchange and solubility of hydrophobic organic compounds. Additionally, carbon and nitrogen are important nutrients for benthic organisms, and their concentrations are indicators of biological and sedimentary processes.

The sediments were analyzed for total N, C and S 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 C, N, and S analysis using the manufacturer's recommended settings. As a primary standard, Sulfanilamide was used. Blanks were run at the beginning of the analyses and after 12 to 15 unknowns (samples) and standards. Replicates of every eighth sample were run. For QA/QC purposes, one of two SRMs was run after every 6 to 7 sediment samples. The precision of the analyses is within 1% (relative standard deviation) and the accuracy generally better than 5% variance from the certified value (Table II). The analytical results are given in Appendix II.

Table II. Results of N, C and S analyses of NIST SRM 1646a and 2702 , compared to the certified or known values. MGS values were obtained by averaging the results of all SRM analyses run with the unknowns.

	Nitrogen		Carbon		Sulfur
NIST SRM1646a-Chesapeake Bay					
Average	0.061		0.585		0.323
Std Dev	0.002		0.012		0.007
Referenced Values	0.056	h	0.583	h	**0.352**
% Recovery	110		100		92
NIST SRM 2702- Baltimore Harbor					
Average	0.261		3.246		1.460
Std Dev	0.010		0.038		0.166
Referenced Values	0.250	h	3.360	nc	1.500
% Recovery	104		97		97

*Note: c – Certified value certified by NIST or CRC.
nc - non-certified value reported by NIST or CRC.
h - Value obtained from repeated analyses in-house and by other laboratories (Haake Buchler Labs and U.S. Dept. of Agriculture).

DISCUSSION

Target Metal Assessment

The approach used to assess target metal levels in this study and the earlier baseline and post construction studies at the site, is based on the interpretive techniques developed for exterior monitoring around HMI DMCF. This technique is a sensitive indicator of metals loading which uses an established regional baseline, determined prior to any construction or operation activities. The baseline behavior is determined by correlating metals concentration with grain size on the reference data set from which all comparisons are made. The reference set, for the HMI DMCF study area, is data collected between 1983 and 1988. Samples collected during this time showed no aberrant behavior in target metal levels. Normalization of grain size induced variability of target metal concentrations was accomplished by fitting the data to the following equation:

$$X = a(\text{Sand}) + b(\text{Silt}) + c(\text{Clay}) \qquad (1)$$

where X = the element 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 (Table III). The correlations are excellent for all of the elements, except Cd, indicating that the concentrations of these metals are directly related to the grain size of the sediment. The correlation for Cd is weaker, though still statistically significant. The poor correlation arises from the low levels of Cd that were near the detection level in the baseline samples.

Table III: Coefficients and R^2 for a best fit of target metal data as a linear function of sediment grain size based on data from the HMI DMCF Baseline Study.

X = [a*Sand + b*Silt + c*Clay]/100

	Cr	Mn	Fe	Ni	Cu	Zn	Pb	Cd
a	25.27	668	0.553	15.3	12.3	44.4	6.81	0.32
b	71.92	218	1.17	0	18.7	0	4.10	0.14
c	160.8	4158	7.57	136	70.8	472	77	1.373
R^2	0.733	0.36	0.91	0.82	0.61	0.77	0.88	0.12

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. This can be done by substituting the coefficients from Table III along with the measured grain size at any location into equation (1); the resulting value is the predicted metal concentration 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.

This technique normalizes grain size induced variability; therefore normal Gaussian statistics can be used to compute the standard deviation (sigma level) of the baseline data. Data within two sigma levels are within the expected regional background, data exceeding this level have been influenced by some process or loading atypical to the region. This is a highly sensitive technique that provides results that are quantified in relation to established background levels.

Grain Size

The summary statistics for the study area, for the past three monitoring years, is given graphically in Figure 2. The average for each parameter is shown by a black line, the standard deviation by the yellow shading and the maximum and minimum values by the red line. Generally the area is fine grained with an average sand content near 20%. There is little variation in the gross data between the three years; there is a slight fining of the sediments in 2008, as compared to the 2007 data, reflected in the lowering of sand and an increase in clay. Figures 3 and 4 show the distribution of the grain size using the % sand and the % clay to mud ratio (CMR: note - mud = silt + clay).

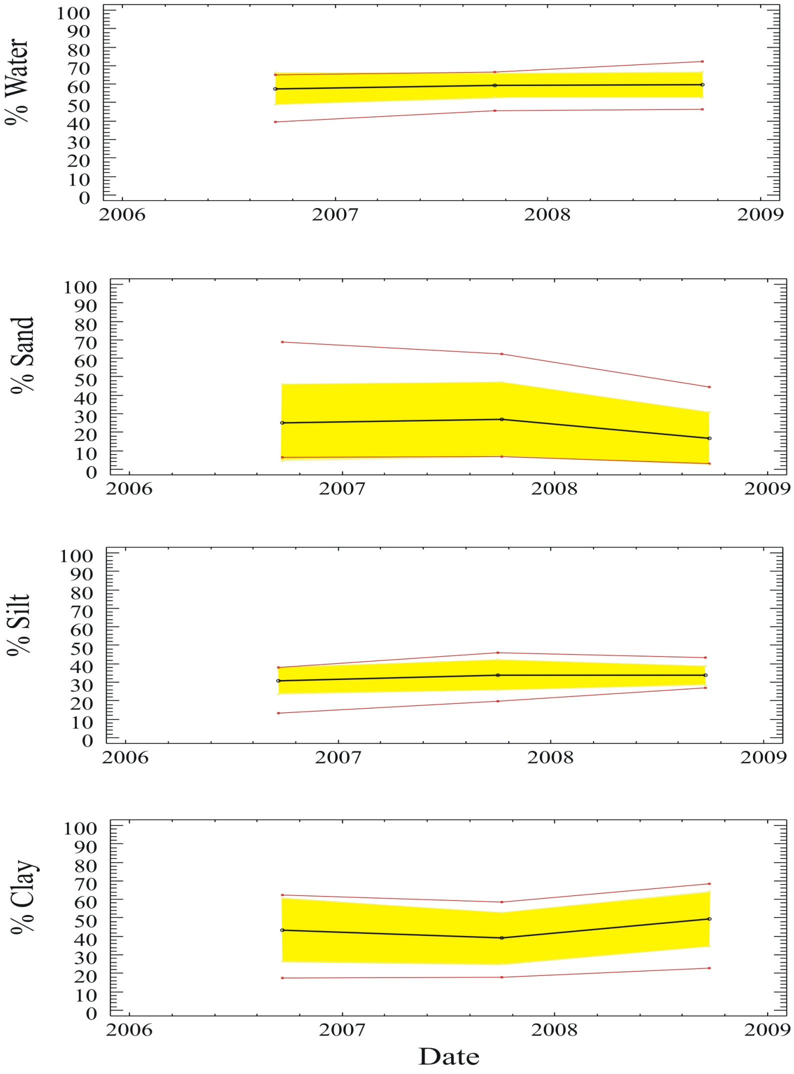


Figure 2. Trend plot of physical properties for Cox Creek DMCF showing: the average (black line), standard deviation (yellow shading), and the minimum and maximum for the data sets. Data are from the monitoring years 2006 through 2008.

Figure 3. % Sand distribution for Cox Creek study area for the monitoring years 2006 – 2008.

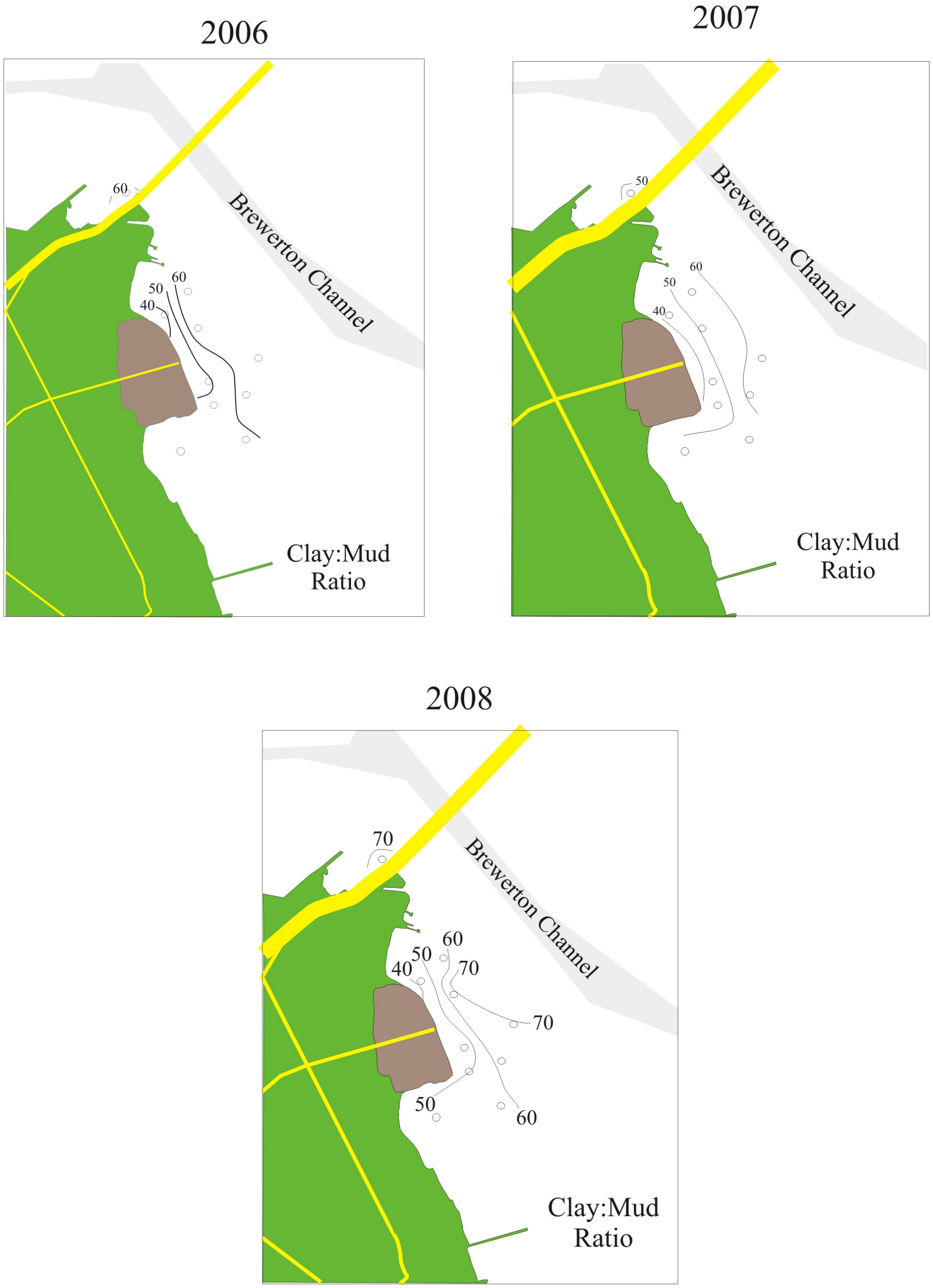


Figure 4. Distribution of the % clay to mud ratio for the Cox Creek study area for the monitoring years 2006 – 2008.

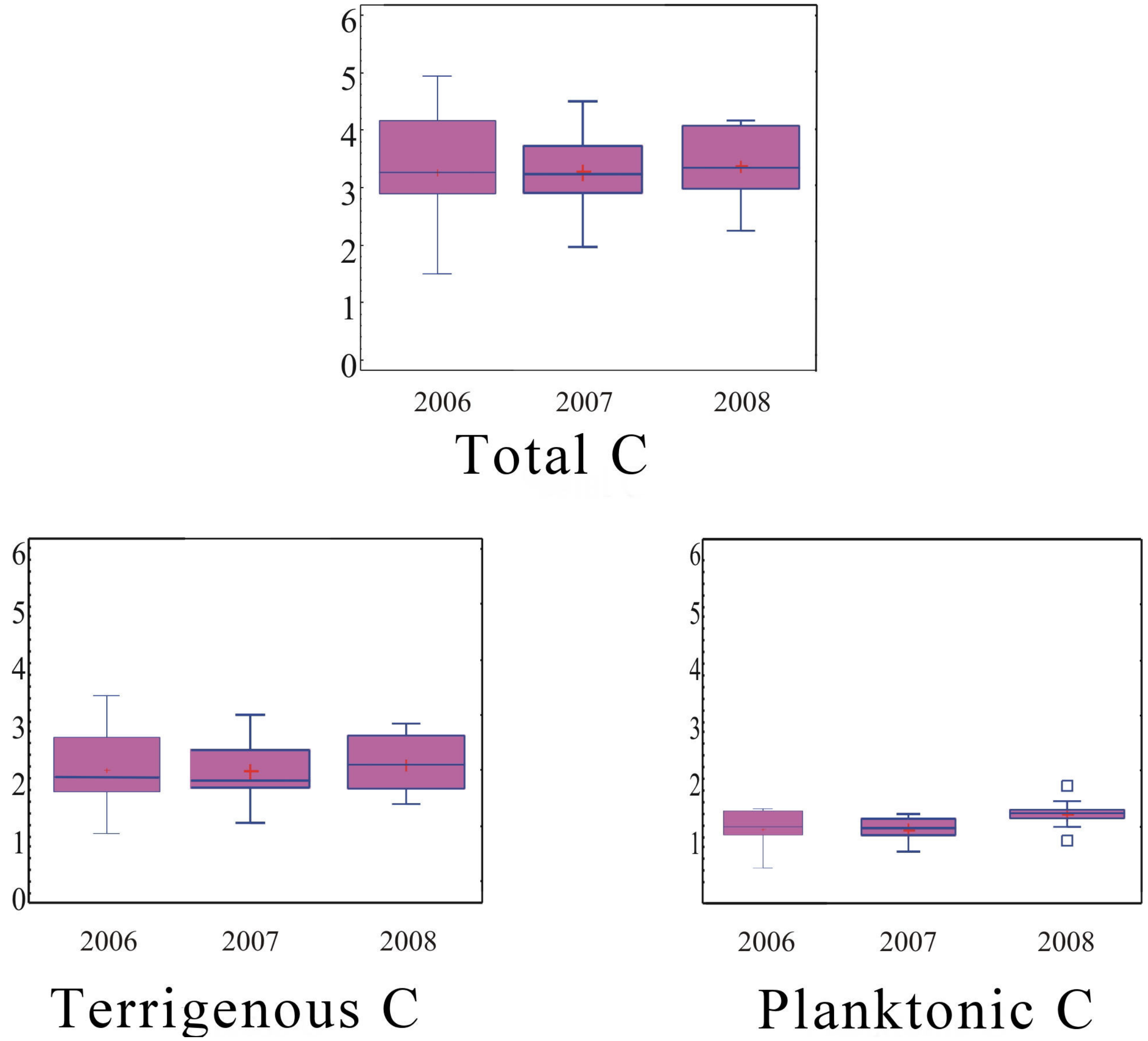
The sediment distribution pattern shows a pattern of coarse grading to fine proceeding from the containment area to the shipping channel. This is evident both from the sand content, which goes from greater than 40% to less than 10%, and the CMR which increases from 40% to >70%. The current study more closely resembles the 2006 conditions than the 2007. The unique feature in 2008 is the finer grain size, seen in the CMR exceeding 70% in the samples nearer the channel. The reference station exhibited the greatest change in the area going from > 60% sand to 3%, and the CMR increased from ~ 50% to >70%; the previous two monitoring years were relatively consistent with one another, though varying from the other sites.

Carbon, Nitrogen and Sulfur

C, N, and S are indicators of the geochemical depositional environment. The concentration of C, N, and S in the sediment is related to the grain size; higher concentrations of these elements are found associated with fine grain sediments. Total C (for this discussion, total carbon is referred as C) in the sediment is comprised of planktonic C ($C_{planktonic}$)and terrigenous C ($C_{terrigenous}$). $C_{planktonic}$ is organic detritus from primary production in the water column. It is derived from plankton that has a mol ratio of 16:106 (N:C) based on the work of Redfield et al. (1963). $C_{terrigenous}$ is organic material from land run-off, coal from mining and industrial sources; $C_{terrigenous}$ has virtually no N content (Hennessee et al., 1986). Consequently, by using the N content with Redfield's ratio 16:106 (N:C) the terrigenous component can be separated from the planktonic. This is shown in Figure 5, which shows the behavior of different measured and calculated species of C; $C_{terrigenous}$, and $C_{planktonic}$. The $C_{planktonic}$, based on the measured N content (see Figure 6) and the Redfield ratio, is consistent with findings in the central portion of Baltimore Harbor [outside of the main shipping channel]. This is expected due to the relative uniformity of the environmental conditions. Factors that effect water column productivity, and the settling of the detritus from the plankton do not vary significantly; *i.e.* there is very little difference in the water column chemistry, the water depths, proximity to land, or hydrodynamic setting to warrant major differences. Consequently, N is similar to the central portion of the Harbor and by extension so is the $C_{planktonic}$. The $C_{terrigenous}$, total C minus $C_{planktonic}$, is significantly higher than further into the Harbor. Cox Creek DMCF is close to Sparrow's Point and the mouth of the Harbor, both are potential sources of coal; either from industrial usage or from the upper Bay which receives a significant amount of coal from mining along the Susquehanna River (Hennessee et al., 1986; Hill et al. 2001). The $C_{terrigenous}$ input is greater than primary productivity ($C_{planktonic}$).

S is different from C and N in that it is predominantly a result of bacterially mediated diagenetic reactions between sulfate in the water column and reactive C in the sediment. The ultimate result is the depletion in C content and the production of metal sulfide minerals in the sediment (Berner, 1970). The amount of sulfide found in the sediment is a result of a variety of factors including the amount of reactive C (principally $C_{planktonic}$), transport related factors allowing for movement of sulfate into the sediment, and the length of time the sediment interacts with the water column. The latter is determined by the sedimentation rate and biological mixing. An indicator of the progress of this process is the S:C ratio; the higher the ratio, the more C consumed in the production of sulfide minerals. Figure 6 shows two S:C ratios; the ratio using total S and C, and the ratio using $C_{planktonic}$ (to reflect the amount of reactive C in the sediment). Generally, the S:$C_{planktonic}$ is within the range typical of mid-Bay samples while the S:C is low. The relativley high proportion of $C_{terrigenous}$ accounts for the low S:C_{total} ratios

The data for all of the monitoring periods are virtually the same. This indicates a relatively stable depositional/geochemical environment.

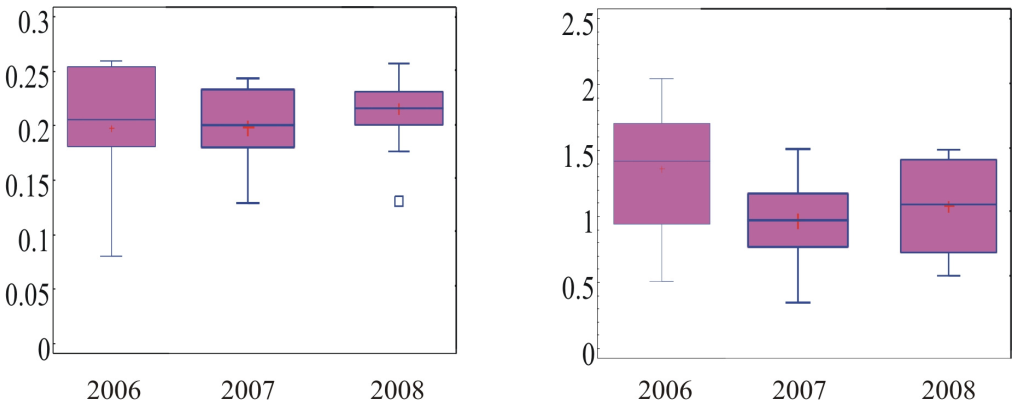


Total C

Terrigenous C

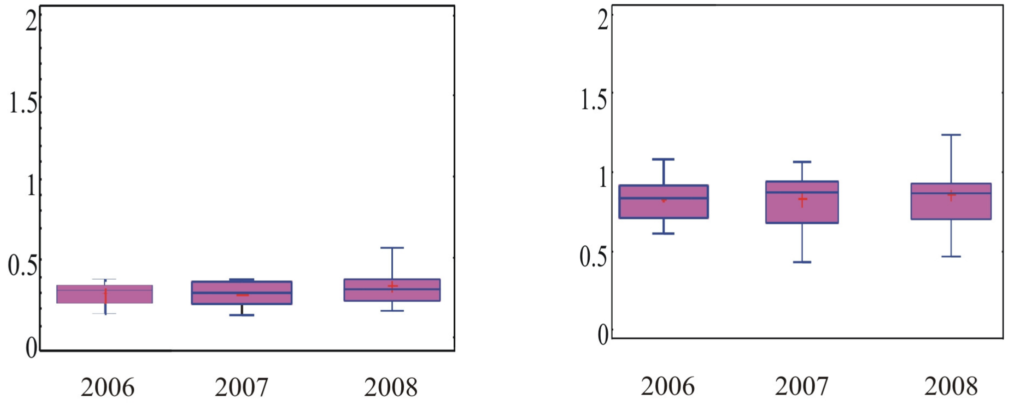
Planktonic C

Figure 5. Box and whisker diagrams showing range and distribution of total C, terrigenous C and planktonic C.



Total N

Total S



Ratio S:C

Ratio $S:C_{Planktonic}$

Figure 6. Box and whisker diagrams showing range and distribution of total N and S and the ratios of S:C and $S:C_{planktonic}$

Target Metals

The concentrations of the target metals of interest are high, as would be expected in fine grain northern Chesapeake Bay sediments in Baltimore Harbor. The summary statistics for the samples in the study area are given in Table IV, along with the Effects Range Low (ERL) and Effects Range Median (ERM) threshold values (Long et al., 1995) for reference. All of the samples, for all of the elements where ERL values exist, are above the ERL values for 2008; Cd was higher this year than previous years. Cr, Ni and Zn have samples above the ERM, consistent with the previous two monitoring years. However, as discussed in an earlier section, the more appropriate way of viewing the data is in the context of the metals concentrations normalized to the grain size data for the main stem of the Chesapeake Bay. All three monitoring years have shown levels of Cr, Cu, Pb, and Zn elevated with respect to the northern Bay reference levels. These elevated levels are consistent with the findings of the Baltimore Harbor Spatial Mapping study (Baker et al, 1997).

Table IV. Summary statistics for target metals for monitoring years 2006 through 2008. Included for reference are the ERL and ERM values from Long et al. (1995).

		2006	2007	2008			2006	2007	2008
Cd (ppm)	Ave.	0.8	1.0	1.4	**Mn (ppm)**	Ave.	1447	1218	1302
	std	0.2	0.2	0.4		std	515	268	213
	Min.	0.3	0.7	0.9		Min.	427	563	978
	Max.	1.1	1.1	2.2		Max.	2080	1540	1690
	n	10	10	10		n	10	10	
	ERL	1.3	1.3	1.3		ERL	n/a	n/a	n/a
	n>ERL	0	0	3		n>ERL			
	ERM	9.5	9.5	9.5		ERM	n/a	n/a	n/a
	n>ERM	0.0	0.0	0.0		n>ERM			
Cr (ppm)	Ave.	292	301	318	**Ni (ppm)**	Ave.	57	53	61
	std	88	60	83		std	17	9	9
	Min.	199	230	190		Min.	27	34	46
	Max.	479	388	478		Max.	81	64	73
	n	10	10	10		n	10	10	10
	ERL	81	81	81		ERL	21	21	21
	n>ERL	10	10	10		n>ERL	10	10	10
	ERM	370	370	370		ERM	52	52	52
	n>ERM	2	2	2		n>ERM	8	6	8
Cu (ppm)	Ave.	117	113	118	**Pb (ppm)**	Ave.	116	116	107
	std	41	27	43		std	38	28	27
	Min.	53	77	73		Min.	43	85	59
	Max.	200	157	201		Max.	180	165	151
	n	10	10	10		n	10	10	10
	ERL	34	34	34		ERL	47	47	47
	n>ERL	10	10	10		n>ERL	9	10	10
	ERM	270	270	270		ERM	218	218	218
	n>ERM	0	0	0		n>ERM	0	0	0
Fe (%)	Ave.	6.83	7.45	7.264	**Zn (ppm)**	Ave.	447	437	421
	std	2.26	1.86	1.5367		std	230	149	152
	Min.	3.72	4.92	4.67		Min.	166	283	226
	Max.	12.10	11.40	10.5		Max.	1040	811	757
	n	10	10	10		n	10	10	10
	ERL	n/a	n/a	n/a		ERL	150	150	150
	n>ERL					n>ERL	10	10	10
	ERM	n/a	n/a	n/a		ERM	410	410	410
	n>ERM					n>ERM	5	6	4

Figure 7 shows box and whisker diagrams for the sigma value of the elevated metals for all of the sampling sites for all three monitoring years. Samples within + or - 2 sigma are within the regional background levels; 3 sigma is borderline, and greater than 3 sigma is statistically significantly influenced by local sources or processes. The data in the figure show only minor variations from year to year.

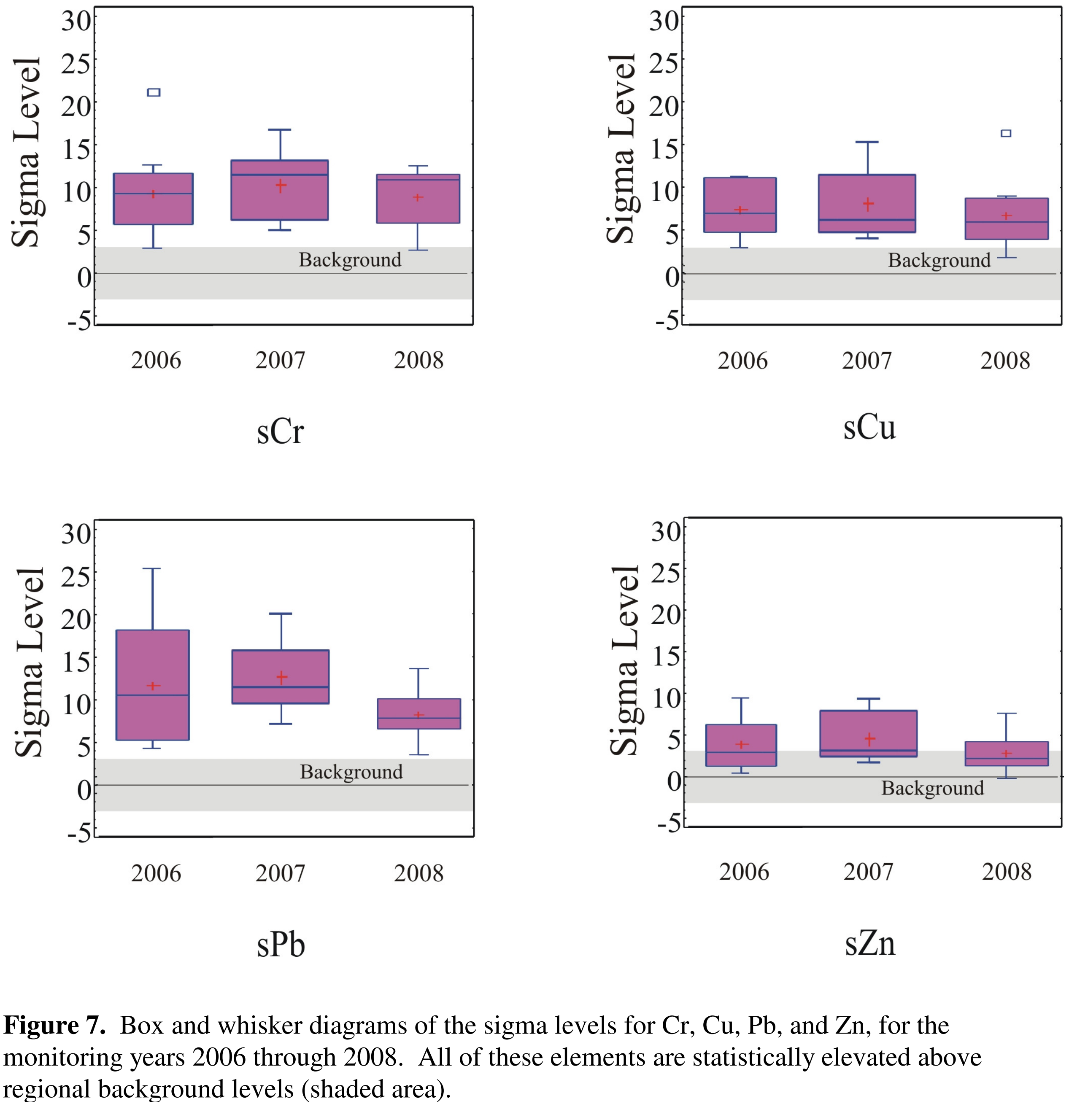


Figure 7. Box and whisker diagrams of the sigma levels for Cr, Cu, Pb, and Zn, for the monitoring years 2006 through 2008. All of these elements are statistically elevated above regional background levels (shaded area).

Figures 8 a - d show the distribution of the sigma values for Cr, Cu, Pb, and Zn for the Cox Creek DMCF study area, comparing monitoring years 2006 through 2008. The contours shown are in increments of 2 sigma (starting with 4 sigma); the areas of statistically significant enrichment (greater than three sigma) are shaded. The features to note from these figures are as follows.

1. Generally the levels of enrichment are lower in 2008.
2. The distributions in 2008 more closely resemble the patterns in 2006.
3. The entire area is significantly enriched for Cr, Cu and Pb for years 2006 and 2007; in 2008 both Cr and Cu had levels that dropped to background closer to the channel.
4. There appears to be a source of enriched material from the central area of the Cox Creek DMCF , for all the elevated metals (including Fe, not shown). This is shown in a plume extending, from the center of the dike going toward the mouth of the Harbor.
5. Zn is within background levels, except for the plume,
6. The reference site in years 2006 and 2007 had some of the highest values in the area for all of the enriched metals. The year 2008 reference samples for Cu, Pb, and Zn were more in line with the low to mid range values of enrichment for the site.

In general, the three years are comparable with only minor variations. In general, the 2008 had lower levels of enrichment as compared to the preceding years; the distribution of the enrichment more closely resembled the 2006 sampling period than the 2007 samples. These variations do not significantly alter the overall pattern of enrichment in the area, and indicate operations at the DMCF have not significantly changed the external environment.

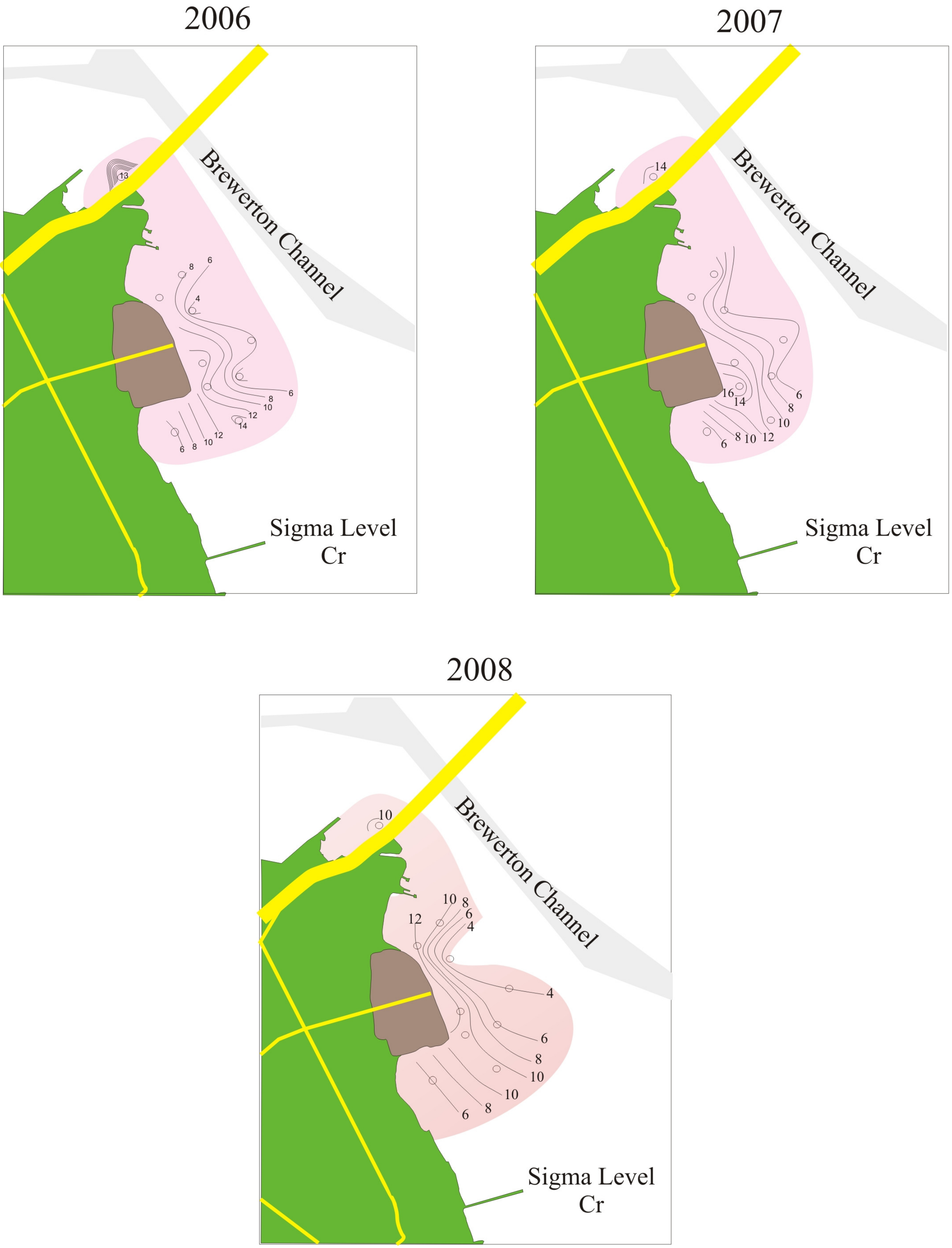


Figure 8a. Sigma levels for Cr in the Cox Creek study area for monitoring years 2006 through 2008. Shaded areas are significantly enriched; contour levels are in increments of 2 sigma

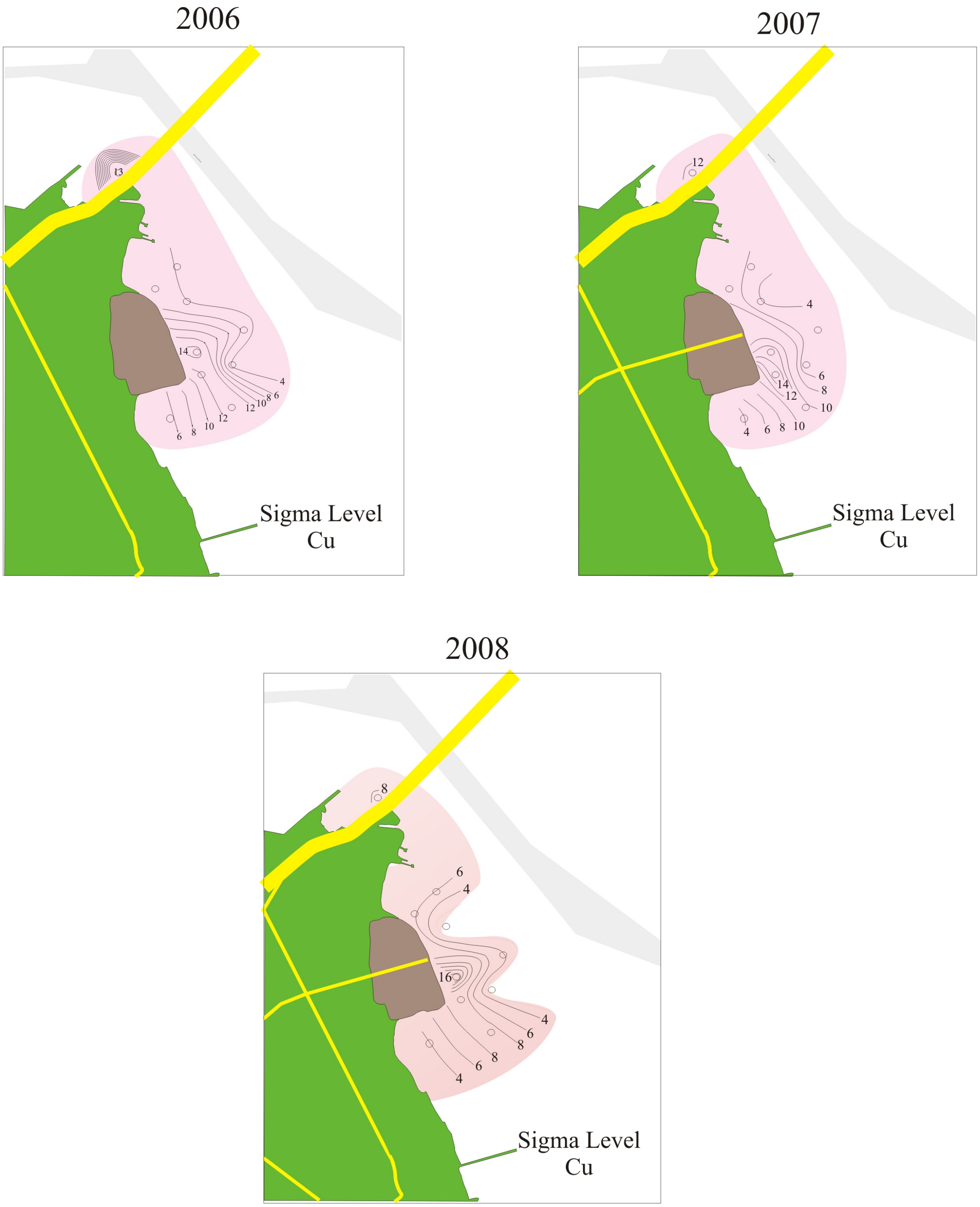


Figure 8b. Sigma levels for Cu in the Cox Creek study area for monitoring years 2006 through 2008. Shaded areas are significantly enriched; contour levels are in increments of 2 sigma

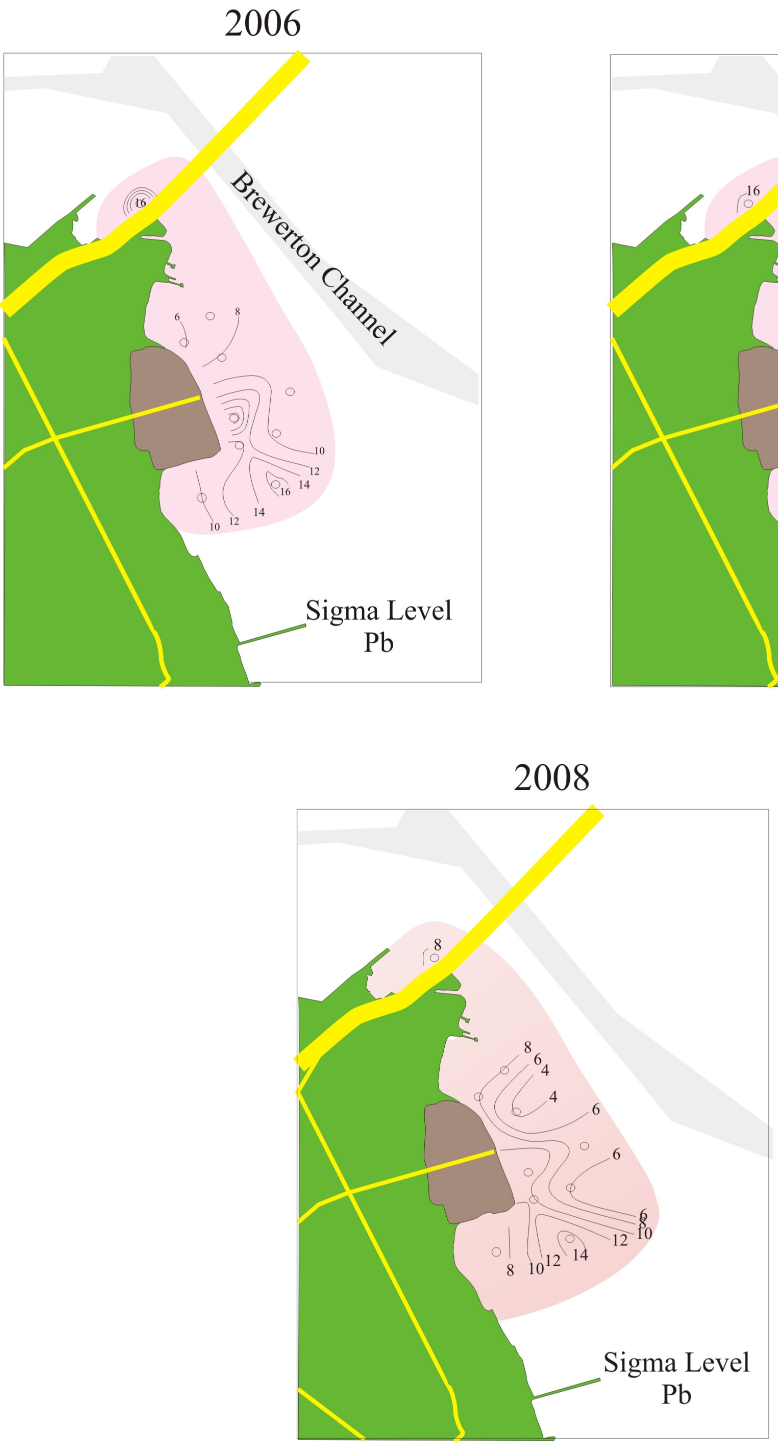


Figure 8c. Sigma levels for Pb in the Cox Creek study area for monitoring years 2006 through 2008. Shaded areas are significantly enriched; contour levels are in increments of 2 sigma

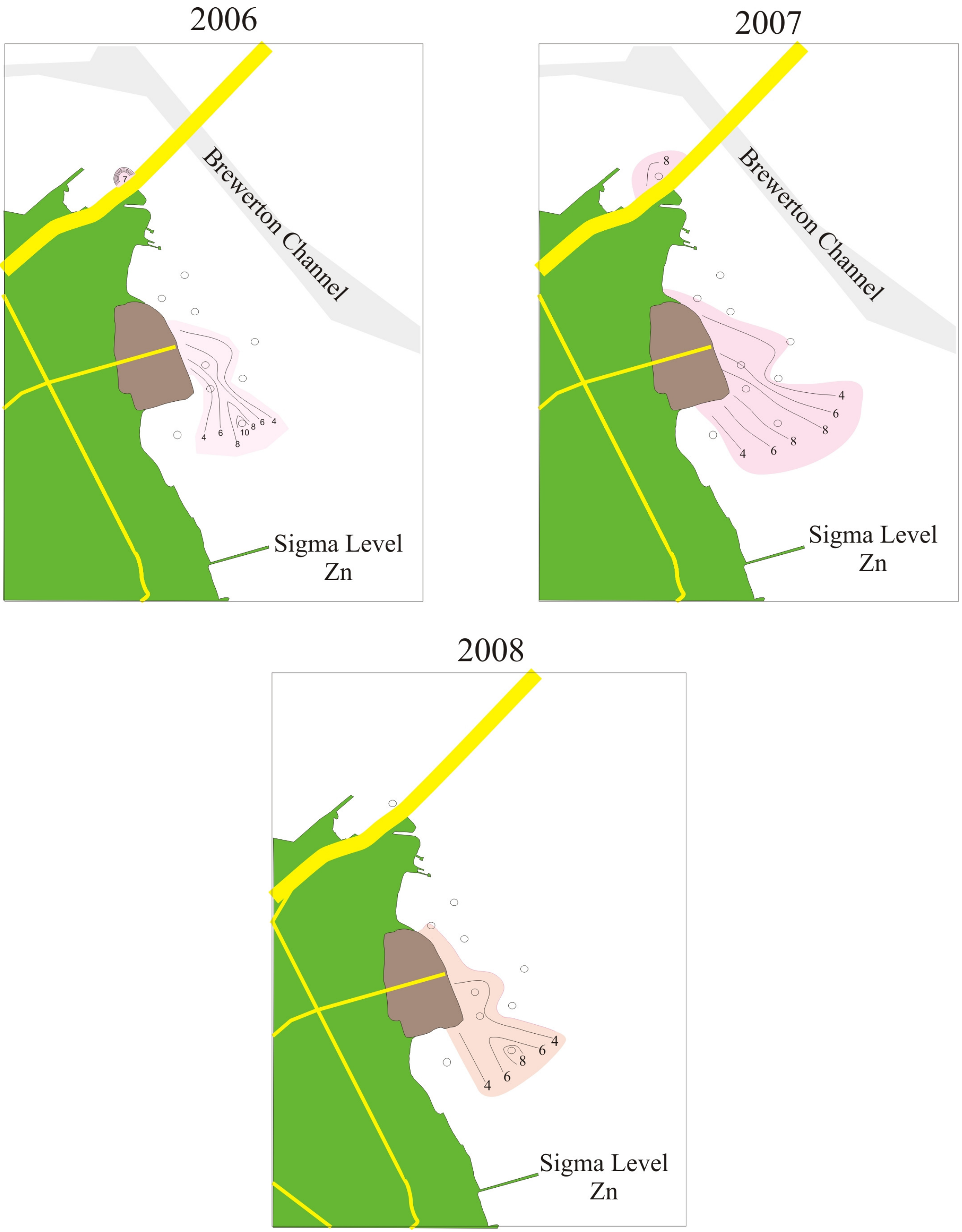


Figure 8d. Sigma levels for Zn in the Cox Creek study area for monitoring years 2006 through 2008. Shaded areas are significantly enriched; contour levels are in increments of 2 sigma

SUMMARY

1. Sediments are generally fine grained with a gradient of higher sand content close to the dike, sand content diminishing away from the dike toward the channel.
2. Based on the total N content of the sediment the Cox Creek DMCF study area has a greater $C_{terrigenous}$ input compared to input from primary production.
3. In monitoring years 2006 and 2007 Cd, Mn, Ni and 25% of the Zn sites were within background levels found for the Northern Chesapeake Bay. The number of samples and the number of elements within background increased in year 2008: Cd, Mn, and Ni, remained at background for all sites; the number of sites for Zn increased from 25% to 70%, and 10 % of the samples had Cr and Cu levels within background.
4. Target metals in the study areas follow the general pattern seen in the 1994 - 1997 Baltimore Harbor study. Site specific variations at the Cox Creek DMCF appear to be a strong source of Fe and Pb, and a lesser source of Cr, Cu and Zn to the external sedimentary environment.
5. The reference site is not representative of the area. Both physically and chemically the site is not representative of the DMCF. This monitoring year the greatest variation occurred at the reference site; for example the % sand dropped more than 50% (>60% in 2007 to < 10% in 2008) and the CMR increased more than 20%
6. General distribution patterns and concentrations for measured parameters are comparable for all three monitoring years indicating effects from the operations of the DMCF are not significantly altering the exterior environment.

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Appendix I

Sampling Locations and Analytical Data

Physical Parameters
Target Metals
Ancillary Elements
Total C, N, & S

Sampling Locations

Cox Creek DMCF		
ID	**Northing**	**Easting**
CCE-01	559782.2	1445199.3
CCE-02	560496.5	1445903.7
CCE-03	559366.3	1446207.1
CCE-04	557761.5	1446533.3
CCE-05	557339.9	1447678.5
CCE-06	557036.1	1446023.5
CCE-07	558457.1	1448073.3
CCE-08	555965.4	1447659.8
CCE-09	555608.7	1445676.6
CCE-REF	563502.1	1444013.7

Physical Parameters

Station	% Water Content	Bulk Density	% GRAVEL	% SAND	% SILT	% CLAY	SHEPARD'S CLASS	PEJRUP CLASS
CCE-01	46.47	1.51	0.00	44.66	32.41	22.93	Sand-Silt-Clay	C,III
CCE-02	62.75	1.31	0.00	16.37	34.63	49.01	Silty-Clay	C,II
CCE-03	59.55	1.34	0.00	13.36	27.12	59.52	Silty-Clay	C,II
CCE-04	59.39	1.35	0.00	18.50	43.45	38.05	Clayey-Silt	C,III
CCE-05	60.38	1.33	0.00	6.31	34.47	59.22	Silty-Clay	D,II
CCE-06	52.57	1.43	0.00	38.18	30.86	30.96	Sand-Silt-Clay	C,II
CCE-07	63.41	1.30	0.00	5.97	29.16	64.87	Silty-Clay	D,II
CCE-08	62.04	1.32	2.95	11.16	37.82	48.06	Silty-Clay	C,II
CCE-09	58.36	1.36	0.00	8.39	38.91	52.70	Silty-Clay	D,II
CCE-REF	72.29	1.21	0.00	2.83	28.78	68.38	Silty-Clay	D,II

Target Metals

Concentrations in ppm unless otherwise noted: bdl= delow detection limit

Sample ID	**P (%)**	**Cd**	**Cr**	**Cu**	**Fe (%)**	**Mn**	**Ni**	**Pb**	**Zn**	**Hg (ppb)**
Detection Limit	0.001	0.3	2	1	0.01	1	1	3	1	5
CCE-01	0.066	0.9	274	74	4.67	978	46	59	226	200
CCE-02	0.125	1.2	365	110	6.81	1110	55	108	371	363
CCE-03	0.085	0.9	190	73	5.86	1470	50	83	273	260
CCE-04	0.126	1.5	376	201	8.23	1270	70	109	484	385
CCE-05	0.147	1.2	291	91	8.07	1200	60	109	415	924
CCE-06	0.129	1.3	295	109	7.16	1160	57	86	367	840
CCE-07	0.114	1.4	255	107	7.07	1480	60	125	404	403
CCE-08	0.225	1.8	387	146	10.5	1440	70	151	757	473
CCE-09	0.11	1.2	268	96	6.81	1690	68	101	352	341
CCE-REF	0.18	2.2	478	175	7.46	1220	73	140	565	468

Ancillary Metals

Concentrations in ppm unless otherwise noted: bdl= delow detection limit

Sample ID	**Au**	**Ag**	**Mo**	**Al (%)**	**As**	**Ba**	**Be**	**Bi**	**Br**	**Ca (%)**
Detection Limit	2	0.3	1	0	0.5	50	1	2	0.5	0.01
CCE-01	bdl	0.8	2	5	29.1	360	2	bdl	42	0.48
CCE-02	8	0.8	3	7.9	61.2	620	3	bdl	69	0.44
CCE-03	bdl	0.6	4	8.3	38.8	bdl	3	bdl	57	0.37
CCE-04	bdl	0.9	3	6.6	53.4	bdl	3	bdl	65	0.57
CCE-05	bdl	0.7	4	5.2	61.8	580	3	bdl	70	0.25
CCE-06	17	1.2	5	6.4	39.6	450	3	bdl	56	0.76
CCE-07	bdl	0.7	4	8.8	56.4	bdl	3	bdl	68	0.36
CCE-08	bdl	1.2	7	7.3	78.9	750	3	bdl	80	0.52
CCE-09	bdl	0.6	3	8.1	55	bdl	3	bdl	68	0.49
CCE-REF	bdl	1.7	5	9.2	51.7	660	4	bdl	93	0.44

Ancillary Metals

Concentrations in ppm unless otherwise noted: bdl= delow detection limit

Sample ID	**Co**	**Cs**	**Eu**	**Hf**	**Ir (ppb)**	**K (%)**	**Mg (%)**	**Na (%)**	**Rb**	**Sb**
Detection Limit	1	1	0.2	1	5	0.01	0	0	15	0.1
CCE-01	14	4	1.6	17	bdl	1.03	1	0.6	69	6.7
CCE-02	23	4	2.1	19	bdl	1.49	1	0.9	120	36.4
CCE-03	22	5	2.1	7	bdl	2.29	1	0.9	133	3
CCE-04	27	bdl	2	14	bdl	1.27	1	0.8	66	10.6
CCE-05	28	7	2.1	9	bdl	1.5	1	0.9	bdl	5.1
CCE-06	22	3	2	15	bdl	1.22	1	0.7	bdl	8
CCE-07	28	6	2	7	bdl	1.95	1	1	99	4.8
CCE-08	33	bdl	2.3	12	bdl	1.38	1	0.9	bdl	8.3
CCE-09	27	6	2.1	12	bdl	1.73	1	0.9	81	3.8
CCE-REF	34	7	2	15	bdl	1.9	1	1.2	bdl	8.7

Ancillary Metals *Concentrations in ppm unless otherwise noted: bdl= delow detection limit*										
Sample ID	**Sc**	**Se**	**Sr**	**Ta**	**Ti (%)**	**Th**	**U**	**V**	**W**	**Y**
Detection Limit	0.1	3	1	0.5	0.01	0.2	1	2	1	1
CCE-01	17.1	bdl	84	bdl	0.66	7.2	4	202	bdl	26
CCE-02	27.2	12	117	11	1.15	16.1	10	179	14	31
CCE-03	18.1	bdl	112	2.8	0.67	8.9	7	194	bdl	42
CCE-04	24.8	bdl	117	5.1	0.72	10.7	12	329	11	31
CCE-05	21.2	bdl	67	6.5	0.65	10.9	9	274	10	24
CCE-06	20.7	bdl	103	4.2	0.86	8.5	7	352	8	30
CCE-07	19.5	bdl	100	bdl	0.64	9.4	8	239	7	35
CCE-08	23.6	bdl	105	6.1	0.8	9.9	13	406	bdl	36
CCE-09	20.7	bdl	113	3.9	0.73	9.6	8	258	bdl	36
CCE-REF	25.2	bdl	128	11	0.95	12.5	11	446	bdl	38

Ancillary Metals

Concentrations in ppm unless otherwise noted: bdl= delow detection limit

Sample ID	**La**	**Ce**	**Nd**	**Sm**	**Sn (%)**	**Tb**	**Yb**	**Lu**		
Detection Limit	**0.5**	**3**	**5**	**0.1**	**0.01**	**0.5**	**0**	**0.1**		
CCE-01	43.4	89	25	6.1	bdl	bdl	4	0.4		
CCE-02	66	108	42	8.8	bdl	bdl	5	0.4		
CCE-03	52	99	28	8.7	bdl	1.6	4	0.6		
CCE-04	73.2	120	51	9.9	bdl	bdl	5	0.7		
CCE-05	70.1	119	45	9.6	bdl	1.7	4	0.6		
CCE-06	50.2	97	45	7.7	bdl	bdl	4	0.6		
CCE-07	60.8	114	46	9.2	bdl	1.7	4	0.5		
CCE-08	74.7	121	51	9.7	bdl	bdl	5	0.7		
CCE-09	58.3	119	51	9.5	bdl	bdl	5	0.6		
CCE-REF	175	193	107	14	bdl	1.4	4	0.7		

Total C, N, & S (wt. %)			
Station	**N**	**C**	**S**
CCE-01	0.128	2.206	0.506
CCE-02	0.226	4.135	1.12
CCE-03	0.199	2.536	1.402
CCE-04	0.2	3.388	1.022
CCE-05	0.23	3.261	0.955
CCE-06	0.174	3.629	0.678
CCE-07	0.223	2.935	1.444
CCE-08	0.256	4.088	0.678
CCE-09	0.208	3.136	1.098
CCE-REF	0.304	4.058	1.478