# Magnitude and Extent of Contaminated Sediment and Toxicity in Chesapeake Bay



S. Ian Hartwell and Jawed Hameedi



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## **Table of Contents**

LIST OF TABLES	ii
LIST OF FIGURES	iv
LIST OF ACRONYMS	vii
EXECUTIVE SUMMARY	ix
I. INTRODUCTION	1
II. SITE DESCRIPTION	4
III. METHODS	17
IV. RESULTS	46
V. DISCUSSION	169
ACKNOWLEDGMENTS	198
REFERENCES	199
APPENDIX A	206

### List of Tables

#		Pg					
1	Elemental quantification techniques	31					
2	Polynuclear aromatic hydrocarbons analyzed in Chesapeake Bay sediment samples	34					
3	Chlorinated pesticides and PCBs analyzed in Chesapeake Bay sediment samples	36					
4	Chemicals and chemical groups for which ERLs and ERMs have been derived						
5	List of metrics used in principal component analyses	44					
6	Percent homolog distribution of PCBs in Baltimore Harbor and the Elizabeth River	77					
7	Concentrations (ng/kg) of planar PCBs detected in Chesapeake Bay sediments in 1998.						
8	Chesapeake Bay stations with 7 or more ERL exceedances (90 <sup>th</sup> percentile) and/or ERM exceedance, including specific chemicals.	101					
9	B[a]P equivalents from HRGS P450 bioassays using two incubation times.	107					
10	Spatial extent (km <sup>2</sup> ) of areas where bioassays demonstrated statistically significant responses in Chesapeake Bay sediments.	108					
11	Spatial extent (km <sup>2</sup> ) of areas where bioassays demonstrated probable toxicity in 65 strata in Chesapeake Bay sediments.	109					
12	Number of species and abundance () after various manipulations of the benthic community data set.	115					
13	List of the most widespread taxa found in Chesapeake Bay sediments. (LPIL indicates lowest possible identification level)						
14	List of the 25 most abundant taxa, and the number of stations where they were found in Chesapeake Bay sediments.	117					
15	Number of unique (occurring at only one station) and rare (occurring at only 2 stations) species from Chesapeake Bay sampling sites	131					
16	Spearman-rank correlation coefficients and significance level between sediment toxicity tests and trace elements, chlorinated pesticides, butyl tins, and PCBs.	137					
17	Spearman-rank correlation coefficients and significance level between sediment toxicity tests and PAHs.	139					
18	Spearman-rank correlation coefficients and significance levels between sediment community attributes and trace elements, chlorinated pesticides, butyl tins, and PCBs.	141					
19	Spearman-rank correlation coefficients and significance levels between sediment community attributes and PAHs.	143					
20	Spearman-rank correlation coefficients and significance level between contaminant classes vs toxicity bioassay results and community characteristics.	145					
21	Spearman–rank correlation coefficients and significance level between toxicity bioassay responses and benthic community attributes.	147					
22	Slope estimates and regression coefficients (%) for toxicity, community, contaminant and selected habitat indices.	148					
23	Slope estimates and regression coefficients (%) for toxicity, community,	149					

	contaminant and habitat indices using data normalized for grain size (%silt	
24	Dringing component analysis factor leadings on chemical community and	
24	toxicity metrics.	156
25	Mean-normalized metals concentrations adjusted for grain size.	185
26	Spearman-rank correlation coefficients and significance level between B_IBI	
	and related sediment quality triad attributes.	189
27	Total mass and mass/km <sup>2</sup> of contaminants in sediments in selected regions of	
	Chesapeake Bay.	195
28	Enrichment values for trace elements in selected regions and specific locations	
	in Chesapeake Bay.	197

#		Pg
1	The Chesapeake Bay system.	5
2	Map of upper Chesapeake Bay showing strata boundaries and sampling sites.	19
3	Map of central Chesapeake Bay showing strata boundaries and sampling sites.	20
4	Map of lower Chesapeake Bay showing strata boundaries and sampling sites.	21
5	Distribution of zones in Chesapeake Bay, divided into mainstem, embayment	
	and tributary sites.	47
6	Grain size distribution at Chesapeake Bay sampling stations, expressed as	
	percent silt + clay	48
7	Total organic carbon content at Chesapeake Bay sampling stations	50
8	Correspondence of measured bottom water salinity and measured salinity of	
	pore water (solid line).	51
9	Surface and bottom salinity in the Chesapeake Bay.	52
10	Surface and bottom water temperature in the Chesapeake Bay.	55
11	Surface and bottom dissolved oxygen in the Chesapeake Bay.	58
12	Normalized sediment contaminant concentrations in the Chesapeake Bay.	62
13	Total PAH concentrations in Chesapeake Bay sediment samples.	65
14	High weight and low weight PAH concentrations in Chesapeake Bay	
	tributaries.	66
15	Concentrations of base and alkyl-substituted low weight PAHs in sediments of	
	the Chesapeake Bay.	67
16	Concentrations of base and alkyl-substituted high weight PAHs in sediments of	
	the Chesapeake Bay.	70
17	Concentration of measured PCBs in sediments of the Chesapeake Bay.	74
18	Mean normalized concentrations of 15 elements (Ag, Al, As, Cd, Cr, Cu, Fe,	
	Hg, Ni, Pb, Sb, Se, Sn, Tl, Zn) in sediments of the Chesapeake Bay mainstem.	79
19	Concentrations of DDT and metabolites in sediments of the Chesapeake Bay	
	mainstem.	83
20	Concentrations of chlordanes and related cyclodienes in sediments of the	
	Chesapeake Bay mainstem.	86
21	Concentrations of total HCH in sediments of the Chesapeake Bay mainstem.	89
22	Concentrations of total chlorinated benzenes in sediments of the Chesapeake	
	Bay mainstem.	92
23	Concentrations of chlorpyrifos in sediments of the Chesapeake Bay mainstem.	95
24	Concentrations of total Butyltins (bars) and TBT (diamonds) in sediments of	
	the Chesapeake Bay mainstem.	98
25	Distribution of mean ERM quotient values in Chesapeake Bay sediments.	103
26	Distribution of amphipod bioassay responses in whole sediment toxicity	
ļ	bioassays for Chesapeake Bay.	104
27	Distribution of sea urchin fertilization bioassay responses in sediment pore	
L	water toxicity bioassays for Chesapeake Bay.	105
28	Distribution of P450 bioassay responses in sediment extract toxicity bioassays	
	for Chesapeake Bay.	106

29	Toxicity response scores from sediment bioassays of the Chesapeake Bay	
	mainstem.	111
30	Distribution of toxicity score values in Chesapeake Bay sediments.	114
31	Number of taxa found in sediments of the Chesapeake Bay mainstem.	118
32	Species abundance in Chesapeake Bay mainstem sampling stations.	122
33	Species diversity in Chesapeake Bay mainstem sampling stations.	125
34	Species evenness in Chesapeake Bay mainstem sampling stations.	128
35	Species richness in Chesapeake Bay sampling strata.	132
36	Benthic organism abundance in Chesapeake Bay sampling strata.	134
37	Mean species diversity in Chesapeake Bay sampling strata.	135
38	Mean species evenness in Chesapeake Bay sampling strata.	136
39	Plot of residuals from regression of number of species on toxicity score on data	
	normalized for %silt/clay in Chesapeake Bay sediment samples.	151
40	Nodal analysis results from combining species and site cluster analyses of	
	Chesapeake Bay benthic community data.	152
41	Distribution of species association nodes in Chesapeake Bay.	153
42	Distribution of species association nodes in Chesapeake Bay, excluding	
	contaminated sites.	155
43	Principal component analysis results for all Chesapeake Bay stations	
	(excluding the deep trough).	157
44	Principal component analysis results for Susquehanna Flats stations.	159
45	Principal component analysis results for the combined Upper Bay/tributaries	
	and node #9 stations.	160
46	Principal component analysis results for the combined Tangier Sound/lower	
	tributaries and node 6, 7, and 8 stations.	161
47	Principal component analysis results for the Bay Mouth node.	162
48	Principal component analysis results for stations in the Sand node.	163
49	Example tri-axial plots of Sediment Quality Triad data from Chesapeake Bay	1.5.4
50	sediment samples.	164
50	Values of example habitat parameters plotted as a function of calculated areas	1.65
<u> </u>	of SQ1 triangles from Chesapeake Bay sediment samples.	165
51	Relationship between the area of triad plots and the standard deviation of the	1.67
50	Internal angles of the triangles.	10/
52	Plot of Effects Range-Median quotient (ERMiq) and surface area of Sediment	169
52	Palationship between observed toxicity response index and mean EDM	100
33	Relationship between observed toxicity response index and mean ERM	170
51	Palationship between observed toxicity response index and mean EDM	170
54	cupitient in independent studies of Delaware and Chesapeake Bays	171
55	Relationship between species diversity and mean FRM quotient values in	1/1
55	sediment samples from Chesaneake Bay	172
56	Relationship between species diversity and mean FRM quotient above and	1/2
50	below a value of 0.1.	173
57	Relationship between mean ERM quotient and grain size in Chesapeake Bay	115
	sediments.	174
		- · ·

58	Distribution of diversity index values in Chesapeake Bay sediments.	176
59	Diversity, normalized by % silt/clay content, plotted as a function of the mean	
	ERM quotient for Susquehanna Flats stations.	178
60	Diversity, normalized by % silt/clay content, plotted as a function of the mean	
	ERM quotient for upper Chesapeake Bay stations.	180
61	Diversity, normalized by % silt/clay content, plotted as a function of the mean	
	ERM quotient for Tangier Sound/lower tributary stations.	181
62	Distribution of PAHs, normalized for TOC, in Chesapeake Bay sediments.	183
63	Locations of stations with Effects Range-Median quotients (ERMq) above and	
	below the regression line of Sediment Quality Triad triangular areas and mean	
	ERMq.	186
64	Benthic Index of Biotic Integrity (B_IBI) classification of benthic community	
	condition in Chesapeake Bay.	188
65	Relationship between Benthic Index of Biotic Integrity (B_IBI) and sediment	
	contaminant indicators in Chesapeake Bay.	191

## List of Acronyms

AAS	Atomic Absorption Spectroscopy
Ag	Silver
Al	Aluminum
As	Arsenic
APHA	American Public Health Association
ASTM	American Society of Testing and Materials
B[a]P	Benzo-a-pyrene
CBP	Chesapeake Bay Program
Cd	Cadmium
Cr	Chromium
Cu	Copper
EPA	Environmental Protection Agency
ERL	Effects Range - Low
ERM	Effects Range - Median
Fe	Iron
GC/ECD	Gas Chromatography/Electron Capture Detector+B9
GC/MS	Gas Chromatography/Mass Spectroscopy
gm	gram
Η'	Diversity (Shannon-Weiner)
HCH	Hexachloro-Cyclohexane
Hg	Mercury
HRGS	Human Reporter Gene System
J'	Evenness (Pileu)
km	kilometers
MDL	Method Detection Limit
mg	milligram
Mn	Manganese
MS	Matrix Spike
MSD	Matrix Spike Duplicate
Ni	Nickel
NIST	National Institute of Standards and Technology
NOAA	National Oceanographic and Atmospheric Administration
NS&T	National Status and Trends
PAH	Polynuclear Aromatic Hydrocarbon
Pb	Lead
PCA	Principal Component Analysis
PCB	Poly-Chlorinated Biphenyl
POTW	Publicaly Owned Treatment Plants

ppt	parts per thousand
Se	Selenium
SQT	Sediment Quality Triad
SRM	Standard Reference Material
TBT	Tri-Butyl-Tin
TCDD	Tetrachlorodibenzo-p-dioxin
TOC	Total Organic Carbon
TRI	Toxics Release Inventory
ug	microgram
USGS	US Geologic Survey
Zn	Zinc



NOAA ship Ferrel

#### **EXECUTIVE SUMMARY**

#### INTRODUCTION

This report summarizes the results of NOAA's sediment toxicity, chemistry, and benthic community studies in the Chesapeake Bay estuary. As part of the National Status and Trends (NS&T) Program, NOAA has conducted studies to determine the spatial extent and severity of chemical contamination and associated adverse biological effects in coastal bays and estuaries of the United States since 1991. Sediment contamination in U.S. coastal areas is a major environmental issue because of its potential toxic effects on biological resources and often, indirectly, on human health. Thus, characterizing and delineating areas of sediment contamination and toxicity and demonstrating their effect(s) on benthic living resources are viewed as important goals of coastal resource management. Benthic community studies have a history of use in regional estuarine monitoring programs and have been shown to be an effective indicator for describing the extent and magnitude of pollution impacts in estuarine ecosystems, as well as for assessing the effectiveness of management actions.

Chesapeake Bay is the largest estuarine system in the United States. Including tidal tributaries, the Bay has approximately 18,694 km of shoreline (more than the entire US West Coast). The watershed is over 165,000 km<sup>2</sup> (64,000 miles<sup>2</sup>), and includes portions of six states (Delaware, Maryland, New York, Pennsylvania, Virginia, and West Virginia) and the District of Columbia. The population of the watershed exceeds 15 million people. There are 150 rivers and streams in the Chesapeake drainage basin. Within the watershed, five major rivers - the Susquehanna, Potomac, Rappahannock, York and James - provide almost 90% of the freshwater to the Bay. The Bay receives an equal volume of water from the Atlantic Ocean.

In the upper Bay and tributaries, sediments are fine-grained silts and clays. Sediments in the middle Bay are mostly made of silts and clays derived from shoreline erosion. In the lower Bay, by contrast, the sediments are sandy. These particles come from shore erosion and inputs from the Atlantic Ocean. The introduction of European-style agriculture and large scale clearing of the watershed produced massive shifts in sediment dynamics of the Bay watershed. As early as the mid 1700s, some navigable rivers were filled in by sediment and sedimentation caused several colonial seaports to become landlocked.

Toxic contaminants enter the Bay *via* atmospheric deposition, dissolved and particulate runoff from the watershed or direct discharge. While contaminants enter the Bay from several sources, sediments accumulate many toxic contaminants and thus reveal the status of input for these constituents. In the watershed, loading estimates indicate that the major sources of contaminants are point sources, stormwater runoff, atmospheric deposition, and spills. Point sources and urban runoff in the Bay proper contribute large quantities of contaminants. Pesticide inputs to the Bay have not been quantified. Baltimore Harbor and the Elizabeth River remain among the most contaminated areas in the Unites States.

In the mainstem, deep sediment core analyses indicate that sediment accumulation rates are 2-10 times higher in the northern Bay than in the middle and lower Bay, and that sedimentation rates are 2-10 times higher than before European settlement throughout the Bay (NOAA 1998). The core samples show a decline in selected PAH compounds over the past several decades, but absolute concentrations are still 1 to 2 orders of magnitude above 'pristine' conditions. Core data also indicate that concentrations of PAHs, PCBs and, organochlorine pesticides do not demonstrate consistent trends over 25 years, but remain 10 times lower than sediments in the tributaries. In contrast, tri-butyl-tin (TBT) concentrations in the deep cores have declined significantly since it's use was severely restricted.

#### METHODS

The NS&T Program uses a stratified-random sampling design to determine the spatial extent of sediment contamination and toxicity. Chesapeake Bay was divided into sixty-five strata based on the knowledge and recommendations of scientific researchers and resource management agencies. A minimum of three sampling sites within each stratum were selected on a random basis. The focus of the sampling design was the larger open expanses of the Bay system. A total of 210 sites were sampled.

Sediment samples were taken at each site in accordance with standard methods developed by the NS&T Program. Samples were taken for toxicity bioassays, chemical contaminant analysis, and benthic community assessment. Only the upper 2-3 cm of the sediment was taken in order to

assure collection of recently deposited materials.

Amphipod mortality, sea urchin fertilization impairment, Microtox® luminesence, and cytochrome P450 Human Reporter Gene System (HRGS) tests were carried out by contract laboratories on sediment samples or extracts. A broad suite of chemicals were analyzed at each station, including 13 metals, butyl-tins, PAHs, chlorinated compounds (PCBs, chlorinated pesticides, furans and dioxins). In addition several physicochemical measures of sediment properties (*e.g.* grain size, TOC, etc.) were determined. Quantitative benthic community characterizations included enumeration of species composition and calculation of density, species richness, evenness, and diversity indices.

Correlation coefficients were calculated between all chemical, toxicological and biological metrics. Regressions were calculated to assess relationships between toxicological, community, contaminant, and habitat attributes. Regressions of toxicity, community, contaminant and habitat indices against % silt clay content were calculated and the residuals were used to assess regression relationships between them in the absence of the influence of grain size. Multivariate cluster analysis was used to group site and species data. A nodal analysis routine was then applied to those results combining the cluster analyses in a graphical array. The objective of the nodal analysis was to produce a coherent pattern of association between results for sites and species clusters. Principal component analysis (PCA) was used to group the sampling sites using benthic community, contaminant, and toxicity metrics. Calculation of a Sediment Quality Triad (SQT) index was developed to quantify impact, and results were compared to the distribution of known stressors (contamination, hypoxia).

#### RESULTS

Sediments in the tributaries tended to be muddier upstream and coarser near the mouths of the rivers, however sandbars were present in all locations. Sediments in eastern shore embayments also tended to have finer grained sediments than the mainstem. Sediments in the deep trough were uniformly fine grained depositional material. Most of the sampled locations in the Susquehanna Flats contained fine grained material.

xi

Most of the mainstem of the Bay was relatively uncontaminated. Depositional areas in the Susquehanna Flats area and the upper portions of the deep trough had higher concentrations of contaminants than the middle and lower Bay. Most tributaries had higher contaminant concentrations than the mainstem. Of the large western tributaries, the Potomac and the James Rivers showed the most elevated concentrations. Most embayments were as clean as the lower mainstem, with the exception of areas off the Gunpowder River above Baltimore, and nearshore stations in Tangier and Pocomoke Sounds, where pesticide concentrations were elevated. Virtually all of the sites comprising the top 10<sup>th</sup> percentile of contaminated sites were found in the Elizabeth River, Baltimore Harbor, and the Susquehanna Flats or the deep trough (Figure A). In the tributaries, the load of PAHs have a larger proportion of pyrogenic (e.g. combustion byproducts) compounds than in the mainstem. The distribution of metals was similar to the organic contaminants. Metals concentrations were elevated at the one station in the vicinity of Hart Miller Island. Chlorinated pesticides were found throughout the Bay. The distribution of elevated concentrations was compound specific. Concentrations of TBT in the Susquehanna flats, while elevated compared to the lower mainstem sites, were not typically as high as several of the tributary stations.

Most significant toxicity responses were from stations in the Susquehanna Flats and the tributaries, however this was test-specific. None of the amphipod bioassays yielded significant toxicity. In contrast, 73 of the sea urchin fertilization bioassays were significant. The HRGS P450 bioassay showed responses at most of the stations in the Susquehanna Flats, the deep trough, the Potomac and Elizabeth Rivers, and some other scattered sites. The spatial extent of impaired habitat (as defined by significant observed toxicity) varied widely. Based on strata areas, the spatial extent of impaired habitat ranged from zero to 30.6% depending on the selected bioassay.

A total of 20,609 organisms, representing 287 taxa were enumerated. Polychaete and oligochaete worms were the most dominant group, both in terms of organism abundance and number of taxa. Clams and snails were the next most abundant taxa, but were characterized by very high numbers of a relatively few species. The vast majority of crustaceans were amphipods. Species richness was site specific, varying considerably from one site to the next. Abundance varied by several

xii

orders of magnitude, even in adjacent sampling stations.

A pattern of species distribution appears when the data are condensed on a stratum by stratum basis. The constricted region of the Bay west of Kent Island and south of the Bay Bridge had a generally low species richness. This area is dominated by deep trough habitats and the associated low oxygen stress. There were fewer species in the western tributaries corresponding to the deep areas in the Patuxent, Potomac, and Rappahannock Rivers. The lowest values in the mainstem were from the central deep trough. The highest values were near the mouth of the Bay. Abundance by strata generally followed the same outline as species richness, but with greater variability between strata.

The community attributes of species richness, abundance, and diversity were significantly, and negatively correlated with all but one of the contaminant groups. They were also consistently negatively correlated with the bioassay results. All significant regression slopes were negative. Observed toxicity and contaminant parameters showed positive, and highly significant regression relationships. The percent silt/clay, TOC and chemical concentrations all demonstrated relatively high correlation. Using the residuals from regression of the community, toxicity, and contaminant parameters on percent silt/clay, none of the community attributes demonstrated significant regressions with the chemical contaminant indices. In contrast, species number, abundance and diversity still showed significant negative regression relationship with toxicity.

Cluster analyses resolved into nodes for 1-Susquehanna Flats, 2- the upper Bay between Baltimore and the Choptank River plus the upper reaches of the major western tributaries, 3-Tangier Sound and the lower reaches of the western tributaries, 4- sandy sites throughout the lower Bay, 5- the Bay mouth. These latter three had overlapping, but distinct community makeup. In contrast, the Susquehanna Flats node and upper Bay/upper tributary node shared fewer species, and these tended to be cosmopolitan taxa. The percent of variation explained by the PCA procedure never exceeded 5% for any single component. This was true for the entire data set and the individual nodes. However, certain patterns were discernable. The most contaminated sites in the Elizabeth River and Baltimore Harbor were separated from all other sites. The SQT calculations indicated a relationship between chemical contamination and species

xiii

diversity. Furthermore, sites that are stressed primarily by chemical contamination can be distinguished from sites with other impacts (e.g. hypoxia), but the latter sites are generally subject to multiple stressors.

#### DISCUSSION

Salinity and grain size were the primary factors which determine community distributions in the Chesapeake Bay mainstem. Each of the major western tributaries also contained distinct mesohaline and polyhaline communities that mimicked the distribution in the mainstem, although they were not physically connected and maintain themselves independently in each subsystem.

Chemical contamination and toxicity responses are more closely correlated to each other than either of these two parameters are with benthic community metrics. When viewed in detail, the benthic community does respond to contamination in measurable fashion, however, certain relationships need to be understood to clarify the relationships.

Diversity, and number of species declined with increasing chemical concentrations. This was partly due to the distribution of fine grained sediments, where elevated contaminant levels were found, and the characteristics of the resident communities in fine grained vs sandy sediments. The nodal analysis demonstrated that the resident communities found in those areas are inherently different from the areas with coarser grained sediments. However, observed toxicity increased with increasing contaminant values, and that impact cannot be ignored when evaluating community impact patterns. When viewed in terms of a habitat-specific community assemblage, as derived from the nodal analysis, biological indices indicated detectable impact of contaminants. Abundance did not decline as sharply as species numbers with increasing contaminated areas in the absence of competitors, predators, and/or indirect effects on the habitat. In the most stressed areas, all biological indices declined.

Using samples collected by NOAA, the Chesapeake Bay Program applied it's Benthic Index of Biotic Integrity (B\_IBI) calculation to the benthic community data. Since 1996, the condition of

xiv

the benthos has been considered to be degraded or marginally degraded in more than 50% of the areal extent of the Bay. Virtually all the CBP B\_IBI results from the NOAA benthic infaunal samples from the deep trough region were classified as degraded, as were most of the tributary sites. A surprising number of mainstem sites in the lower Bay were considered degraded. Conversely, most of the sites in the Susquehanna Flats area, where a large proportion of contaminated sites are found, are classified as being in good condition. The B\_IBI responds to a variety of potential stressors, especially hypoxia, but this reduces predictive power with respect to cause and effect. Response to a toxicity signal is overwhelmed by other metrics used in the index. The predominantly 'good' classification of the Susquehanna Flats stations is more problematic, and may reflect the reduced effectiveness of the B\_IBI in fresher waters

Normalizing community indices for grain size yielded a relationship between them and contaminant level. The lowest normalized diversity values were from the sites dominated by pollution tolerant species. Thus, low values of grain size normalized diversity was a consistent indicator of stressed conditions in all areas, but distinguishing contaminant stress responses from other stressors (e.g. hypoxia) may not be possible with this approach. The SQT approach does distinguish between contaminant vs other stressors, but it cannot distinguish the relative contribution of different types of stressors.

Grain size distribution also explained the variation in the distribution of contaminated and uncontaminated areas in Baltimore Harbor and the Elizabeth River. Within those systems, sandy sites did not contain contaminants at levels as high as those found at the muddy sites. TOC normalized PAH data illustrates that all Elizabeth River and the Baltimore Harbor sites had elevated PAH concentrations relative to most other areas. Normalized concentrations in the deep trough were relatively low away from the mouths of tributaries, but concentrations in the Susquehanna Flats were not. Normalization for grain size yielded a similar picture for metals. Thus loading rates (and/or residual deposits) in the Elizabeth River and in the vicinity of Baltimore Harbor and the Susquehanna River are elevated.

Previous studies in Baltimore Harbor demonstrate steep gradients in contaminant concentrations from the heads of the various tributaries down into the Patapsco subestuary (Baker *et. al.* 1997).

X۷

Concentrations reported in this NS&T study were considerably lower than what has been reported at locations upstream in the Patapsco system. In previous studies of the Elizabeth River, contaminant concentrations were also seen to be highly variable on a site specific basis due to a combination of historical sources of pollution and sediment characteristics. The Eastern Branch contaminant concentrations were as high, if not higher, than the Southern Branch even though the Eastern Branch is primarily residential along the shoreline of the upper reaches.

The Hart Miller Island containment facility is the repository for dredge spoil from Baltimore Harbor and approach channels. The single NS&T station in the Hart Miller Island area showed elevated metals levels relative to the surrounding area. Even after grain size normalization, the station demonstrated higher concentrations of metals relative to other stations.

The distribution of high and low weight PAHs, and the degree of alkylation indicated a pyrogenic source for the high molecular weight PAHs. The low molecular weight PAHs are likely a mixture of pyrogenic sources and fuel spills. The median concentration of PAHs in the tributaries was five times that found in the mainstem or embayments.

The mass of various contaminants in the upper 10 cm of sediment for different depositional compartments of the Chesapeake Bay mainstem were calculated (Table A). The northern portion of the Bay, including Susquehanna Flats, the Patapsco, and Chester Rivers contain a much higher reservoir of contaminants than other areas. On an areal basis however, the concentrations found in the deep trough were comparable. In contrast, Tangier Sound contained vastly less contamination than Susquehanna Flats. The Elizabeth River, although relatively small in size contained significant quantities of contaminants. The concentrations of PAHs were an order of magnitude higher in the Elizabeth River than any other region. Average metal concentrations were found in the Elizabeth River at concentrations comparable to those in the northern region of the Bay. The areas in Hampton Roads and Norfolk cannot be compared in the same way because the sediments are sandy. While industrial, and shipping-related activity is intense, sediment in Hampton Roads were not as contaminated as one might presume because it is not a depositional environment, and it is well flushed.

xvi

Relative to background values, the Chesapeake is enriched for most elements even in the relatively clean area of Tangier sound. This is due to the depositional nature of an estuary. Enrichment in the Susquehanna Flats exceeded Tangier Sound for every element except Cr. Enrichment levels in Elizabeth River were low for As, Cr, and Ni, but higher for all the others. Enrichment of Se and Hg were especially high. The single muddy site in Baltimore Harbor (# 23) showed the highest enrichment rates of any location in the Bay. The Elizabeth River was also contaminated with metals, but not to the same concentrations as the Patapsco.



Figure A. Distribution of sites in the top  $10^{th}$  percentile of contaminant concentration.

Region	Northern Bay 1-9		Deep Trough 11,14,19		Tangier Sound 33-40		Elizabeth River 62-64	
Strata								
Area (km <sup>2</sup> )	1135.0		333.5		1174.1		14.9	
		kg/km <sup>2</sup>	kg	kg/km <sup>2</sup>	kg	kg/km <sup>2</sup>	kg	kg/km <sup>2</sup>
РАН	219,415	193	44,845	134	50,017	43	16,420	1,100
PCB	1,667	1	326	1	716	1	89	6
DDT kg	454	0.4	35	0.1	145	0.1	42	3
Chlordanes	113	0.1	14	0.04	77	0.07	12	1
As	1,738,872	1,532	642,942	1,928	758,368	646	21,283	1,426
Cd	82,798	73	25,243	76	23,106	20	1,047	70
Cr	12,006,975	10,579	3,850,546	11,545	5,341,199	4,549	115,201	7,717
Cu	5,579,045	4,915	1,580,890	4,740	1,456,042	1,240	126,507	8,474
Pb	6,599,546	5,814	1,887,153	5,658	2,300,265	1,959	102,645	6,876
Hg	23,165	20	5,063	15	3,661	3	560	38
Ag	58,803	52	13,067	39	6,295	5	620	42
Ni	7,555,691	6,657	1,910,015	5,727	2,232,902	1,902	46,254	3,098
Se	128,775	113	48,571	146	56,465	48	2,605	174
Zn	32,824,582	28,920	9,613,109	28,824	9,056,296	7,713	502,461	33,657

Table A. Total mass and kg/km<sup>2</sup> of contaminants in sediments in selected regions of Chesapeake Bay.

#### **INTRODUCTION**

This report summarizes the results of NOAA's sediment toxicity, chemistry, and benthic community studies in the Chesapeake Bay estuary. As part of the National Status and Trends (NS&T) Program, NOAA conducts studies to determine the spatial extent and severity of chemical contamination and associated adverse biological effects in coastal bays and estuaries of the United States. This program encompasses a broad spectrum of research and monitoring studies to evaluate sediment contamination and toxicity in U.S. coastal waters, including the long-term, nationwide monitoring of contaminant concentrations in sediments and bivalves; sediment toxicity assessments in specific coastal areas; the evaluation and application of biomarkers; and the development of ecological indices (Turgeon et al., 1998). The National Status and Trends Program has conducted sediment toxicity assessment studies in coastal water bodies since 1991. Results from previous NS&T sediment toxicity studies in over 20 coastal waters and estuaries have been published (Long et al., 1996; Turgeon et al., 1998; Long, 2000a). Regions for sediment toxicity assessment studies are selected based on a variety of parameters, including: (1) concentrations of contamination in oysters or mussels as determined by NOAA's NS&T Mussel Watch Program; (2) the likelihood of adverse biological effects of contamination based on state and local environmental data; and (3) collaboration with other Federal, state, and local agencies, and academic institutions.

Sediment contamination in U.S. coastal areas is a major environmental issue because of its potential toxic effects on biological resources and often, indirectly, on human health. A large variety of contaminants from industrial, agricultural, urban, and maritime activities are associated with bottom sediments, including synthetic organic chemicals, polycyclic aromatic hydrocarbons (PAHs), and trace elements.

Critical habitats and food chains supporting many estuarine fish and wildlife species involve the benthic environment. Contaminants in the sediments often pose both ecological and humanhealth risks through degraded habitats, loss of fauna, biomagnification of contaminants in the coastal ecosystem, and human consumption of contaminated fish and wildlife. In many instances, fish consumption advisories are coincident with severely degraded sediments in

coastal water bodies. Thus, characterizing and delineating areas of sediment contamination and toxicity are viewed as important goals of coastal resource management.

Macrobenthic organisms play an important role in the estuarine environment. As secondary consumers in the estuarine ecosystem, they represent an important link between primary producers and higher trophic levels for both planktonic and detritus-based food webs. They are a particularly important food source for juvenile fish and crustaceans. Macrobenthic filter feeding activities can remove large amounts of particulate material from the water, especially in shallow (<10 m) estuaries, improving water quality by increasing water clarity and limiting phytoplankton production. Benthic assemblages are composed of diverse taxa with a variety of reproductive modes, feeding guilds, life history characteristics, and physiological tolerances to environmental stressors, both natural and anthropogenic. Responses of some species (e.g., organisms that burrow in or feed on sediments) are indicative of changes in sediment quality. Benthic species composition, abundance, and biomass also are influenced by habitat conditions including salinity and sediment type. Distributions of benthic organisms, however, are predictable along estuarine gradients and are characterized by similar groups of species over broad latitudinal ranges. Information on changes in benthic population and community parameters due to habitat characteristics can be useful for separating natural variation from changes associated with human activities. Furthermore, most benthic species have limited mobility and cannot physically avoid stressful environmental conditions. Benthic assemblages thus cannot avoid and must respond to a variety of stressors such as toxic contamination, eutrophication, sediment quality, habitat modification, and seasonal weather changes. Benthic community studies have a history of use in regional estuarine monitoring programs and have been proven to serve as an effective indicator for describing the extent and magnitude of pollution impacts in estuarine ecosystems, as well as for assessing the effectiveness of management actions Llanso et al., 2004; Long et al., 1995).

NOAA uses a suite of sediment toxicity tests to assess different modes of contaminant exposure (bulk sediment, sediment porewater, and chemical extracts of contaminants from sediment) to a variety of species (invertebrates, bacteria, and vertebrate cells) and different assessment endpoints (i.e., mortality, impaired reproduction, physiological stress, and enzymatic response).

Since the test results are not necessarily axiomatic and biological effects of contaminants occur at different levels of biological organization, i.e., from cells to ecosystems, results from a suite of toxicity tests are used in the "weight of evidence" context to infer the incidence and severity of environmental toxicity (Chapman, 1996). Typically, the amphipod mortality bioassay, the sea urchin fertilization impairment bioassay, the Microtox<sup>TM</sup> test, and, in recent years, a Human Reporter Gene System (HRGS) test are used in each study area. Other tests, based on promising new techniques, e.g. full life-cycle tests, and genotoxicity, have also been used in some areas on a trial basis or in response to a specific information need. The overall purpose of this study was to characterize the environmental conditions in the Chesapeake Bay mainstem and major tributaries in terms of sediment contamination and associated adverse biological effects. The objectives were to determine the incidence and degree of surficial sediment toxicity; determine the spatial patterns or gradients in chemical contamination and toxicity; and determine the association among measures of sediment contamination, toxicity and the benthic macroinvertebrate community structure.



Chesapeake Bay Bridge

#### SITE DESCRIPTION

Chesapeake Bay is the largest estuarine system in the United States. The mainstem is approximately 320 km long, from Havre de Grace, Maryland, south to Norfolk, Virginia. It varies in width from about 5.4 km near Aberdeen, Maryland, to 56 km at its widest point, near the mouth of the Potomac River. The surface area of the Bay and its tidal tributaries is approximately 10,643  $\text{km}^2$  (4,109 miles<sup>2</sup>). The tidal portion of the Potomac River sub-estuary by itself is as large as the entire San Francisco Bay system. The volume of the Bay is over 74 billion cubic meters. Including tidal tributaries, the Bay has approximately 18,694 km of shoreline (more than the entire US West Coast). The watershed is over 165,000 km<sup>2</sup> (64,000 miles<sup>2</sup>), and includes portions of six states (Delaware, Maryland, New York, Pennsylvania, Virginia, and West Virginia) and the District of Columbia. The population of the watershed exceeds 15 million people. The Bay is relatively shallow. Average depth, including all tidal tributaries, is about 6.4 m with a few deep troughs that reach 53 m in depth. The surface area of the submerged bottom is only 0.007% larger than the surface area of the water. The deep troughs that run along much of the length of the Bay are remnants of the ancient Susquehanna River channel eroded during glacial periods of Pleistocene age. The Bay assumed its present dimensions about 3,000 years ago from a complex array of drowned river valleys at the end of the last ice age (Fig. 1). The convergence of the major Virginia tributaries with the Susquehanna are believed to be a result of land subsidence due to an Eocene epoch meteor strike near the tip of the Delmarva Peninsula (Poag, 1997). This is why the James and York Rivers turn northeast near their mouths to join the ancient Susquehanna channel. There are 150 rivers and streams in the Chesapeake drainage basin. At the northern end of the Chesapeake, the Susquehanna River provides about 50% of the freshwater coming into the Bay. Within the watershed, five major rivers - the Susquehanna, Potomac, Rappahannock, York and James-provide almost 90% of the freshwater to the Bay. The Bay receives an equal volume of water from the Atlantic Ocean. The Bay's salinity ranges from freshwater (0-0.5 parts per thousand or ppt) near the Susquehanna River to nearly oceanic (30-35 ppt) at the Chesapeake's mouth.

Water circulation is driven primarily by the movements of freshwater from the north and saltwater from the south. The warmer, lighter freshwater flows seaward over a layer of saltier



Figure 1. The Chesapeake Bay system.

and denser water flowing upstream on the bottom. The volumes of these water masses are roughly equal over time (Schubel and Prichard, 1986). The opposing movement of these two flows forms saltwater fronts or gradients that move up and down the Bay in response to the input of freshwater. These fronts are characterized by intensive mixing. Stratification varies within any season depending on rainfall and winds. Stratification is usually highest in the spring as the amount of freshwater in the Bay increases due to snow melt and frequent rain. Stratification is maintained throughout summer due to the warming of surface waters. This is significant for the benthic habitat because stratification and the concomitant algal blooms in the surface waters result in hypoxia in the deeper areas as a consequence of remineralization of organic matter as it sinks. This is particularly severe in the deep trough regions of the upper Bay. This phenomenon is exacerbated by the presence of Rappahannock shoals which can act as a hydraulic control point in the mainstem, and cuts off upstream-flowing bottom water (Chao and Paluszkiewicz, 1991). Hypoxia and anoxia have continued to be an increasing problem in the Bay over several decades. During summer, the deep parts of some tributaries like the Patuxent, Potomac, and Rappahannock rivers become anoxic. The benthic community in the deep reaches of the mainstem, and the shoulders of the channels have become progressively depauperate. Winds can tilt the pycnocline laterally causing deep water to overflow sills at the mouths of tributaries or into depressions, introducing salty, low oxygen waters into the mouths of the sub-estuaries (Sanford and Boicourt, 1990). These pools of water may be trapped behind the sills introducing long term hypoxic conditions on the bottom.

While the Chesapeake is often referred to as a classic two-layered salt wedge estuary, salinity can vary widely, both seasonally and from place to place and year to year, depending on local conditions. Because the greatest volume of freshwater enters the Bay from northern and western tributaries, isohalines tend to show a southwest to northeast tilt. The Bay is large enough that the Coriolis effect can be seen, which deflects fresh water flowing down the Bay to the west and saltier ocean water moving up the Bay toward the eastern shore. Winds can disrupt or reinforce this two-layered flow. Wind can raise or lower the level of surface waters and occasionally reverse the direction of flow. Strong northwest winds, associated with high pressure areas, push water away from the Atlantic Coast, creating exceptionally low tides. Strong northeast winds, associated with low pressure areas, produce exceptionally high tides. Because the Bay is so

shallow, its heat capacity is relatively small. Water temperature fluctuates throughout the year, ranging from 1 to 29° C. In autumn, fresher surface waters cool faster than deeper waters and sink. Vertical mixing of the two water layers occurs rapidly, usually overnight. During the winter, water temperature and salinity are relatively constant from surface to bottom.

Tidal currents are also significant forces moving water and sediments. Because the Bay is long enough to contain the entire wavelength of the tidal cycle within itself (Boicourt *et al.*, 1999), and frictional interaction with the bottom results in time lags with depth, the current velocity structure within the Bay as a whole is very complex. In addition, internal seiches appear to be a significant parameter in Bay circulation. Finally, plumes and convergence zones from the tributaries interact with all of these phenomena at small and large scales and impact biogeochemical transformations and biological productivity in the water column and on the bottom.

Different sources of freshwater that enter the Bay have different characteristics, depending on the geology of the watershed from which they originate. The watershed includes the Atlantic Coastal Plain, the Piedmont and the Appalachian Mountains. The Atlantic Coastal Plain is a flat lowland area with a maximum elevation of about 90 m. It is underlain by crystalline rock, covered primarily with marine sedimentary deposits of relatively unconsolidated sand, clay and gravel that dip in southeasterly layers. The Coastal Plain extends to the fall line 25 to 145 km west of the Bay. The fall line is the geologic boundary between the Piedmont and the Coastal Plain that runs along the east coast from New York City to Georgia. Ground elevation rises abruptly to over 300 m. The base of the fall line is also the head of tidal influence. A line of cities including Richmond, Va., Fredricksburg Va., the District of Columbia, and Baltimore, Md. developed along the fall line to take advantage of the hydro power provided by water falls (thus the fall line). Since colonial ships could not sail past the fall line, cargo would be transferred to canals or overland shipping. Cities along the fall line became important areas for commerce and grew into major population centers. In the north, the Piedmont is divided into two geologically distinct regions (CBP, 2005). The types of rock found in the east include slates, schists, marble and granite. These are relatively impermeable, and water flowing from the eastern side is soft, low in calcium and magnesium. In contrast, the western side consists of sandstones, shales and

siltstones, underlain by limestone. This limestone bedrock contributes calcium and magnesium to its water, making it hard water. Water from the western side flow into the Potomac River. The southern tributaries in Virginia cut across the entire width of the Piedmont to the foothills of the Appalachians. The Appalachian Province lies in the western and northern parts of the watershed. Sandstone, siltstone, shale and limestone form the bedrock. These areas are characterized by mountains and valleys with high stream flow rates and seasonal flash flooding. Water from this province flows to the Bay mainly via the Susquehanna River and the upper Potomac, including the Shenandoah Valley to the south.

The waters of the Chesapeake and its tributaries transport huge quantities of sediment from the watersheds. For example, the annual load of suspended sediment delivered to the Bay from the Susquehanna River alone was calculated to be over 1.9 million metric tons (CBP, 1996). Export of sediment from tributaries to the mainstem of the Bay is a complex process. Some researchers suggest that much of the sediment transported by the major tidal tributaries is deposited in the tributaries. Others have suggested substantially more sediment is exported out of tributaries and into the Bay during extreme weather events or sustained periods of high freshwater inflow, when a substantial amount of sediment can be exported into the mainstem of the Bay (Langland and Cronin, 2003). Sediment transport is of critical importance in understanding the sources and sinks of contaminant distribution within the Bay system. The long term fate of many contaminants, and restoration of managed habitats will be influenced by natural processes over which we have little control.

In the upper Bay and tributaries, sediments are fine-grained silts and clays that are carried long distances in the fresh, upper layer of water. As they move into the Bay and water velocities slow, the particles slowly descend into the denser saline layer. Here, the particles may reverse direction and flow back up toward tidal tributaries with the lower layer of water. As the upstream flow decreases and as flocculation occurs, the sediments settle to the bottom. The mainstem and the major tributaries each contain a maximum turbidity zone feature at the nexus of the freshwater flow and saltwater estuary.

Sediments in the middle Bay are mostly made of silts and clays derived from shoreline erosion. In the lower Bay, by contrast, the sediments are sandy. These particles come from shore erosion and inputs from the Atlantic Ocean. These sediments settle fairly rapidly, remain near their original source and are less likely to be resuspended than finer sediments. The introduction of European-style agriculture and large scale clearing of the watershed produced massive shifts in sediment dynamics of the Bay watershed. By the mid 1700s, some navigable rivers were filled in by sediment. Sedimentation caused several colonial seaports, like Port Tobacco, Maryland, to become landlocked. Joppatown, Maryland, once a seaport, is now more than two miles from open water.

Toxic contaminants enter the Bay via atmospheric deposition, dissolved and particulate runoff from the watershed or direct discharge. Groundwater inputs are largely unexplored. While contaminants enter via the water or air, sediments accumulate most toxic contaminants and thus reveal the current status of input for most of the important constituents. Exceptions to this generalization include highly water soluble materials, such as certain metals and some pesticides (e.g., triazines). With an understanding of physical and chemical sediment dynamics, the history of contaminant loading over time can be evaluated. The utility of historical comparisons is in the evaluation of progress in controlling contaminant releases to the Bay.

#### SITE CONDITIONS

**Tributaries-** The Maryland sediment monitoring program analyzed surficial sediment from 30+ tributary locations annually. The data demonstrates a general trend of higher to lower concentrations of trace metals from the northern and western tributaries toward the southern and Eastern Shore tributaries and bays (Eskin *et al.*, 1996). One exception to this pattern is for cadmium, which shows higher concentrations in the Patuxent River and certain south-eastern tributaries. Since 1986, the general trends in concentrations have been static or decreasing, with some site-specific exceptions. However, this is a relatively short time interval with which to assess temporal trends. Data from more limited spatial scales, but covering decadal time scales, and analysis of sediment cores, which may cover up to hundreds of years, show a general decline in recent sediment metals concentrations. On a Bay-wide basis, peak concentrations were seen in the 1970s and '80s, followed by subsequent declines (CBP, 1994). Declines to pristine conditions

have not been achieved. Trends in oyster tissue concentrations also show a general decline in arsenic, cadmium, mercury and zinc from the 1970s and early 1980s (CBP, 1994). Organic contaminant analyses show a similar trend of higher to lower concentrations from northwest to southeast, but the current data base is inadequate for assessment of short term trends. Bieri *et al.* (1982) reported that sediment contaminant concentrations at the mouths of the Patuxent, Potomac, Rappahannock, York , and James Rivers were generally higher than concentrations seen in the Eastern Shore, particularly the lower Eastern Shore, or mainstem locations. Mainstem sediment core samples show a decline in selected PAH compounds over the past several decades, but absolute concentrations are still one to two orders of magnitude above 'pristine' conditions (CBP, 1994).

The NS&T Program has derived a series of numerical sediment quality guidelines for a variety of chemicals (9 metals, 11 PAHs, 8 persistent chlorinated pesticides, and PCBs) based on empirical data from laboratory and field studies (Long and Morgan, 1990; Long *et al.*, 1995). The ERM guideline (Effects Range Median) is that concentration at which acutely toxic impacts are observed in at least 50% of cases, and is considered the threshold concentration, above which toxic effects are predicted to be seen in the field. The ERL (Effects Range Low) is the 10th percentile concentration where effects were measured, and is considered the lower threshold concentration, above which toxic effects might begin to be seen in the field.

In the Maryland sediment monitoring data base, ERLs are exceeded for most of the PAHs and chlordane, total DDTs, and dieldrin in selected tributaries. The Magothy and Severn Rivers were consistently in this group, as well as sporadic exceedances in the Middle, South, West/Rhode and, Northeast Rivers. None of the observed concentrations approach ERM levels in magnitude. Eastern Shore tributaries and embayments generally do not exceed ERLs for any constituent. A 1991 sample from the Sassafrass River showed high concentrations of PAHs, but subsequent sampling at that location has never demonstrated similar results, which was most likely either a spurious sample, or a local spill. Metal concentrations comparisons are not possible because the guidelines are based on 'total' concentrations, but the sediment data base contains only 'recoverable' metal concentrations (see below).

Baltimore Harbor remains one of the most contaminated locations in the country (NOAA, 1994). Sediment concentrations at the Ft. McHenry station are in the top 10<sup>th</sup> percentile nationwide for toxic metals, chlordane, PCBs, and PAHs. Patapsco River sediments exceed the ERMs for PCBs, chlordane, zinc, lead and chromium. Stations at Bodkin Point., Mountain Point Bar (Magothy River) and, Hackett Point. Bar (Severn River) are generally at or above the 75<sup>th</sup> percentile nationwide. Two stations in the Potomac River, at Swan Point. and Mattox Creek. also show metals levels at or above the 75<sup>th</sup> percentile range. At Norfolk, in the southern portion of the Bay, the Elizabeth River is also heavily contaminated with metals and organic contaminants. Concentrations are at or above the 75<sup>th</sup> percentile rank for 8 of 10 constituents, including being one of only a handful of places in the nation that exceeds the ERM for PAHs. Other areas of the lower James River (e.g. Willoughby Bay, Newport News) have also been observed to contain toxic sediments. Further up the James River, extensive contaminant data are lacking, but the river still has health advisories due to historical Kepone contamination.

**Mainstem-** Deep sediment core analyses indicate that mainstem sediment accumulation rates are 2-10 times higher in the northern Bay than in the middle and lower Bay, and that sedimentation rates are 2-10 times higher than before European settlement throughout the Bay (NOAA, 1998). Sedimentation rates are primarily storm driven, and have not declined significantly in recent times. Toxic metal enrichment rates (concentrations above background) of sediment depositing in the northern Bay are higher than those in the middle and lower Bay. Metals enrichment rates peaked in the early 1980s and have declined since then. However, enrichment rates are still elevated in the northern Bay for manganese, nickel, chromium and lead by factors of 1.5-2X (NOAA, 1998). Enrichment rates for copper and zinc are elevated by factors of 1.5-3.5X throughout the Bay, indicating wider dispersion mechanisms (e.g., atmospheric deposition, sediment/water column exchange). A US Geologic Survey (USGS) study of river-borne input arrived at similar enrichment rates for particulate material delivered to the Bay from the Susquehanna River, but also calculated an enrichment rate of 110X for cadmium (CBP, 1996). The deep core data indicated that concentrations of PAHs, PCBs and, organochlorine compounds do not demonstrate consistent trends over 25 years, but remain 10 times lower than sediments in the tributaries. In contrast, butyl-tins (TBT) concentrations in the deep cores have declined significantly since it's use was severely restricted.

Contaminant Loadings - A USGS study of contaminant loading rates at the fall line of major rivers to the Bay (CBP, 1996) concluded that the bulk of toxic contaminants was delivered to the Bay in particulate form (suspended sediment, algae, etc.) as opposed to dissolved in the water column. On a volume basis, the largest loadings are delivered by the Susquehanna River. The Susquehanna, Potomac, and James Rivers account for 99% of total Bay-wide loads derived from the watershed above the fall line. This does not include sources below the fall line (e.g., Baltimore and Norfolk Harbors, shoreline erosion, atmospheric deposition, etc.). The watersheds' yield of organic contaminants was highest for organophosphate-type pesticides, followed by PAHs, organochlorine pesticides, and PCBs. On the Eastern Shore, the Choptank and Nanticoke watershed loads are higher for many pesticides, cadmium, iron, manganese, nickel, lead and zinc than western shore tributaries when calculated on a per acre yield basis. This was the case for spring runoff, but not in the fall season. Clearly, some combination of geochemistry and land use practices contribute to this circumstance. Comparable data for other Eastern Shore rivers have not been generated. The 1994 basinwide toxics reduction strategy revaluation report (CBP, 1994) estimated that in addition to input at the fall line, point sources and urban runoff were the other major sources of toxic metals. The most significant sources of organic contaminants were urban runoff, atmospheric deposition and coastal plain point sources in addition to inputs at the fall line.

Current-use pesticide loading is a difficult parameter to estimate. Except for targeted studies, or monitoring related to drinking water quality, most non-persistent pesticides are not analyzed for on a routine basis. Except for farm fields directly adjacent to estuarine waters, agricultural pesticides are introduced into the Bay via freshwater input, where the largest environmental impacts would be expected to occur. Excluding wood preservation operations (using chromated copper arsenate) nearly 2.95 million kg (6.5 million pounds) of pesticide <u>active ingredient</u> was applied to the watershed in Maryland alone in 2000 (MDA, 2002), mostly in agricultural applications. This does not account for all pesticides applied by private agricultural operators, but does include some use by commercial applicators in urban settings. The ultimate load of pesticides actually delivered to the Bay from these applications is unknown. Pesticides are subject to variable rates of degradation and permanent deposition en route to the Bay. Urban-use
pesticide loads (turf management, termiticides, etc.) have proven difficult to quantify. A total application of 524,565 kg (1,154,042 lbs) of active ingredient in anti-foulants was also reported in 1994, most of which would presumably have been applied to boat hulls.

The EPA Toxics Release Inventory (TRI ) tracks trends in releases of certain toxic chemicals from selected industries. Since 1989, data from within the Chesapeake Bay basin has reflected overall declines in chemical releases. As with pesticide applications, a release in the watershed is not necessarily equivalent to a loading directly to the Bay. Direct loadings to the Bay from industrial and Publicly Owned Treatment Plants (POTW) point source discharges have shown declines (CBP, 1994). Releases to the air have not shown proportional declines, and may account for substantial loading of selected contaminants to the Bay via direct rainfall and stormwater runoff. In spite of progress in direct discharge reductions in the Patapsco River, over the 5-year period from 1990 through 1994, 1,058,692 kg (2,329,123 lbs) of toxic contaminants have been discharged into the water, including 345,000 kg (759,000 lbs) of metals to Old Road Bay alone (EWG, 1997).

Interpretation of the current and historical contamination patterns are complicated by technical advances in analytical chemistry over time and differing methods employed by various monitoring and research programs. The ability to detect ever smaller concentrations of chemicals improves accuracy, but it is difficult to assess trends when older data had detection limits above currently detectable concentrations. Non-detects may have been arbitrarily assigned a value of zero, the detection limit, or in some instances ½ the reported detection limit. These benchmarks may have changed several times over a decade as methods improved. This problem also applies to other parameters such as calculating changes in loading rates.

Different monitoring and assessment programs have used different analytical procedures which yield incompatible results. Chemical and geological evaluations of trace metals use analytical methods that measure the 'total' amount of each metal, including the elemental content of the minerals that make up the sediment particles. This yields data on the absolute content of an environment, which is necessary to evaluate real loadings to the ecosystem. Biological evaluations tend to only measure the 'recoverable' metals; that portion which is readily available

to organisms. This approach yields data that are useful for evaluating impacts on living resources. The two sets of numbers are useful for different applications, but they are not interchangeable.

Comparison of sediment chemical concentration data from different locations or time frames is only valid if the data are 'normalized' for physical sediment characteristics. For example, sediments with high amounts of organic matter will tend to accumulate higher concentrations of organic contaminants, such as PAHs (Di Toro and De Rosa, 1998). Thus, concentrations of organic contaminants should be adjusted for the relative bulk of organic matter in a given sediment sample. Similarly, metals tend to accumulate in fine grained sediment (silt and clay) more so than in coarse grained sediment (sand), and metals' concentrations should be normalized to mean grain size (Hanson *et al.*, 1993). It is these corrections for the bias introduced by the physical background which allows for comparisons, over space and through time, of the underlying contaminant distribution pattern.

For most contaminants, sediment concentrations are a useful indicator of the effectiveness of pollution control strategies, including releases of toxic chemicals. However, the location and concentration of contaminants in sediments are a product of both loading to the Bay and the geophysical properties of sediments. For example, there is a gradient of increasing grain size from north to south in the Bay. Fine grained sediments are found in depositional areas. Fine grained sediments also tend to have higher organic content for a variety of reasons. Fine grained, organically rich sediments, will accumulate higher concentrations of metallic and organic contaminants. Since they are found in depositional zones, they tend to accumulate unless a large storm surge resuspends them. Thus, loadings to the upper Bay, from any source, will tend to remain there longer than the same loading in the lower Bay. It is the relative dynamic between accumulation rate and sediment loss rate that will drive the distribution pattern. In addition, the accumulation rate is a product of chemical delivery and degradation rates, as well as biological recycling and bioconcentration processes.

Presumably, most of the contaminants found in the mainstem were not originally introduced there, they were transported there. Gradients of contaminant concentration may indicate where

the actual source of a contaminant is. More soluble contaminants and airborne contaminants tend to have a more uniform distribution than sediment-bound chemicals. Every contaminant has it's own characteristic affinity for water vs. sediment. The uniformity or concentration of a chemical's distribution is therefore a product of both the loading rate and it's mobility in the environment, as mediated by the sediment transport processes noted above.

# **BIOLOGICAL ASSESSMENTS**

**Ambient Toxicity-** To assess contaminant impacts on living resources in the estuarine tributaries of the Bay, a variety of ambient toxicity tests have been performed (Hall and Alden, 1997; Hartwell *et al.*, 1995a, 1995b, 1997; Pinkney *et al.*, 1991, 2005; Roberts *et al.*, 2001; Wright *et al.*, 1989). One of the basic assumptions of the ambient toxicity approach is that bioassays will identify areas where contamination is of biological significance, whereas scans of standard chemical contaminants may not predict biological significance due to omitted chemicals and lack of knowledge on synergistic effects. All of the above referenced studies have avoided testing in the mixing zones of known discharges. Toxic impacts have been seen primarily, but not exclusively, in the sediment, as opposed to the water column. Lethal and/or sublethal conditions have been observed in the Potomac, Patuxent, South, Severn, Magothy, Patapsco, Rock, Chester, Wye, and James Rivers. Data from four independent labs have shown that virtually every test location in the Patapsco River system is acutely toxic to some or all test species. Toxicity gradients have been seen in the South, Magothy and Chester Rivers. In larger systems such as the Potomac and Patuxent Rivers, impacted zones appear to be separated by relatively clean areas. None of these studies dealt with the Chesapeake Bay mainstem.

There is no single class of chemicals which explain these data. In the absence of compelling evidence, it must be assumed that the combined effect of a multitude of measured and unmeasured chemical contaminants are the cause of such widespread toxicity. Clear relationships exist between trends in mortality levels and trends in cumulative chemical concentrations, as has been observed in other locations in the nation (Long, 2000b). Mortality from toxic contaminants has not been observed in the Middle, Sassafras, Choptank, Nanticoke, Rappahannock, or York Rivers but other parameters (e.g. pH) have been implicated in selected tributaries (Uphoff, 1989; Secor and Houde, 1998).

**Benthic community assessment-** The Chesapeake Bay Program (CBP), in conjunction with the States of Maryland and Virginia, has established sampling sites throughout the Bay to monitor the condition of the benthic community. While the major focus of the Bay Program is nutrients and the condition of the tributaries, the benthic assessment program has included permanent sites in the mainstem and the tidal tributaries for trend analysis since 1985, and randomly chosen sites in a stratified sampling pattern, similar to NS&T. Since 1996, the condition of the benthos has been considered to be degraded or marginally degraded in approximately 50% of the areal extent of the Bay (Llanso *et al.*, 2004). Most of the locations considered to be degraded are in tidal tributary areas or the deep trough. Most of the fixed sites do not demonstrate any long term trends, either improving or degrading, especially in the mainstem. The benthic community condition may respond to a variety of environmental factors such as eutrophication, sedimentation, climate change, etc. in addition to contaminant impacts.



Sampler deployment, York R., Va.

#### **METHODS**

# SAMPLING DESIGN

NOAA uses a stratified-random design for selection of sampling sites to determine the spatial extent of sediment toxicity in US coastal waters. One of the design principles is to apply the same suite of tests synoptically to all areas so that comparisons can be made without the confounding interference of using different methods in different areas. Thus, comparison of spatial extent of impact between areas is possible even if the areas are not contiguous. Chesapeake Bay was divided into sixty-five strata. Strata boundaries were developed in conjunction with regional scientists and resource mangers, and were intended to enclose relatively uniform habitats within each stratum. Strata boundaries were established based on bathymetric, hydrographic, regional environmental considerations, and previous studies detailing geochemical reservoirs, sediment grain size distribution, hydrographic model results, organic carbon maps, distribution patterns of benthic fauna, occurrence of seasonally anoxic conditions, and regional contamination databases indicating potential problem areas. Based on background data, large strata were established in the open waters of the bay where topographic features and oceanographic conditions were relatively uniform and toxicant concentrations were expected to be low. In contrast, smaller strata were established in tributaries and specific areas near suspected sources of contamination or where environmental conditions were expected to be heterogeneous or transitional, especially channels. The larger western tributaries were sampled well up into the sub-estuaries, but smaller tributaries were not thoroughly sampled beyond the embayments into which they empty. The focus of the sampling design was the larger open expanses of the Bay system. The tributaries and tidal-fresh portions of the system have been adequately assessed byongoing State and regional programs (Hall and Alden, 1997; Hartwell et al., 1995b, 1997; McGee et al., 2001; Pinkney et al., 1991, 2005; Wright et al., 1989).

A minimum of three sampling sites were selected on a random basis within each stratum. This sampling strategy allows some control of spacing of samples in the study area and combines the strengths of a stratified design with the random-probabilistic selection of sampling locations. This allows the data generated within each stratum to be attributed to the dimensions of that stratum with a quantifiable degree of confidence (Heimbuch *et al.*, 1995). Two alternate sites

were also selected for each primary sampling site. In instances where the primary site could not be sampled due to accessibility or an unsuitable substratum, the next sequential alternate site was sampled. Examples of reasons for not sampling the primary sites included the site being too shallow, manmade obstructions, hard bottom, or there was no dredging or anchoring allowed in the area.

This sampling approach, is geographically comprehensive but does not account for temporal variability. Due to the size of the Chesapeake Bay system and the large number of requisite sample sites, sampling was conducted in three phases. The northern (63 sites, Fig. 2) and middle (69 sites, Fig. 3) portions of the system were sampled during August and September of 1998 and 1999 respectively. Seventy nine sites in the southern reaches were sampled in September of 2001 (Fig. 4). Sampling was conducted during the late summer period when much of the benthic fauna are at the peak of seasonal development, and inter-annual variability is likely to be low. No sites were sampled in more than one year of the project. Specific sample locations are listed in Appendix A.

#### FIELD SAMPLING PROCEDURES

Two sediment samples were taken at each site in addition to salinity, temperature, and oxygen readings at the surface and bottom of the water column. Samples were collected on board the NOAA ship FERREL or from her launch in shallow water. A total of 210 sites were sampled. Site #165 and all its alternates were inaccessible.

Toxicity and chemistry samples were collected with a Kynar-coated 0.1m2 Young-modified Van Veen grab sampler. Sampling gear was initially washed with soap, rinsed with deionized water, rinsed with acetone, followed by an acid wash with 10% hydrochloric acid and again rinsed with deionized water. At each site, the sampler was rinsed with acetone and deionized water immediately prior to sampling. Only the upper 2-3 cm of the sediment was used in order to assure collection of recently deposited materials. A sediment sample was discarded if the jaws of the grab were open, the sample was partly washed out, or if the sediment sample in the grab was less than 5 cm deep. Sediments were removed with a scoop made of high-impact styrene. Sediment was composited in an acetone rinsed, high-density polyethylene (HDPE) bucket.



Figure 2. Map of upper Chesapeake Bay showing strata boundaries and sampling sites



Figure 3. Map of central Chesapeake Bay showing strata boundaries and sample sites.



Figure 4. Map of lower Chesapeake Bay showing strata boundaries and sampling sites. Strata 53-55 were the south, channel, and north areas of the Rappahannock R respectively (inset). Strata 56-58 were the north, channel, and south areas of the York R. respectively.

Between each deployment of the sampler, the bucket was covered with an HDPE lid to minimize sample oxidation and exposure to atmospheric contamination. Additional grab samples were taken and the top layer of sediment was collected and composited until sufficient volume (7-8 L) of sediment for all the toxicity bioassays and chemical analyses was collected. The material was thoroughly homogenized in the field with an acetone-rinsed, stainless steel mixer attachment on an electric drill. This composite sample was subdivided for distribution to various testing laboratories. Sampling procedures in the smaller launch were exactly the same except a smaller PONAR sampler (0.04 m2 surface area grab) was deployed by hand. All subsamples were either stored on ice or frozen, as appropriate, prior to shipment to laboratories ashore.

A second sample was taken for benthic community analysis with the small PONAR grab sampler. The entire contents of an acceptable sample (at least 5 cm deep) were sieved on site through 0.5mm mesh. All organisms were retained in 500/2500 ml plastic Nalgene bottles and preserved in diluted 10% neutral buffered formalin containing Rose Bengal. For a collaborative effort with the EPA Chesapeake Bay Program, a replicate benthos sample was also taken. This sample was handled exactly the same as the first sample, but the samples were delivered to the Bay Program contract lab for analysis and application of the CBP benthic Index of Biotic Integrity (B\_IBI), (Llanso, 2002). Included in the B\_IBI analysis is a measure of biomass as ash-free dry weight, which requires destruction of the samples after species enumeration.

Samples for toxicity tests were kept chilled on ice until extractions or tests were initiated. Holding times were less than 10 days. Samples for chemical analyses were kept frozen until thawed for analyses. Samples for toxicity testing and chemistry analyses were shipped in ice chests packed with water ice or blue ice to the testing laboratories by overnight courier. All samples were accompanied by chain of custody forms which included the date and time of sample collection and site number.

# SEDIMENT TOXICITY BIOASSAYS

Amphipod mortality, sea urchin fertilization impairment, Microtox® luminesence, and cytochrome P450 Human Reporter Gene System (HRGS) tests were carried out on the sediment samples or extracts. A summary of the toxicity bioassay methods is presented below. All

methods are based on standard methods promulgated by the EPA, American Society for Testing and Materials (ASTM), and/or the American Public Health Association (APHA).

**Amphipod Survival Test-** This test is commonly used in North America for assessing sediment quality, in part because the test integrates the effects of complex contaminant mixtures in relatively unaltered sediment and also because amphipods are fairly common and ecologically important species in coastal waters. *Ampelisca abdita* is the most commonly used species in NOAA's studies, as well as other agencies. This euryhaline species occurs in fine sediments from the intertidal zone to a depth of 60 m, with a distribution range that extends from Newfoundland to south-central Florida, and includes the eastern Gulf of Mexico, and portions of the California coast. *A. abdita* builds soft, membranous tubes and feeds on surface deposited particles as well as particles in suspension. In previous studies, this species has shown relatively little sensitivity to nuisance factors such as grain size, ammonia, and organic carbon (EPA, 1994). The tests are performed using juveniles exposed to relatively unaltered, bulk sediments.

The tests were performed in accordance with a standard guide for conducting 10-day static sediment toxicity tests with amphipods (ASTM, 1999) and additional guidance developed for testing four different amphipod species (EPA, 1994). Briefly, amphipods were exposed to test and control sediments for 10 days under static conditions. The bioassays included 5 replicates, with 20 animals per replicate. During the test, the animals were exposed to constant light in filtered, aerated seawater at 28 ppt salinity. The test chambers were 1L glass vessels, containing 200 mL of sediment. The vessels were monitored daily for water temperature and condition of test organisms. Measurements for salinity, dissolved oxygen, ammonia, and pH were made at least twice during the course of the bioassay. Hydrogen sulfide in sediment pore water was also measured periodically.

A positive control, or reference toxicant test, was used to document the sensitivity of each batch of test organisms. A commonly used industrial detergent, sodium dodecyl sulfate (SDS), also known as sodium lauryl sulfate, was used in 96-hour water-only exposure bioassay as a control test. The LC50 results were recorded in a control chart, and were expected to be within 2 standard deviations of the mean of the previous 20 positive control tests.

Based on statistical analyses of an amphipod survival dataset with 637 bioassay tests (five replicates per test), including power analysis, two criteria were derived to declare test results to be different from the control: first, the t-test must show that the sample survival was statistically lower than in the control, and second, the sample's mean survival must be less than 20% that of the control (Thursby *et al.*, 1997). These thresholds are referred to here as having statistically lower survival, and demonstrating a toxic response, respectively.

**Sea Urchin Fertilization Toxicity Test-** The sea urchin (Arbacia punctulata) fertilization toxicity test (also known as the sperm cell test) involves exposing sea urchin sperm to pore water followed by the addition of eggs. This test is used extensively in assessments of ambient water quality, toxicity of industrial and municipal effluents, and sediment toxicity in coastal waters. It combines the features of testing sediment pore waters (the phase of sediments in which dissolved toxicants may be bioavailable) and exposures of gametes which often are more sensitive than adults.

Pore water was extracted from the sediment by using a pneumatic extraction device. The extractor was made of polyvinyl chloride and uses a 5  $\mu$ m polyester filter. After extraction the sample was centrifuged, and the supernatant collected and frozen at -20 °C. Prior to commencing the experiment, samples were thawed in a water bath, and water quality measurements were made (dissolved oxygen, pH, sulfide, and ammonia). Each porewater sample was tested in a dilution series (100%, 50% and 25%) with five replicates per treatment. Sample temperatures during the tests were maintained at 20±1° C. Sample salinity was measured and adjusted to 30±1 ppt, if necessary, using purified deionized water or concentrated brine. A reference porewater sample collected from Redfish Bay, Texas was included with each test as a negative control.

Adult male and female urchins were stimulated to spawn with a mild electric shock and the gametes were collected separately. The bioassay tests exposed sperm to 5 ml of the pore water for 30 minutes followed by the addition of 2,000 eggs. After an additional 30 minutes of incubation, the test was terminated by the addition of formalin. An aliquot of the egg suspension

was examined under a microscope to determine the presence or absence of a fertilization membrane surrounding the egg, and percent fertilization was recorded for each replicate.

At the test's conclusion, the fraction of fertilized eggs was recorded. Sodium dodecyl sulfate (SDS) was used as a positive control toxicant. Reduction in mean fertilization success after exposure to pore water, in comparison with the negative control, was the experimental end-point. A detailed outline of the pore water extraction procedure and testing protocol is given by Carr and Chapman (1995).

Statistical treatments of data include analysis of variance and Dunnett's one-tailed t-test on arcsine square root transformed data. The trimmed Spearman-Karber method with Abbott's correction is used to calculate EC50 (concentration that is effective in causing a 50% response in a toxicity test) values based on dilution series tests. In addition to statistically significant differences from control sediment, a detectable significance criterion is used to determine the 95% confidence value based on power analysis of data from similar tests (n=3110). This value is the percent minimum difference from the reference that is necessary to detect a significant response: at ( $\alpha = 0.05$ , it is 15.5%, and at  $\alpha = 0.01$ , it is 19% (Carr and Biedenbach, 1999).

Human Reporter Gene System (Cytochrome P450) Response- This test was used to determine the presence of organic compounds that bind to the Ah (aryl hydrocarbon) receptor and induce the CYP1A locus on the vertebrate chromosome. Under appropriate test conditions, induction of CYP1A is evidence that the cells have been exposed to one or more of these xenobiotic organic compounds, including dioxins, furans, planar PCBs, and several polycyclic aromatic hydrocarbons. Differences in the ability of the P450 enzyme to metabolize chlorinated and non-chlorinated compounds allow for differentiation between these classes of compounds in environmental samples. Since most PAHs are metabolized, they exhibit a maximum response in 6 hours, at which point the response begins to fade. Chlorinated hydrocarbons (dioxins, furans, and certain PCBs), on the other hand are not degraded and continue to induce CYP1A, resulting in increasing responses after 16 hours following exposure.

The details of this test are provided as a standard method, Method 4425, of the US Environmental Protection Agency (EPA, 1999), the American Public Health Association (APHA, 1998) and American Society of Testing and Material (ASTM, 1999). The test uses a transgenic cell line (101L), derived from the human hepatoma cell line (HepG2), in which the flanking sequences of the CYP1A gene, containing the xenobiotic response elements (XREs), have been stably linked to the firefly luciferase gene (Postlind *et al.*, 1993). As a result, the enzyme luciferase is produced in the presence of compounds that bind the XREs.

Sediment was extracted and processed within 10 days following collection in accordance with the EPA Method 3550. Details of the extraction procedure are provided elsewhere (EPA, 1996; Johnson and Long, 1998). Briefly, after removal of debris and pebbles, the sediment was homogenized and dried with anhydrous sodium sulfate. Twenty grams of sediment was extracted by sonication with dichloromethane (DCM). The extract was concentrated under nitrogen, and exchanged into mixture of dimethylsulfoxide (DMSO), toluene and isopropyl alcohol (2:1:1) to achieve a final volume of 2 mL. Before testing, the extracts were diluted 1:10 with DMSO. The extraction procedure is well suited for extraction of neutral, non-ionic organic compounds, such as aromatic and chlorinated hydrocarbons. Extraction of other classes of toxicants, such as metals and polar organic compounds, is not efficient. DMSO is compatible with this test because of its low toxicity and high solvent properties with a broad spectrum of nonpolar chemicals.

Detection of enzyme induction in this assay is relatively rapid and simple to measure since binding of a xenobiotic with the Ah receptor results in the production of luciferase. After incubation with the extract, the cells were washed and lysed. Cell lysates were centrifuged, and the supernatant was mixed with buffering chemicals. Enzyme reaction was initiated by injection of luciferin. The resulting luminescence is measured with a luminometer and expressed in relative light units (RLUs). A solvent blank and a reference toxicant (Tetrachlorodibenzo-pdioxin [TCDD, dioxin] at a concentration of 1 ng/mL) were used with each batch of samples.

The relative increase in RLU over background (enzyme fold induction) is calculated as the mean RLU of the test solution divided by the mean RLU of the solvent blank. From the standard concentration-response curve for benzo[a]pyrene (B[a]P), the HRGS response to  $1 \mu g/mL$  is

approximately 60. Data are converted to µg of B[a]P equivalents per g of sediment using this factor. Since testing at only one time interval (16 h) does not allow discrimination between PAHs and chlorinated hydrocarbons, the data are also expressed as Toxic Equivalents (TEQs) in ng/g based on a standard curve with a dioxin/furan mixture.

Quality control tests were run with clean extracts spiked with tetrachlorodibenzo-p-dioxin (TCDD) and B[a]P to ensure compliance with results of previous tests. Tests were rerun if the coefficient of variation for replicates is greater than 20%, and if fold induction was over the linear range (100 fold). Sediment extracts from Redfish Bay, Texas, were used as a negative control. For samples in which fold induction (=sample/solvent blank) was 100 or greater, a dilution series was conducted to obtain final response values. At selected stations these tests were evaluated at both 6 and 16 hrs incubation to assess the relative contribution of PAHs as opposed to chlorinated dioxins, furans and, PCBs to the observed responses.

There are no clearly defined assessment end-points for P450 induction that signify a threshold of biological damage, and statistical procedures must be employed to arrive at decision points. Two parameters that have been employed are confidence intervals and prediction intervals.

Anderson *et al.* (1999a) calculated the mean and 95% confidence interval of HRGS values from 527 sampling points in the NOAA biological effects database to be 22.7 + 10.1 (CI=12.6-32.8) mg B[a]P Eq/kg. Hence, values less than 12.6, forming the tail of the distribution in the direction of low induction (or impact), could be interpreted as a minimal (background) level. This is consistent with data from pristine sites in Alaska and California where HRGS values did not exceed 10.4 mg B[a]P Eq/kg (Anderson *et al.*, 1999b; Fairey *et al.*, 1996). Fairey *et al.* (1996) also demonstrated that HRGS values above 60 mg B[a]P Eq/kg were highly correlated with degraded benthic communities in San Diego and Mission Bays, and also PAH concentrations above the 9,600 ug/kg Probable Effects Level (PEL) guideline (McDonald, 1993). Based on these data, HRGS values greater than 10 and 60 mg B[a]P Eq/kg were considered to represent marginal and highly contaminated thresholds, respectively.

Microtox<sup>TM</sup> bioluminescence inhibition tests were conducted on organic extracts of sediments. However due to technical difficulties with the tests, the data are not used in these analyses.

Integrated Toxicity Response Index- A ranking scheme was used to evaluate the toxicological results on a site by site basis (Hartwell, 1997). The ranking system quantifies relative toxicological impact, not merely cataloging presence or absence of toxic effects. The simplified version of the ranking scheme is the sum of the products of endpoint severity and percent response divided by  $\sqrt{N}$ .

Site Score = { $\Sigma$  [(Severity) (% Response)]}  $\sqrt{N}$ 

The sum was divided by the square root of the number of test endpoints (N) for each site, to compensate for bias between different sites where different amounts of data may be present. Severity refers to the degree of effect which the bioassay endpoints measure. Mortality is considered the most severe response, followed by impaired reproduction and exposure. They were arbitrarily set as integers of mortality = 3, reduced fecundity = 2 and elevated exposure = 1. Thus, more weight is given to more critical endpoints.

Degree of response is the measure of the proportion of response in each bioassay regardless of statistical significance (e.g. 5% mortality, 45% reproductive inhibition, etc.). Low level impacts may have significant population level ramifications if present over widespread areas or for long time periods. In this regard, it is as important to know what percentage of the organisms responded as it is to know whether it was `statistically significant'. The response values were adjusted for mean control values in their calculation formulas. Negative values were assigned a value of zero. The following equations were used to calculate degree of response:

mortality % response = {(test # dead - control # dead)/start total #} X 100 reproductive impairment % response= {(control - test)/control} X 100 exposure% response = calculated B[a]P equivalents The number of endpoints measured at each site refers to the number of bioassays which are monitored. For statistical and experimental reasons, the number of tests run at each site ideally should be the same. However, given the uncertainties of experimental work, this is not always possible. This score is a useful technique for comparing individual sites and for examining spatial trends in sediment or temporal trends in water samples.

Site	Endpoint	Severity	Response	Subscore	Sum	Ν	Site
							Score
1	Amphipod	3	10	30	100	4	50
	Mortality						
1	Sea Urchin	2	10	20			
	Fertilization						
1	P450	1	20	20			
1	Microtox	1	30	30			
2	Amphipod	3	15	45	200	4	100
	Mortality						
2	Sea Urchin	2	25	50			
	Fertilization						
2	P450	1	50	50			
2	Microtox	1	55	55			

An example calculation is shown here;

# CHEMICAL ANALYSES

Chemical analyses followed procedures used in the NOAA NS&T program (Lauenstein and Cantillo, 1998). A broad suite of chemicals were analyzed at each station, including 13 metals, butyl-tins, PAHs, chlorinated compounds (PCBs, chlorinated pesticides, furans and dioxins). In addition several physicochemical measurements of sediment quality (e.g. grain size, TOC, etc.) were determined.

**Metals-** Sediment samples were stored frozen until processing and analysis. Samples were prepared for atomic absorption analysis and activation analysis by freeze drying and wet digestion. Dried sediment samples were homogenized, weighed and digested in a sequence of heating steps in Teflon bombs with HNO3, HF, and H3BO3, except Hg. Analyses were performed using either flame or graphite furnace atomic absorption spectroscopy (AAS), (Table 1). Recalibration standards were run every 12 samples, and matrix modifiers were used as necessary.

Quality control samples were processed in a manner identical to actual samples. A method blank was run with every 20 samples, or with every sample set, whichever was more frequent. If corrected blank concentrations for any component were above three times the method detection limit (MDL), the whole sample set was re-extracted and reanalyzed. If insufficient sample was available for re-extraction, the data was reported and appropriately qualified. Matrix spike/matrix spike duplicate (MS/MSD) samples were run with every 20 samples, or with every sample set, whichever was more frequent. The appropriate spiking level was ten times the MDL. Reference materials were extracted with each set of sample and were analyzed when available. The method detection limit was determined following the procedures outlined in CFR 40, part 136 (1999).

For analysis of Hg, sediment samples were digested using a modified version of EPA method 245.5, using a concentrated H2SO4 and HNO3 digestion, followed by addition of KMnO4, and K2S2O8, and the samples were again digested. Before analysis, 5 mL of 10% (w/w) NH2OH . HCl were added to reduce excess permanganate and the volume brought to 40 mL with distilled water.

**TBT-** An aliquot of freeze dried sediment was weighed and appropriate amounts of surrogate standards (approximately 10 times the MDL) were added to all samples, matrix spikes, and blanks. Samples were extracted three times by agitation with tropolone in dichloromethane. The sample extract was concentrated in a hot water bath, and the extract was centrifuged and further concentrated. The solvent was exchanged to hexane and concentrated to a final volume of about 10 - 20 mL at which point only hexane remained. Hexylmagnesium bromide (2 M; Grignard reagent) was added to the sample extract under nitrogen and heated to hexylate the sample.

Table 1. Elemental quantification techniques by element.

Analyte	Method		
Mercury	CVAA		
Aluminum	FAA		
Iron	FAA		
Manganese	FAA		
Zinc	FAA		
Arsenic	GFAA		
Cadmium	GFAA		
Chromium	GFAA		
Copper	GFAA		
Lead	GFAA		
Nickel	GFAA		
Selenium	GFAA		
Silver	GFAA		

CVAA - Cold vapor atomic absorption FAA - Flame atomic absorption GFAA - Graphite furnace atomic absorption After separation from the organic phase, pentane:CH2Cl2 (3/1, v/v) was added to the aqueous phase and the sample shaken vigorously. The pentane:CH2Cl2 extraction was done twice. The hexylated extract was dried by addition of anhydrous Na2SO4 and then concentrated. The extract was purified using silica gel/alumina column chromatography. The eluent was collected and concentrated on a water bath.

The quantitative method was based on high resolution, capillary gas chromatography using flame photometric detection (GC/FPD). This method quantitatively determined tetrabutyltin (4BT), tributyltin (TBT), dibutyltin (DBT) and monobutyltin (MBT).

Quality control samples were processed in a manner identical to actual samples. A method blank was run with every 20 samples, or with every sample set, whichever was more frequent. If corrected blank concentrations for any component were above three times MDL, the whole sample set was re-extracted and reanalyzed. If insufficient sample was available for re-extraction, the data was reported and appropriately qualified. Matrix spike/matrix spike duplicate (MS/MSD) samples were run with every 20 samples, or with every sample set, whichever was more frequent. The appropriate spiking level was ten times the MDL. Reference materials were extracted with each set of sample and were analyzed when available. The method detection limit was determined following the procedures outlined in CFR 40, part 136 (1999).

**Organics (PAHs, PCBs, chlorinated pesticides)-** Samples were shipped frozen to the laboratory and stored at -20 °C until analysis. An aliquot of approximately 1 g of sample was weighed and oven dried at 63 - 56 °C to constant weight to determine wet/dry weight.

For analyses, an aliquot of homogenized sample was chemically dried with sodium sulfate. After samples were spiked with surrogates the samples were extracted in a Soxhlet apparatus with dichloromethane on a hot sand bath for 8 hr. If sediment or other particulates were present in the sample extract, the extracts were filtered through a funnel containing glass wool and sodium sulfate. The sample extract was then concentrated and solvent changed to about 2 mL of hexane. Silica gel/alumina column chromatography was utilized to concentrate and purify the samples before analysis. Quality control samples were processed with each batch of samples in a manner

identical to the samples, including matrix spikes. Extracts were stored in the dark at or below 4 °C.

A method blank was run with every 20 samples, or with every sample set, whichever was more frequent. If blank concentrations for any component were above three times MDL, samples analyzed in that sample set were re-extracted and reanalyzed. If insufficient sample was available for extraction, the data was reported and appropriately qualified. Matrix spike/matrix spike duplicate samples were run with every 20 samples, or with every sample set, whichever was more frequent. Surrogate standards were spiked into every sample and quality control sample.

Quantitation of PAHs and their alkylated homologues was performed by gas chromatography mass spectrometry (GC/MS) in the selected ion monitoring (SIM) mode. Target analytes are listed in Table 2. The compounds in the surrogate solution were deuterated naphthalene-d8, acenaphthene-d10, phenanthrene-d10, chrysene-d12 and perylene-d12. The internal standards were fluorene-d10, and benzo[a]pyrene-d12 at  $4 \mu g/mL$  and were prepared with a certified standard (NIST or equivalent). The GC conditions were set so that the internal standards were resolved, but would elute in close proximity to, the analytes of interest.

A solution containing 2- to 5-ring PAH compounds was used to fortify matrix spike samples. A certified solution (NIST SRM 2260) was diluted to the appropriate working concentration. Dibenzothiophene was not present in the SRM and was added to the solution by weighing neat material to make a concentration of  $1.00 \ \mu g/\mu L$ . The spiking solution was used to fortify samples to a final concentration of approximately ten times the MDL. A solution of a laboratory reference oil was analyzed as an instrument reference solution with each analytical batch. After every 8 - 10 samples, the mass spectrometer response for each PAH relative to the internal standard was determined using check standards. Daily response factors for each compound were compared to the initial calibration curve and recalibration was repeated when necessary. The standard reference oil was analyzed with all analytical batches.

When available, a standard reference material was extracted and analyzed with each batch of samples. Target concentrations were defined as the range of the certified value plus or minus the

Table 2. Polynuclear aromatic hydrocarbons analyzed in Chesapeake Bay sediment samples.

Naphthalene C1-Naphthalenes **C2-Naphthalenes** C3-Naphthalenes C4-Naphthalenes Biphenyl Acenaphthylene Acenaphthene Fluorene **C1-Fluorenes C2-Fluorenes C3-Fluorenes** Anthracene Phenanthrene C1-Phenanthrenes/Anthracenes C2-Phenanthrenes/Anthracenes C3-Phenanthrenes/Anthracenes C4-Phenanthrenes/Anthracenes Dibenzothiophene C1-Dibenzothiophenes C2-Dibenzothiophenes C3-Dibenzothiophenes Fluoranthene C1-Fluoranthenes/Pyrenes C2-Fluoranthenes/Pyrenes C3-Fluoranthenes/Pyrenes Pyrene Benz(a)anthracene Chrysene C1-Chrysenes C2-Chrysenes C3-Chrysenes

C4-Chrysenes Benzo(b)fluoranthene Benzo(k)fluoranthene Benzo(e)pyrene Benzo(a)pyrene Perylene Indeno(1,2,3-c,d)pyrene Dibenzo(a,h)anthracene Benzo(g,h,i)perylene

Additional PAHs 2,6-Dimethylnaphthalene 1-Methylphenanthrene 1-Methylnaphthalene 2-Methylnaphthalene 1,6,7-Trimethylnaphthalene 95% confidence intervals found in the SRM certification. The measured concentration was within  $\pm 30\%$  of the target concentration on average for all analytes either certified or non-certified with concentrations greater than 10 times the MDL. The actual analytical method detection limit (MDL) was determined following procedures outlined in CFR 40, part 136 (1999).

Chlorinated hydrocarbons (chlorinated pesticides and PCBs, Table 3) were quantitatively determined by capillary gas chromatography with an electron capture detector (ECD). If the response for any peak exceeded the highest calibration solution, the extract was diluted, a known amount of surrogate and tetrachloro-m-xylene (TCMX) solution added, and the sample reanalyzed for those analytes that exceeded the calibration range. Analyte concentrations in the samples were based on calculations using the PCB 103 surrogate. The internal standard (TCMX) was used to calculate surrogate recoveries. 4,4'-dibromooctafluorobiphenyl (DBOFB) or PCB 198 was used to calculate selected analytes concentrations, if it was demonstrated that they produced more reliable data (i.e., if matrix interference occurs with PCB 103) based on percent recoveries in spiked blanks, matrix spikes, or reference materials. The calibration solutions that were analyzed as part of the analytical GC/ECD run were preceded by no more than six samples and no more than six samples were run between calibration mixtures.

An acceptable method blank contained no more than two target compounds at concentrations three times greater than the MDL. All samples and quality control samples were spiked with DBOFB, PCB 103 and PCB 198. The surrogate standard solution was spiked into the samples prior to extraction in an attempt to minimize individual sample matrix effects associated with sample preparation and analysis. A matrix spike and a duplicate were analyzed with each sample set or every 20 field samples, whichever was more frequent. The acceptable matrix spike recovery criteria were 50 - 125% recovery for at least 80% of the analytes. Criterion for duplicates was  $\leq$ 30% relative percent difference (RPD). The method detection limit was determined following the procedures outlined in CFR 40, part 136 (1999). Most target compounds, surrogates and internal standard were resolved from one another and from interfering compounds. When they were not, coelutions were documented. A standard reference

Table 3. Chlorinated pesticides and PCBs analyzed in Chesapeake Bay sediment sample

Alpha HCH	Normalized Pesticides
Beta HCH	
Delta HCH	Total Butyl Tins
Gamma HCH	·
Total HCH	PCB28
	PCB44
Heptachlor	PCB52
Heptachlor epoxide	PCB66
Oxychlordane	PCB105
Alphachlordane	PCB118
Gamma Cholrdane	PCB128
Cis-Nonachlor	PCB180
Trans-Nonachlor	PCB187
Aldrin	PCB206
Dieldrin	PCB209
Endrin	PCB101_90
	PCB138_160
Mirex	PCB153_132
Endosulfan	PCB170_190
Chlorpyrofos	PCB18_17
	PCB195_208
2,4' DDD	PCB8_5
2,4' DDE	
2,4' DDT	Co-planar PCBs*
4,4' DDD	PCB81
4,4' DDE	PCB77
4,4' DDT	PCB126
Total DDTs	PCB169
Tetrachlorobenzene 1,2,3,4	
Tetrachlorobenzene 1,2,4,5	
Pentachlorobenzene	
Havaahlarahanzana	*colocitad stations only

Tetrachlorobenzene 1,2,4,5 Pentachlorobenzene Hexachlorobenzene Total Chlorinated Benzene Total Pesticides

\*selected stations only

material sample was analyzed per batch of samples or every 20 samples whichever was more frequent.

## BENTHIC COMMUNITY ASSESSMENT

**Community Metrics-** Benthic infauna samples were sieved through a 0.5-mm mesh screen and preserved with 10% formalin in the field. In the laboratory, samples were inventoried, rinsed gently through a 0.5 mm mesh sieve to remove preservatives and residual sediment, stained with Rose Bengal, and stored in 70% isopropanol solution until processing. Sample material (sediment, detritus, organisms) was placed in white enamel trays for sorting under Wild M-5A dissecting microscopes. All macroinvertebrates were carefully segregated into major taxonomic group (e.g. Polychaete, Mollusk, Arthropod). All sorted macroinvertebrates were identified to the lowest practical identification level (LPIL), which in most cases was to species level unless the specimen was a juvenile, damaged, or otherwise unidentifiable. The number of individuals of each taxon, excluding fragments, was recorded.

Data were reduced to a data summary report for each site, which included a taxonomic species list and benthic community parameters information. Archive data files of species identification and enumeration were prepared. At a minimum, 10 percent of all samples were resorted and recounted on a regular basis. The minimum acceptable sorting efficiency was 95%. Ten percent of samples were randomly selected and re-identified. The minimum acceptable taxonomic efficiency was 95%. A voucher collection composed of representative individuals of each species encountered in the project was accumulated and retained.

Several manipulations of the input data were performed to filter the data and remove confounding effects and bias.

1- Four taxa of epiphytic species such as sea anemones and tunicates were eliminated from the data set as they are not truly infauna.

2 - 'Artificial' species (resulting from failure to identify some specimens all the way down to species) were identified as a data bias. For example, there were many examples where specimens of 2-3 species were identified in genus A, and there were other specimens that were identified only to genus A, or the family to which genus A belongs. This tends to artificially increase

species richness and diversity of the sample when in fact that diversity is an artifact of imperfect taxonomic identification. In some instances, specimens were only identifiable to family, order or class. To address this problem, specimens not identified to species level were eliminated, unless they were identified to a taxonomic level below which no other specimens in the collection belonged. That is, even though they were not identified to species, they were the only representative of that taxonomic line and did represent a non-redundant taxon. From an initial total of 287 taxa, 26 taxa were eliminated in this step. Twenty one of these were only identified to family or a higher level. However, these were not numerous or widespread. Most of them were specimens that were difficult to identify, or were too damaged by sampling gear to completely identify, and only accounted for approximately 5% of the 20,609 individual organisms enumerated.

3 - To minimize loss of important community information there were instances where specimens identified to one level were combined into one taxon with specimens only identified to the next higher level. This retained 2,728 individuals but reduced the number of taxa by 45. In 43 other cases, there were multiple species to choose from so they were not combined. The individual species were kept and the genus was also kept as a separate taxon. This retained 2,439 individuals.

Since taxa are distributed along environmental gradients, there are generally no distinct boundaries between communities. However, the relationships between habitats and benthic assemblages reflect the interactions of physical and biological factors and reveal ecological patterns. Quantitative benthic community characterizations included enumeration of density (#/m2), species richness (S), evenness (J'), and diversity (H'). Density was calculated as the total number of individuals per square meter. Species richness is reported as the total number of taxa represented at a given site. Diversity, was calculated with the Shannon-Weiner Index (Shannon and Weaver, 1949), using the following formula:

$$\mathbf{H'} = -\Sigma \mathbf{p}_i (\ln \mathbf{p}_i)$$

where,

S = is the number of species in the sample, i is the ith species in the sample, and  $p_i$  is the number of individuals of the ith species divided by the total number of individuals in the sample.

Evenness for a given station was estimated as Pielou's Index J' (Pielou, 1966);

J' = H'/1n S

## DATA ANALYSIS

Individual bioassay endpoints (e.g., P450), concentrations of contaminant groups (e.g., PAHs, PCBs), and biological community measurements (e.g., abundance, number of taxa), were arbitrarily termed metrics. Values derived from manipulation and combinations of the metrics are arbitrarily termed indices (e.g., toxicity score, ERMq). A variety of univariate and multivariate statistical analyses were performed on the metrics and indices derived from the data.

Numerical sediment quality guidelines (Table 4) developed by Long and Morgan (1990) and Long *et al.* (1995) known as ERM and ERL (effects range-median, effects range-low) express statistically derived levels of contamination, above which toxic effects would be expected to be observed with some level of frequency (ERM), and below which effects were rarely expected (ERL). The mean ERM quotient (Long *et al.*, 1998) is the average of the ratio of ERM values to sediment concentrations for each chemical. The mean quotient of the ERMs and observed contaminant concentrations were calculated on a site by site basis. The calculation included low weight PAHs, high weight PAHs, total PCBs, total DDT, and the individual metals, except Ni. The ERM for Ni has poor predictive power in marine and estuarine sediments (Long *et al.*, 1995).

Because trace elements and other compounds naturally vary in concentration by several orders of magnitude, normalized values were calculated for the purpose of summarizing contaminant data in consistent units. Data were normalized by dividing the concentration of each element or compound at each station by the overall mean concentration for that specific chemical. This was also applied to summed chemical values (e.g. total PAHs). Thus, all metals can be contrasted against each other, or metals and PCBs.

	ERL	ERM	
Total DDT	1.58	46.1	
pp'-DDE	2.2	27	
Total PCBs	22.7	180	
Total PAHs	4022	44792	
High weight PAHs ( $\geq$ 4 rings)	1700	9600	
Low weight PAHs ( $\leq$ 3 rings)	552	3160	
Acenaphthene	16	500	
Acenaphthylene	44	640	
Anthracene	85.3	1100	
Flourene	19	540	
2-Methyl Naphthalene	70	670	
Naphthalene	160	2100	
Phenanthrene	240	1500	
Benzo-a-anthracene	261	1600	
Benzo-a-pyrene	430	1600	
Chrysene	384	2800	
Dibenzo(a,h)anthracene	63.4	260	
Fluoranthene	600	5100	
Pyrene	665	2600	
As	8.2	70	
Cd	1.2	9.6	
Cr	81	370	
Cu	34	270	
Pb	46.7	218	
Hg	0.15	0.71	
Ni	20.9	51.6	
Ag	1.0	3.7	
Zn	150	410	

Table 4. Chemicals and chemical groups for which ERLs and ERMs have been derived (organics ppb, metals ppm, dry weight).

**Regression and Correlation-** Summary statistics for all metrics were calculated on a site by site basis, and averaged by strata. Simple scatter plots were produced for all community metrics versus toxicity data and chemical constituents, and between toxicity results and contaminant concentrations to assess gross correlation of metrics. Toxicity data were log or arc-sine transformed, as appropriate. Contaminant concentration data were used as both linear and log transformed variables. The contaminant data were run as individual chemicals and broad classes (e.g. metals, PAHs, PCBs, etc.) and in subgroups including individual metals, low and high weight PAHs, alkyl substituted and parent compound PAHs, DDT and metabolites, chlordane and related cyclodienes compounds, TBT, HCH, and HCB.

Spearman- rank correlation coefficients were calculated between all chemical, toxicological and biological metrics. Correlations were also calculated using data condensed into larger groupings such as total PCBs, total PAHS, and between derived indices. Linear and quadratic regressions were calculated for toxicological, community, contaminant, and habitat attributes using log transformed values for those data that spanned multiple orders of magnitude. Regressions of toxicity, community, contaminant and habitat indices against % silt clay content were calculated and the residuals were used to assess regression relationships between them in the absence of the influence of grain size. The B\_IBI values from the CBP were evaluated through Spearman-rank correlation coefficients with statistical community parameters, including the triad area calculations, and spatial comparison with derived habitat classification from the nodal analysis (see below).

**Nodal analysis-** Multivariate cluster analysis was employed to group site and species data. Cluster analysis is a two-step process including; 1) creation of a resemblance data matrix from the raw data, 2) clustering the resemblance coefficients in the matrix. The input resemblance (similarity or dissimilarity) matrix can be created by a number of methods. Input data may or may not be standardized or transformed depending on the requirements of the method (e.g. Bray Curtis). Based on previous research (Hartwell and Claflin, 2005) the Jaccard Coefficient (Goodall, 1973) was used to generate the similarity matrix. The Jaccard Coefficient is calculated by a binary method based only on presence/absence data, and thus ignores abundance values.

This method generates a resemblance matrix of coefficients that reflects the cumulative frequency of species overlap between sites. The calculation method does not include negative frequencies, i.e. for sites in which a given species is missing in both, no value is returned in the calculation routine. Site coefficients are the product of instances in which species are found in common and/or in which species are present in one site but not the other. Cluster analyses were calculated from the matrices using the Unweighted Pair-Group Method Using Arithmetic Averages (UPGMA) procedure which clusters coefficients based on arithmetic mean distance calculations (Sneath and Sokal, 1973).

After the cluster analyses had been evaluated, a nodal analysis routine was applied to the results (Lambert and Williams, 1962). The objective of nodal analysis was to produce a coherent pattern of association between results for sites and species clusters. This consisted of combining the independent cluster analyses in a graphical array. The first analysis clustered sites using species occurrence data. The second calculation clustered species. The intersection of site clusters on the abscissa and species clusters on the ordinate axis yields a pattern of species associations with site clusters, termed nodes. In practice, this is done on large 3'x4' plots of the cluster analysis output. Reduction to normal text page size sacrifices a significant amount of detail. The site and species clusters were also characterized by physicochemical habitat parameters, contaminant concentrations, and other site-specific data. Cluster analyses were run on a set of data with and without the top 10th percentile of contaminated sites, based on the ERMq. Sites which exceeded any individual ERM were also excluded. This was done to analyze communities in the absence of the influence of impacted species assemblages.

To optimize the cluster analysis results, a final filter of the input data was performed to simplify results. 'Rare and unique' taxa, defined as those species that were found at no more than two stations, were eliminated from the data set. Eighty-six taxa were removed in this step. Because of their limited distribution, by definition, they do not provide information on the impact of contaminant gradients in the environment because they do not occur across a gradient. The other difficulty with these species in the analyses is that they caused formation of spurious clusters that disaggregated sites in the cluster analyses which otherwise grouped together. A total of only 507 animals were removed over the entire 86 taxa. Of the 43 taxa kept uncombined in the previously

described taxonomic data filter step (above), 25 were eliminated as rare and unique taxa and only accounted for 60 organisms. The final list of taxa used in the cluster analyses was reduced to 126 from an original total of 287; a 56% decrease. The final count of total abundance was only reduced from 20,609 to 19,100, or approximately 7%. Thus a great deal of spurious taxonomic information was eliminated without a corresponding large loss of abundance information.

Principal Component Analysis- Principal component analysis (PCA) was calculated for all the sampling sites using benthic community, contaminant, and toxicity metrics and indices (Table 5). All sites were included except the deep trough sites with no macrofauna present. PCA calculations were also performed using these data on selected assemblages of sites based on the nodal analysis results. Because the nodal analyses are based on the distribution of species assemblages alone, selected nodal groupings were combined, based upon physical characteristics of the sampling sites. An objective of the analyses is to identify potential indicators of biological impact from anthropogenic stress. By combining site groupings with distinct benthic communities, but which were otherwise similar in location, salinity, and grain size characteristics, it may be possible to derive a pattern of community response to stressors from the data. Nodes were combined into larger assemblages of sites if the range of salinity and % fine grained sediment completely overlapped each other. For node-specific analyses, two different nodal associations were combined based on the salinity and grain size characteristics of the sites. The first included the Upper Bay/tributary node and species cluster #9, one of the clusters with no discernable dominant species. The second was the Tangier Sound/lower tributary node and the single species dominated clusters #7 and #8 (Paraprionospio pinnatao and Nereis succinea), plus the remaining low species/abundance cluster (#6, two sites). The other nodal groupings were unchanged.

Conducting PCA on species presence alone (as was done in the nodal analysis) is not productive, as it is in cluster analysis. Since the mathematical procedures in PCA identify maximum divergence in correlation, PCA based on species abundance primarily responds to species which are rare or narrowly distributed. Thus, the correlation of a site which includes a species that is only found in one or two sites is very large relative to the other sites, which biases the results.

Table 5. List of metrics used in principal component analyses.

Log Abundance Total # Species Diversity

Percent abundance of sensitive species Percent abundance of *Ampelisca* species Percent abundance of Amphipods species Percent abundance of bivalve species Percent abundance of tolerant species Percent abundance of Capitellid species Percent abundance of *Limnodrilus* species Percent abundance of Tubificid species Percent abundance of Spinoid species

Normalized DDT Normalized PCB Normalized PAH Normalized PEST Normalized TBT Normalized METALS Mean ERM quotient

Toxicity Response score

**Sediment Quality Triad Analysis-** The Sediment Quality Triad (SQT) approach is a tool to assess benthic habitats in terms of their community characteristics, observed toxicity, and chemical contamination loads (Chapman *et al.*, 1987). The SQT has traditionally been presented as a weight of evidence matrix of three separate scores. In an attempt to integrate SQT data into a unified score for each site, the three types of data were integrated in a graphical composite to allow comparison between sites and correlation with other parameters. Data for each component of the triad were normalized and scaled from 1 to 100. Results for each site were scaled using the formula:

((Site Value - minimum Value) / (maximum Value – minimum Value)) x 100

This places all values in the range of 0-100, based on the range of the data. The derived Toxicity index (Hartwell, 1997) was scaled in this manner. For contaminants, the ERMq was calculated for each of the trace elements, which were then averaged. The ERMq was also calculated for low and high weight PAHs, PCBs, and total DDT. The overall mean quotient for all these five chemical constituents was then calculated. Because the chemistry data was highly skewed (skewness = 4.4), the  $\log_{10}$  of the average quotient was used in the scaling calculation. The inverse of community species richness was used for the third triad leg. Thus high values in each category represented degraded conditions. The three values were plotted on tri-axial graphs and the surface areas of each resulting triangle was calculated as a measure of impact. The largest triangle possible in this system would have a surface area of 8,660. The angles within the corners of the triangles were also calculated. The standard deviation of the angles represents a measure of the symmetry of the triangles. That is, at sites where there is high contamination, toxicity and low numbers of species, the triangle tends toward an equilateral shape. Sites where one or two metrics are high and the other is low indicates a lack of effective cause and effect linkage between the triad legs (Chapman, 1996). The areas of the triangles were plotted against the standard deviation and the ERMq and other parameters to investigate possible relationships.

# RESULTS

Specific sample locations are shown in Appendix A. Most of the maps in the text show the data only in terms of percentiles to allow for a Bay-wide inspection of the results. Contaminant data are presented by chemical class. Organic contaminants data are summarized into total concentrations of all parameters measured. Benthic community data are presented on a site by site basis. Bioassay data are presented by test method and site. Conventional sediment characteristics (e.g. grain size, TOC, *etc.*) and water quality parameters are also presented. For ease of presentation, graphical data plots are grouped into mainstem, embayments and tributary sites (Fig. 5). Most embayments are on the eastern shore in Tangier and Pocomoke Sounds and behind Kent and Tilghman Islands, away from heavily populated areas. Plots are annotated with specific locations so the reader can assess the data within a general spatial reference.

# HABITAT CONDITIONS

Sediment grain size characteristics demonstrated a distinct gradient from fine to coarse grained particles down the mainstem from north to south (Fig. 6). Sediments in the tributaries tended to be muddier upstream and coarser near the mouths of the rivers (except the deep portions of the mouth of the Potomac), however sandbars were present in various locations due to current regime and depth. Sediments in the eastern shore embayments also tended to have finer grained sediments close to the shoreline and behind protective islands and shoals. Sediments in the deep trough were uniformly fine grained depositional material. Most of the sampled locations in the Susquehanna Flats contained fine grained material. Stations closer to the shoreline in the northern portion of the Bay tended to have coarser grain sizes, reflecting higher energy environments from waves and local currents, shoreline erosion, or anthropogenic alteration (e.g. dredging). The southern 2/3 thirds of the Bay contained primarily sandy sediments reflecting lower depositional rates from terrestrial runoff, a higher energy environment and the influence of oceanic flux from the mouth of the Bay.

Total organic carbon (TOC) ranged from less than 0.1% at site 113 to 10.6% at site 5 in the Susquehanna Flats area. Mean TOC was 1.4% overall. The mean TOC content of the sediment did not vary significantly between the three zones, averaging 1.1, 1.2 and 1.6% in the



Figure 5. Distribution of zones in Chesapeake Bay, divided into mainstem, embayment and tributary sites.



Figure 6. Grain size distribution at Chesapeake Bay sampling stations, expressed as percent silt + clay.
embayments, mainstem and tributaries respectively. There were high and low values on a site specific basis in all zones (Fig. 7). The bulk of the high values were found in depositional areas in the northern end of the Bay. The mainstem stations south of the mouth of the Patuxent River averaged only 0.3% TOC. The tributaries and embayments showed a mix of higher and lower values, correlated with grain size.

Water column data is incomplete due to instrument failure, primarily in the first year of sampling, but the partial record is sufficient to describe conditions on a system-wide basis. Also, bottom salinity can be inferred from the pore water bioassay data set (Fig. 8). Pore water salinity slightly underestimates bottom water salinity over most of the range. Chesapeake Bay salinities shown in Figure 9, use pore water values for missing measurements. Salinity varies from almost fresh in Susquehanna Flats to a maximum of 30 ppt at station 154 at the mouth of the Bay. Stratification of the water column was commonly observed in the mainstem, but not in the tributaries or the embayments. Variation in stratification in the mainstem would be expected as sampling cruises experienced a variety of weather conditions over the course of several weeks, and between sampling years. Surface and bottom temperature data only indicate possible thermal stratification near the mouth of the Bay (Fig. 10). Consistent with a two layered salt wedge estuarine circulation, locations showed cooler temperatures on the bottom than at the surface, but most differences were relatively small.

Most oxygen measurements in the tributaries and embayments showed minor differences between surface and bottom (Fig. 11). Sampling proceeded on 24 hr/day operations, so minor differences in oxygen are not meaningful. The utility of the oxygen data is to identify locations which may have been experiencing hypoxic or anoxic stress. Virtually all the oxygen concentrations were at or above 4mg/l. Two locations show dramatic reductions in bottom oxygen; 166 in Broad Bay within Virginia Beach, and 178 in the Rappahannock River These are most likely due to lowering the oxygen probe too low in the water and interacting with bottom sediments. The oxygen measurements of most interest would have been from the mainstem, particularly in the deep trough area. However all the deep stations were sampled from the RV FERREL, and the CTD on the ship did not include an oxygen meter.



Figure 7. Total organic carbon content at Chesapeake Bay sampling stations. Color scale represents percentile rank.

# Chesapeake Bay Bottom ppt vs Pore Water ppt



Figure 8. Correspondence of measured bottom water salinity and measured salinity of pore water (solid line).

### **Chesapeake Bay Mainstem Salinity**



Figure 9a. Surface and bottom salinity in the Chesapeake Bay mainstem. Selected locations are noted.

# **Chesapeake Bay Embayments Salinity**



Figure 9b. Surface and bottom salinity in Chesapeake Bay embayments. Selected locations are noted.

# **Chesapeake Bay Tributaries Salinity**



Figure 9c. Surface and bottom salinity in Chesapeake Bay tributaries. Selected locations are noted.

### **Chesapeake Bay Mainstem Temperature**



Figure 10a. Surface and bottom temperature in the Chesapeake Bay mainstem. Selected locations are noted.

### **Chesapeake Bay Embayments Temperature**



Figure 10b. Surface and bottom temperature in Chesapeake Bay embayments. Selected locations are noted.

# **Chesapeake Bay Tributaries Temperature**



Figure 10c. Surface and bottom temperature in Chesapeake Bay tributaries. Selected locations are noted.

# Chesapeake Bay Mainstem Dissolved Oxygen



Figure 11a. Surface and bottom dissolved oxygen in the Chesapeake Bay mainstem. Selected locations are noted.

# Chesapeake Bay Embayments Dissolved Oxygen



Figure 11b. Surface and bottom dissolved oxygen in Chesapeake Bay embayments. Selected locations are noted.

# Chesapeake Bay Tributaries Dissolved Oxygen



Figure 11c. Surface and bottom dissolved oxygen in Chesapeake Bay tributaries. Selected locations are noted.

#### CHEMICAL CONTAMINATION

Most of the mainstem of the Bay was relatively uncontaminated. The depositional areas in the Susquehanna Flats area and the upper portions of the deep trough where sedimentation rates are high and sediments are fine grained, have higher concentrations of contaminants than the middle and lower Bay (Fig. 12). Most of the tributaries had higher contaminant concentrations than the mainstem. Most of the embayments were as clean as the lower mainstem, with the exception of areas off the Gunpowder River near Baltimore, and nearshore stations in Tangier and Pocomoke Sounds, where pesticides were somewhat elevated. The Patapsco River at Baltimore and the Elizabeth River in Norfolk yielded the highest numbers in the entire system. Elizabeth River stations in both the south and east branches demonstrated considerably higher values than any other tributary, up to 70 times higher than the Bay-wide average. However, the Patapsco River is a much larger system than the Elizabeth River, and only 2 stations were located in Baltimore Harbor proper. Some of the most contaminated branches of the Patapsco River were not sampled (Baker et al., 1997). Of the large western tributaries, the Potomac and the James showed the most elevated concentrations. A few isolated stations in all zones showed contaminant spikes of one or more compounds, which may represent localized spills or proximity to a particular source area.

Concentrations of measured PAHs were highly variable, ranging from just 4 to over 22,000 ug/kg. Most stations had low concentrations of PAHs, with a small percentage showing highly elevated concentrations (Fig. 13). Only one mainstem and six tributary stations exceeded the ERL for total PAHs. Most of the Susquehanna Flats stations and the upper portion of the deep trough had elevated PAH concentrations relative to the rest of the Bay mainstem stations. Baltimore Harbor, the James and Elizabeth Rivers, and the mouth of the Patuxent River had the highest tributary concentrations. This pattern was not greatly changed by TOC normalization. In the mainstem and embayments, PAHs were evenly split between high weight ( $\geq$  4 rings) and low weight ( $\leq$  3 rings) PAHs. In contrast, the tributaries contained higher concentrations of high weight PAHs (Fig. 14). The difference is most dramatic in the more heavily contaminated areas. Alkyl- substituted PAHs were more prevalent in the low weight category (Fig. 15) than the high weight category (Fig. 16).

61



### **Chesapeake Bay Mainstem Normalized Contaminant Concentrations**

Figure 12a. Normalized sediment contaminant concentrations in the Chesapeake Bay mainstem. Selected locations are noted.



### **Chesapeake Bay Embayments Sediment Normalized Concentrations**

Figure 12b. Normalized sediment contaminant concentrations in Chesapeake Bay embayments. Selected locations are noted.



### **Chesapeake Bay Tributaries Normalized Contaminant Concentrations**

Figure 12c. Normalized sediment contaminant concentrations in Chesapeake Bay embayments. Selected locations are noted.

# **Chesapeake Bay Total PAH Concentrations**



Figure 13. Total PAH concentrations in Chesapeake Bay sediment samples. Dashed line indicates ERL concentration.

**Chesapeake Bay Tributary PAHs** 



Figure 14 High and low molecular weight PAH concentrations in Chesapeake Bay tributaries.



### **Chesapeake Bay Mainstem Low Weight PAHs**

Figure 15a. Concentrations of base and alkyl-substituted low weight PAHs in the Chesapeake Bay mainstem. Selected locations are noted. Horizontal line indicates ERL concentration.



### **Chesapeake Bay Embayments Low Weight PAHs**

Figure 15b. Concentrations of base and alkyl-substituted low weight PAHs in Chesapeake Bay embayments. Selected locations are noted. Horizontal line indicates ERL concentration.



### **Chesapeake Bay Tributaries Low Weight PAHs**

Figure 15c. Concentrations of base and alkyl-substituted low weight PAHs in Chesapeake Bay tributaries. Selected locations are noted. Horizontal lines indicate ERL and ERM concentrations.

# **Chesapeake Bay Mainstem High Weight PAHs**



Figure 16a. Concentrations of base and alkyl-substituted high weight PAHs in the Chesapeake Bay mainstem. Selected locations are noted. Horizontal line indicates ERL concentration.

# **Chesapeake Bay Embayments High Weight PAHs**



Figure 16b. Concentrations of base and alkyl-substituted high weight PAHs in Chesapeake Bay embayments. Selected locations are noted. Horizontal line indicates ERL concentration.

### **Chesapeake Bay Tributaries High Weight PAHs**



Figure 16c. Concentrations of base and alkyl-substituted high weight PAHs in the Chesapeake Bay tributaries. Selected locations are noted. Horizontal lines indicate ERL and ERM concentrations.

The distribution of PCBs was almost identical to that of the PAHs. Most of the Susquehanna Flats stations and the upper portion of the deep trough had elevated PCB concentrations. There were elevated values at selected embayment sites as well. Baltimore Harbor, the James and Elizabeth Rivers, and the mouth of the Patuxent River had the highest concentrations in the tributaries (Fig. 17). Concentrations ranged from below detection to 122 ug/kg. The distribution of PCB homologs in the Elizabeth River and Baltimore Harbor indicate a variety of aroclors contributing to the mixture, including 1260, 1254, and 1248 (Table 6). Since NS&T does not measure all congeners, and these represent weathered samples, it is difficult to precisely assess the inputs. Most of the other locations with a PCB spike contained only one or two dominant congeners, usually PCB28 or 170/190. These are tri- and hepta-chlorinated congeners, respectively. Planar PCBs (congeners 69, 77, 126, 169) were analyzed at 20 selected stations in 1998 only. Only four stations showed reportable concentrations (Table 7). Of the 20 samples, the highest concentrations were found in Baltimore Harbor. PCB169 was not detected anywhere. Dioxins were not analyzed.

The distribution of metals was similar to the organic contaminants, but metals were more frequently found at elevated concentrations in the Susquehanna Flats and the deep trough than other areas (Fig. 18). Baltimore Harbor had very high concentrations of metals. Only some portions of the Elizabeth River showed high metals concentrations. (Because trace elements naturally vary in concentration by several orders of magnitude, Figure 18 uses mean normalized values for each metal. Data were normalized by dividing the concentration of each element at each station by the overall mean concentration for that element for the entire data set.) The large western tributaries had higher concentrations than the lower mainstem, but values were only slightly higher. The distribution of the individual metals is the result of a complex interaction between sediment grain size, proximity to sources, and the inherent particle reactivity of the elements. For example, concentration spikes in zinc are seen in Baltimore Harbor, Susquehanna Flats and the Elizabeth River. In contrast, chromium is elevated in Baltimore Harbor and Susquehanna Flats, but the Elizabeth River is no different than other tributaries in the immediate area. Metals concentrations were elevated at the one station in the vicinity of Hart Miller Island.

73

**Chesapeake Bay Mainstem Total PCBs** 



Figure 17a. Concentration of measured PCBs in the Chesapeake Bay mainstem. Selected locations are noted. Horizontal line indicates ERL concentration.

**Chesapeake Bay Embayments Total PCBs** 



Figure 17b. Concentration of measured PCBs in Chesapeake Bay embayments. Selected locations are noted. Horizontal line indicates ERL concentration.

### **Chesapeake Bay Tributaries Total PCBs**



Figure 17c. Concentration of measured PCBs in Chesapeake Bay tributaries. Selected locations are noted. Horizontal line indicates ERL concentration.

	Station								
Chlorination	23	203	204	205	206				
di	0.17	0.75	1.00	0.66	1.26				
tri	5.10	5.04	5.35	5.02	3.87				
tetra	14.31	21.19	14.92	23.03	12.80				
penta	15.35	18.48	21.55	19.28	26.68				
hexa	22.46	28.71	32.88	29.63	38.93				
hepta	29.88	22.68	20.84	20.06	12.73				
octa	2.75	1.64	1.64	1.53	1.71				
nona	4.68	0.95	1.14	0.20	1.10				
deca	5.30	0.55	0.67	0.58	0.93				

Table 6. Percent homolog distribution of PCBs in Baltimore Harbor and the Elizabeth River.

Table 7. Concentrations (ng/kg) of planar PCBs detected in Chesapeake Bay sediments in 1998. Stations sampled were; 1, 4, 7, 8, 10, 15, 21, 23, 30, 34, 37, 40, 44, 46, 51, 53, 58, 61, 62, and 63.

Site	10	flag	21	flag	23	flag	53	flag
PCB81	15	J <sup>a</sup>	17	J	97		64	
PCB77	51		10	J	104		6	J
PCB126		ND <sup>b</sup>	41		14	J		ND
PCB169		ND		ND	7	J		ND

<sup>a</sup> J= below minimum detection limit <sup>b</sup> ND=not detected

# **Chesapeake Bay Mainstem Metals**



Figure 18a. Mean normalized concentrations of 15 elements (from bottom to top Ag, Al, As, Cd, Cr, Cu, Fe, Hg, Ni, Pb, Sb, Se, Sn, Tl, Zn) in the Chesapeake Bay mainstem. Selected locations are noted.

### **Chesapeake Bay Embayments Metals**



Figure 18b. Mean normalized concentrations of 15 elements (from bottom to top Ag, Al, As, Cd, Cr, Cu, Fe, Hg, Ni, Pb, Sb, Se, Sn, Tl, Zn) in Chesapeake Bay embayments. Selected locations are noted.

### **Chesapeake Bay Tributary Metals**



Figure 18c. Mean normalized concentrations of 15 elements (from bottom to top Ag, Al, As, Cd, Cr, Cu, Fe, Hg, Ni, Pb, Sb, Se, Sn, Tl, Zn) in Chesapeake Bay tributaries. Selected locations are noted.

The distribution of pesticides varied between the types of compound. The insecticide DDT was found throughout the Bay, including the mainstem (Fig. 19). DDT was consistently found at higher concentrations in Susquehanna Flats and Baltimore Harbor, the Potomac River and the Elizabeth River. Isolated spikes were seen in other tributaries. Cyclodiene insecticides (chlordanes, heptachlors, nonachlors, aldrin, dieldrin, endrin and endosulfan) were also found throughout the Bay but were only found at high concentrations in the Elizabeth River, primarily in the east branch (Fig. 20). In contrast, hexachlorocyclohexane (HCH, includes lindane) concentrations were elevated in the Patuxent, Potomac, and Eastern Shore tributaries and embayments but not in the upper Bay or the Elizabeth River (Fig. 21). None of the concentrations were above 5ug/kg, including the isolated spike in the deep trough. Chlorinated benzenes are used as fungicides and insecticides. They were found throughout the Bay, but most of the higher concentrations were in the northern Bay and tributaries. Baltimore Harbor had the highest concentration. No station was at or above 6 ug/kg (Fig. 22). Mirex was only rarely above detection limits and was never at or above 0.5ug/kg. Chlorpyrifos was frequently below detection limits, with a peak concentration of 1.6 ug/kg in the Elizabeth River Eastern Branch (Fig. 23).

Butyltins were detected throughout the Bay (Fig. 24). Concentrations in the Susquehanna flats, while elevated compared to the lower mainstem sites, were not typically as high as several of the tributary stations. Most stations were below 10ug/kg Sn. Large spikes of butyltins were detected in isolated stations in the mainstem near Hart Miller Island, the Potomac River , the Rappahannock River, and the Elizabeth River. Tributyltin (TBT) was the dominant compound in most cases. Ninety nine stations did not exceed any ERLs. The top 10<sup>th</sup> percentile (24 stations) of all stations exceeded 7 or more ERLs (Table 8). Virtually all of these stations were found in the Elizabeth River, Baltimore Harbor, and the Susquehanna Flats or the deep trough. The exceptions were station 81 near the Patuxent Naval Air Base, station 47 located south of Deale MD, stations 83 and 91 which were located in deep areas in the middle of the Potomac River, station 28 in the Magothy River, and station 170 far up a small feeder to the Rappahannock River. Exceedances of the DDT ERL were common, but the DDT ERM was only exceeded in the Elizabeth River. Nine stations had ERM exceedances, including two that were not in the top 10<sup>th</sup> percentile for ERL exceedances. The ERM quotient (ERM-Q) ranged from

82



### **Chesapeake Bay Mainstem Total DDT**

Figure 19a. Concentrations of DDT and metabolites in the Chesapeake Bay mainstem. Selected locations are noted. Horizontal line indicates the ERL concentration for total DDTs.



# **Chesapeake Bay Embayments Total DDT**

Figure 19b. Concentrations of DDT and metabolites in Chesapeake Bay embayments. Selected locations are noted. Horizontal line indicates the ERL concentration for total DDTs.


#### **Chesapeake Bay Tributaries Total DDT**

Figure 19c. Concentrations of DDT and metabolites in Chesapeake Bay embayments. Selected locations are noted. Horizontal lines indicate the ERL and ERM concentrations for total DDTs.

**Chesapeake Bay Tributaries Total DDT** 



# **Chesapeake Bay Mainstem Total Cyclodienes**

Figure 20a. Concentrations of chlordanes and related cyclodienes in the Chesapeake Bay mainstem. Selected locations are noted. .



# **Chesapeake Bay Embayments Total Cyclodienes**

Figure 20b. Concentrations of chlordanes and related cyclodienes in Chesapeake Bay embayments. Selected locations are noted.



# **Chesapeake Bay Tributaries Total Cyclodienes**

Figure 20c. Concentrations of chlordanes and related cyclodienes in Chesapeake Bay tributaries. Selected locations are noted.

# **Chesapeake Bay Mainstem Total HCH**



Figure 21a. Concentrations of total HCH in the Chesapeake Bay mainstem. Selected locations are noted.



# **Chesapeake Bay Embayments Total HCH**

Figure 21b. Concentrations of total HCH in Chesapeake Bay embayments. Selected locations are noted.

# **Chesapeake Bay Tributaries Total HCH**



Figure 21c. Concentrations of total HCH in Chesapeake Bay tributaries. Selected locations are noted.



# **Chesapeake Bay Mainstem Total Chlorinated Benzenes**

Figure 22a. Concentrations of chlorinated benzenes in the Chesapeake Bay mainstem. Selected locations are noted.



# **Chesapeake Bay Embayments Total Chlorinated Benzenes**

Figure 22b. Concentrations of chlorinated benzenes in Chesapeake Bay embayments. Selected locations are noted.



# **Chesapeake Bay Tributaries Total Chlorinated Benzenes**

Figure 22c. Concentrations of chlorinated benzenes in Chesapeake Bay tributaries. Selected locations are noted.



# **Chesapeake Bay Mainstem Chlorpyrifos**

Figure 23a. Concentrations of chlorpyrifos in the Chesapeake Bay mainstem. Selected locations are noted.

# **Chesapeake Bay Embayments Chlorpyrifos**



Figure 23b. Concentrations of chlorpyrifos in Chesapeake Bay embayments. Selected locations are noted.

# **Chesapeake Bay Tributaries Chlorpyrifos**



Figure 23c. Concentrations of Chlorpyrifos in Chesapeake Bay tributaries. Selected locations are noted.



Figure 24a. Concentrations of total Butyltins (bars) and TBT (diamonds) in the Chesapeake Bay mainstem. Selected locations are noted. .

#### **Chesapeake Bay Embayments Butyltins**



Figure 24b. Concentrations of total Butyltins (bars) and TBT (diamonds) in Chesapeake Bay embayments. Selected locations are noted.

#### **Chesapeake Bay Tributary Butyltins**



Figure 24c. Concentrations of total Butyltins (bars) and TBT (diamonds) in Chesapeake Bay tributaries. Selected locations are noted.

Table 8. Chesapeake Bay stations with seven or more ERL exceedances ( $90^{th}$  percentile) and/or ERM exceedances, including specific chemicals. Mean ERM-Qs are also shown. (Zone T= tributary, M=mainstem, E=embayment)

Stratum	Station	Zone	# ERLs	# ERMs	ERM chemical	ERM-Q
64	206	Т	21	3	LW PAHs, HW PAHs, Dibenzo(a,h)Anthracene	0.72
63	205	Т	20	1	total DDT	0.49
63	204	Т	18	0		0.41
63	203	Т	17	1	LW PAHs	0.58
7	23	Т	14	1	Zn	0.54
11	39	М	12	0		0.24
64	207	Т	11	0		0.23
2	6	М	10	0		0.23
6	19	Е	9	0		0.29
5	15	М	9	0		0.27
1	1	Т	9	0		0.22
4	10	Т	9	0		0.22
4	12	Т	9	0		0.25
23	81	Т	9	0		0.20
8	29	М	8	1	Zn	0.27
8	27	М	8	0		0.21
3	9	Т	8	0		0.20
62	201	Т	8	0		0.21
6	20	М	7	1	Zn	0.29
13	47	М	7	1	Ag	0.32
2	5	М	7	0		0.20
3	7	Т	7	0		0.19
24	83	Т	7	0		0.18
27	91	Т	7	0		0.17
8	28	Т	6	1	Zn	0.33
52	170	Т	3	1	4,4-DDE	0.13

0.0 to 0.72. Many locations exceeded a mean ERM quotient of 0.1. More than half of the tributary stations had elevated ERM quotients. The 90<sup>th</sup> percentile mean ERM-Q was 0.2. Only seven stations exceeded a mean ERM-Q of 0.3 (Fig. 25). These stations were either in Baltimore Harbor or the Elizabeth River, plus one station (#28) in the Magothy River and one station (#47) in the mainstem below Deale, Md. The Magothy River had several elevated metals. Station #47 had a very high concentration of silver but was otherwise very similar to adjacent stations. The highest value was at station 206 in the industrialized south branch Elizabeth River, but all the stations in the residential east branch were high as well.

#### SEDIMENT TOXICITY

Most of the bioassay toxic responses were seen at stations from the Susquehanna Flats and the tributaries, however this was test-specific. Only 19 stations showed significant effects in the amphipod bioassay, and most of these were in the area between Kent and Tilghman Islands (Fig. 26). None of the amphipod bioassays resulted in >20% mortality relative to controls. In contrast, 73 of the pore water bioassays were significant and 69 of those showed >20% effect (Fig. 27). The HRGS P450 bioassay showed responses at most of the stations in the Susquehanna Flats, the deep trough, the Potomac, and Elizabeth Rivers, and some other scattered sites (Fig. 28). Nine of the P450 values were at or above the threshold value of 60ug B[a]P equivalents.

In the 1999 sampling year, additional P450 tests were performed with 6 and 16 hr incubations to assess the relative contribution of PAHs vs chlorinated compounds at those stations with the highest observed B[a]P equivalents (Table 9). All tests showed significant reduction in induction except stations 79 and 99. These tests were repeated with diluted samples to test for the possible effect of excessive PAH that can overwhelm the cell's ability to metabolize them. This indicates that planar PCBs (or other unmeasured inducers) were not a significant cause of the P450 response.

Using the individual bioassay results, the spatial extent of impaired habitat varied widely depending on the selected bioassay (Tables 10 and 11). Based on strata areas, the cumulative spatial extent of marginally impaired habitat (threshold response relative to controls) in Chesapeake Bay ranged from 0.8 to 21.2%. The spatial extent of highly impaired habitat



Figure 25. Distribution of mean ERM quotient values in Chesapeake Bay sediments.



Figure 26. Distribution of amphipod bioassay responses in whole sediment toxicity bioassays for Chesapeake Bay.



Figure 27. Distribution of sea urchin fertilization bioassay responses in sediment pore water toxicity bioassays for Chesapeake Bay.



Figure 28. Distribution of P450 bioassay responses in sediment extract toxicity bioassays for Chesapeake Bay.

Table 9. B[a]P equivalents from HRGS P450 bioassays using two incubation times.

Station	6hr BaPeq	16hr B[a]Peq
79	73.8	36.3
79(1:4)	215.8	26.7
81	112.3	27.6
83	152.1	13.5
84	114.7	9.4
85	89.7	10.4
91	97.8	10.0
99	95.8	87.6
99(1:4)	255.2	61.3

STRATUM	Total area*	Amphipod Mortality	P450 B[a]Peq	SeaUrchin Fertilization	STRATUM	Total area*	Amphipod Mortality	P450 B[a]Peq	SeaUrchin Fertilization
1	75.9	0.0	75.9	0.0	34	41.0	0.0	0.0	0.0
2	92.1	0.0	30.7	0.0	35	371.0	0.0	18.9	0.0
3	39.0	0.0	13.0	0.0	36	28.1	0.0	0.0	0.0
4	36.8	0.0	24.5	12.3	37	27.7	0.0	0.0	0.0
5	250.0	50.0	250.0	0.0	38	56.6	0.0	12.4	0.0
6	247.6	0.0	198.1	0.0	39	21.9	0.0	0.0	0.0
7	44.0	0.0	22.0	0.0	40	197.1	0.0	0.0	0.0
8	132.1	0.0	99.1	0.0	41	53.9	0.0	0.0	0.0
9	97.3	24.3	24.3	0.0	42	444.6	0.0	0.0	0.0
10	109.8	54.9	27.5	0.0	43	837.2	0.0	0.0	0.0
11	66.3	22.1	22.1	0.0	44	426.0	0.0	106.5	0.0
12	95.3	47.6	23.8	0.0	45	254.5	0.0	0.0	0.0
13	133.6	66.8	66.8	0.0	46	209.7	0.0	0.0	0.0
14	108.1	36.0	108.1	0.0	47	253.1	0.0	0.0	0.0
15	102.7	68.4	0.0	0.0	48	31.7	0.0	0.0	0.0
16	146.3	97.5	0.0	0.0	49	168.3	0.0	56.1	0.0
17	154.2	0.0	30.8	0.0	50	73.1	0.0	0.0	0.0
18	95.4	26.5	0.0	0.0	51	26.2	0.0	0.0	0.0
19	324.0	0.0	108.0	0.0	52	100.6	0.0	0.0	0.0
20	412.2	0.0	137.4	0.0	53	66.3	0.0	0.0	0.0
21	46.2	0.0	0.0	0.0	54	49.4	0.0	0.0	16.5
22	34.3	0.0	0.0	0.0	55	48.1	0.0	0.0	0.0
23	18.6	0.0	82.3	0.0	56	46.8	0.0	0.0	0.0
24	105.9	0.0	176.9	0.0	57	30.2	0.0	10.1	0.0
25	79.0	0.0	28.5	0.0	58	42.0	0.0	0.0	0.0
26	69.3	29.5	29.5	0.0	59	46.3	15.4	0.0	15.4
27	177.1	0.0	92.4	0.0	60	27.4	0.0	9.1	0.0
28	85.4	0.0	47.1	0.0	61	86.7	0.0	0.0	28.9
29	371.5	0.0	0.0	0.0	62	33.2	0.0	0.0	0.0
30	519.8	0.3	0.0	0.0	63	5.7	0.0	3.8	0.0
31	123.5	13.7	0.0	0.0	64	6.5	0.0	2.2	0.0
32	235.8	0.0	0.0	0.0	65	119.5	0.0	0.0	0.0
33	259.8	0.0	0.0	0.0	Total km	9119.5	553.3	1937.9	73.1
					%		6.1	21.2	0.8

Table 10. Spatial extent (km<sup>2</sup>) of areas where bioassays demonstrated significant response in Chesapeake Bay sediments.

\*strata area adjusted for alternate site selection

STRATUM	Total area*	Amphipod Mortality	P450 B[a]Peq	Sea Urchin Fertilization	STRATUM	Total area*	Amphipod Mortality	P450 B[a]Peq	Sea Urchin Fertilization
1	75.9	0.0	0.0	0.0	34	41.0	0.0	0.0	0.0
2	92.1	0.0	61.4	92.1	35	371.0	0.0	0.0	0.0
3	39.0	0.0	13.0	13.0	36	28.1	0.0	0.0	0.0
4	36.8	0.0	12.3	12.3	37	27.7	0.0	0.0	0.0
5	250.0	0.0	0.0	200.0	38	56.6	0.0	0.0	0.0
6	247.6	0.0	0.0	0.0	39	21.9	0.0	0.0	14.6
7	44.0	0.0	22.0	22.0	40	197.1	0.0	0.0	65.7
8	132.1	0.0	0.0	33.0	41	53.9	0.0	0.0	0.0
9	97.3	0.0	0.0	0.0	42	444.6	0.0	0.0	222.3
10	109.8	0.0	0.0	27.5	43	837.2	0.0	0.0	669.7
11	66.3	0.0	22.1	44.2	44	426.0	0.0	0.0	106.5
12	95.3	0.0	0.0	47.6	45	254.5	0.0	0.0	0.0
13	133.6	0.0	0.0	66.8	46	209.7	0.0	0.0	69.9
14	108.1	0.0	0.0	36.0	47	253.1	0.0	0.0	0.0
15	102.7	0.0	0.0	68.4	48	31.7	0.0	0.0	0.0
16	146.3	0.0	0.0	0.0	49	168.3	0.0	0.0	0.0
17	154.2	0.0	0.0	30.8	50	73.1	0.0	0.0	36.6
18	95.4	0.0	0.0	0.0	51	17.5	0.0	0.0	8.7
19	324.0	0.0	0.0	216.0	52	100.6	0.0	0.0	42.3
20	412.2	0.0	0.0	137.4	53	66.3	0.0	0.0	22.1
21	46.2	0.0	0.0	0.0	54	49.4	0.0	0.0	33.0
22	34.3	0.0	0.0	22.9	55	48.1	0.0	0.0	0.0
23	18.6	0.0	0.0	0.0	56	46.8	0.0	0.0	15.6
24	105.9	0.0	0.0	70.6	57	30.2	0.0	0.0	20.2
25	79.0	0.0	0.0	0.0	58	42.0	0.0	0.0	14.0
26	69.3	0.0	0.0	69.3	59	46.3	0.0	0.0	15.4
27	177.1	0.0	0.0	177.1	60	27.4	0.0	0.0	9.1
28	85.4	0.0	0.0	56.9	61	86.7	0.0	0.0	0.0
29	371.5	0.0	123.8	0.0	62	33.2	0.0	0.0	33.2
30	519.8	0.0	0.0	0.0	 63	5.7	0.0	0.0	0.0
31	123.5	0.0	0.0	0.0	 64	6.5	0.0	2.2	2.2
32	235.8	0.0	0.0	0.0	 65	119.5	0.0	0.0	119.5
33	259.8	0.0	0.0	0.0	Total km	9119.5	0.0	256.8	2964.7
					%		0.0	2.82	32.51

Table 11. Spatial extent (km<sup>2</sup>) of areas where bioassays demonstrated probable toxicity in Chesapeake Bay sediments.

\*strata area adjusted for alternate site selection

(statistically significant toxic response) ranged from zero to 32.6%. Most of the elevated P450 bioassays yielded marginal results, whereas most of the significant pore water bioassays yielded high level results. The amphipod bioassays showed fewer significant results than either of the other tests, and none indicated highly toxic conditions. Summary results are illustrated on a regional basis in Figure 29. The combined scores are dominated by the pore water bioassay. Given that the series of bioassays were conducted over a three year period, the spatial and temporal consistency of the results, and the relative agreement with the general patterns of contaminant concentrations, indicate a high degree of reliability in the results. The distribution of the integrated toxicity score values are mapped in Figure 30.

#### BENTHIC COMMUNITY CHARACTERIZATION

A complete species listing for all sites including abundance data is available from NOAA. A total of 20,609 organisms, representing 287 taxa were enumerated. Following elimination of epiphytes and the 'artificial' species there were 209 taxa and 19,607 organisms (Table 12). Polychaetes were the most dominant group, both in terms of abundance and number of taxa. Virtually all of the Oligochaetes were Tubificids, but most were not identified beyond family level. Bivalves were the next most abundant taxa, but were characterized by very high numbers of a relatively few species. The same was true for gastropods. The vast majority of Malacostracans were Amphipods. Approximately half of the miscellaneous organisms were either Rhynchocoels or Branchiostomidae (*Amphioxus*). The most widespread taxa are listed in Table 13. The list is dominated by Polychaete worms. Rhynchocoels would appear to be more widespread, but that is an artifact of them seldom being keyed out below family level. The same is true for the Tubificids. The most numerous taxa were mollusks and polychaetes (Table 14).

Specific stations would occasionally contain high numbers of a particular species. For example, station 90 held 77,200 *Gemma gemma* /m<sup>2</sup> and 31,650 *Odostomia* sp. /m<sup>2</sup>. Seventy nine percent of all the *G. gemma* in the collection came from that one station. Species richness is shown in Figure 31. Variation in species richness did not follow the patterns seen in contaminant concentrations. The region where the Bay is constricted west of Kent Island and south of the Bay Bridge has a generally low species richness. This area is dominated by deep trough habitats and

# **Chesapeake Bay Mainstem Toxicity Scores**



Figure 29a. Toxicity response scores from sediment bioassays of the Chesapeake Bay mainstem.

# **Chesapeake Bay Embayments Toxicity Scores**



Figure 29b. Toxicity response scores from sediment bioassays of Chesapeake Bay embayments.



#### Chesapeake Bay Tributary Toxicity Scores

Figure 29c. Toxicity response scores from sediment bioassays of Chesapeake Bay tributaries. .



Figure 30. Distribution of toxicity score values in Chesapeake Bay sediments. Color scale represents percentile rank.

Taxa	All Data	W/O Epiphytes	W/O Rare and	
		& Artificial taxa	Unique taxa	
Polychaetes	110	84	51	
	(7,089)	(7,025)	(6,856)	
Oligochaetes	8	6	6	
	(1,741)	(1,670)	(1,670)	
Gastropods	30	20	9	
	(3,042)	(2,943)	(2,902)	
Bivalves	31	24	13	
	(5,486)	(5,257)	(5,092)	
Malacostracans	70	51	31	
	(1,843)	(1,787)	(1,692)	
Amphipods	44	32	19	
	(1,316)	(1,265)	(1,222)	
Misc	38	24	16	
	(1,374)	(925)	(888)	
Total	287	209	126	
	(20,609)	(19,607)	(19,100)	

Table 12. Number of species and abundance () after various manipulations of the benthic community data set.

Table 13. List of the most widespread taxa found in Chesapeake Bay sediments. (LPIL indicates lowest possible identification level)

# Stations	Phylum	Class	Taxa Name
112	Rhynchocoela	Anopla	LINEIDAE (LPIL)
100	Annelida	Polychaeta	MEDIOMASTUS (LPIL)
96	Annelida	Polychaeta	PARAPRIONOSPIO PINNATA
95	Annelida	Polychaeta	GLYCINDE SOLITARIA
94	Annelida	Polychaeta	NEREIS SUCCINEA
89	Annelida	Oligochaeta	TUBIFICIDAE (LPIL)
84	Mollusca	Gastropoda	ACTEOCINA CANALICULATA
66	Annelida	Polychaeta	STREBLOSPIO BENEDICTI
55	Annelida	Polychaeta	LOIMIA MEDUSA
54	Annelida	Polychaeta	HETEROMASTUS FILIFORMIS
49	Annelida	Polychaeta	LEITOSCOLOPLOS (LPIL)
43	Annelida	Polychaeta	NEREIDIDAE (LPIL)
41	Arthropoda	Malacostraca	LISTRIELLA BARNARDI
38	Annelida	Oligochaeta	TUBIFICOIDES (LPIL)
35	Mollusca	Gastropoda	ODOSTOMIA (LPIL)
34	Annelida	Polychaeta	SPIOCHAETOPTERUS OCULATUS
33	Arthropoda	Malacostraca	LEUCON AMERICANUS
30	Mollusca	Bivalvia	GEMMA GEMMA
30	Arthropoda	Malacostraca	CYATHURA POLITA
29	Mollusca	Bivalvia	TELLINA AGILIS
29	Chordata	Leptocardia	BRANCHIOSTOMA (LPIL)
25	Arthropoda	Malacostraca	LEPTOCHEIRUS PLUMULOSUS
25	Arthropoda	Malacostraca	EDOTEA TRILOBA
25	Annelida	Polychaeta	MARENZELLERIA VIRIDIS
25	Annelida	Polychaeta	PECTINARIA (LPIL)

Total	#	l	I	
abundance	# Stations	Phylum	Class	Taxa Name
3916	30	Mollusca	Bivalvia	GEMMA GEMMA
1676	100	Annelida	Polychaeta	MEDIOMASTUS (LPIL)
1459	35	Mollusca	Gastropoda	ODOSTOMIA (LPIL)
1296	84	Mollusca	Gastropoda	ACTEOCINA CANALICULATA
1063	89	Annelida	Oligochaeta	TUBIFICIDAE (LPIL)
835	96	Annelida	Polychaeta	PARAPRIONOSPIO PINNATA
761	66	Annelida	Polychaeta	STREBLOSPIO BENEDICTI
593	25	Arthropoda	Malacostraca	LEPTOCHEIRUS PLUMULOSUS
514	94	Annelida	Polychaeta	NEREIS SUCCINEA
504	22	Mollusca	Bivalvia	RANGIA CUNEATA
376	95	Annelida	Polychaeta	GLYCINDE SOLITARIA
318	5	Annelida	Polychaeta	THARYX ACUTUS
302	20	Mollusca	Bivalvia	TELLINA (LPIL)
278	15	Annelida	Polychaeta	POLYDORA CORNUTA
276	112	Rhynchocoela	Anopla	LINEIDAE (LPIL)
271	55	Annelida	Polychaeta	LOIMIA MEDUSA
250	54	Annelida	Polychaeta	HETEROMASTUS FILIFORMIS
249	38	Annelida	Oligochaeta	TUBIFICOIDES (LPIL)
246	29	Chordata	Leptocardia	BRANCHIOSTOMA (LPIL)
223	8	Annelida	Oligochaeta	LUMBRICULIDAE (LPIL)
173	43	Annelida	Polychaeta	NEREIDIDAE (LPIL)
169	30	Arthropoda	Malacostraca	CYATHURA POLITA
140	13	Annelida	Polychaeta	CIRRATULIDAE (LPIL)
139	41	Arthropoda	Malacostraca	LISTRIELLA BARNARDI
124	49	Annelida	Polychaeta	LEITOSCOLOPLOS (LPIL)

Table 14. List of the 25 most abundant taxa, and the number of stations where they were found in Chesapeake Bay sediments. Abundance is the cumulative number of animals taken in 0.04m<sup>2</sup> grabs. (LIPL indicates lowest possible identification level.)

**Chesapeake Bay Mainstem Species Richness** 



Figure 31a. Number of taxa in the Chesapeake Bay mainstem. Selected locations are noted. .

# **Chesapeake Bay Embayments Species Richness**



Figure 31b. Number of taxa in Chesapeake Bay embayments. Selected locations are noted.

# **Chesapeake Bay Tributaries Species Richness**



Figure 31c. Number of taxa in Chesapeake Bay tributaries. Selected locations are noted.
the associated low oxygen stress. In other areas, species richness is site specific from one location to the next. Abundance varied by several orders of magnitude, even in adjacent sampling stations (Fig. 32). Abundance does follow the pattern of species richness to some extent, in that the deep trough region had generally low values. In other areas abundance varied seemingly arbitrarily, being driven by salinity, grain size, and other local conditions. For example, the deep central stations in the Potomac River tended to have low numbers of species and low abundance. Sandbars in the upper reaches of the Bay had low numbers of species and abundance, while sandbars in the lower Bay had medium to high species richness and abundance.

Diversity (Fig. 33) and evenness (Fig. 34) are indices derived from abundance and number of taxa. Both reflect the highly variable species richness and abundance data. At those stations with elevated numbers of a particular species, diversity and evenness are very low, even though the habitat apparently supports a vigorous, if asymmetrical, community. Excluding zero and one species stations, the mean diversity index for the mainstem, embayments and tributaries were 1.73, 1.80, and 1.52 respectively. All zones had standard deviations between 0.5 and 0.7.

Rare and unique taxa were not randomly distributed. Only a few cases of rare or unique taxa were found in tributaries. Scattered locations, mostly in the lower mainstem, had rare and unique taxa. Most of the rare and unique taxa were found at the confluence of the Susquehanna River and the Bay, and at the mouth of the Bay in the vicinity of Norfolk (Table 15). These areas are the transition points between major ecological systems and a mixture of species at the edges is to be expected.

The distribution of species is clearer when viewed on a stratum by stratum basis (Fig. 35). Considered this way, Susquehanna Flats and the upper Bay strata are fairly similar. The low values in the western tributaries correspond to the deep areas in the Patuxent, Potomac, and Rappahannock Rivers. The lowest value in the James River was from stratum 60 at the uppermost set of samples (Fig. 4). The deep area of the channel in the upstream portion of the James River (stratum 49) was not sampled by chance, due to the randomized site selection process. The lowest values in the Bay are from the central deep trough. The highest values are

121



# **Chesapeake Bay Mainstem Species Abundance**

Figure 32a. Species abundance in the Chesapeake Bay mainstem. Selected locations are noted.

#### **Chesapeake Bay Embayments Species Abundance**



Figure 32b. Species abundance in Chesapeake Bay embayments. Selected locations are noted.



**Chesapeake Bay Tributaries Abundance** 

Figure 32c. Species abundance in Chesapeake Bay tributaries. Selected locations are noted.



#### Chesapeake Bay Mainstem Species Diversity

Figure 33a. Species diversity in the Chesapeake Bay mainstem. Selected locations are noted.



# Chesapeake Bay Embayments Species Diversity

Figure 33b. Species diversity in Chesapeake Bay embayments. Selected locations are noted.



#### Chesapeake Bay Tributaries Species Diversity

Figure 33c. Species diversity in Chesapeake Bay tributaries. Selected locations are noted.



# **Chesapeake Bay Mainstem Species Evenness**

Figure 34a. Species evenness in the Chesapeake Bay mainstem. Selected locations are noted.



# **Chesapeake Bay Embayments Species Evenness**

Figure 34b. Species evenness in Chesapeake Bay embayments. Selected locations are noted.



# **Chesapeake Bay Tributaries Species Evenness**

Figure 34c. Species evenness in Chesapeake Bay tributaries. Selected locations are noted.

Table 15. Number of unique (occurring at only one station) and rare (occurring at only two stations) taxa in Chesapeake Bay sediment samples.

Site	Unique	Rare	Total
1		1	1
2	2	1	3
3	1	2	3
4	1	1	2
5		2	2
9	3	1	4
11	1		1
13	1		1
24		1	1
46		1	1
57		1	1
66		1	1
70	1		1
100	1		1
103	1		1
110		1	1
111	1		1
113	1		1
114		1	1
115	1		1
130		1	1
134	1	1	2
135	1		1
136		2	2
138	1		1
139	1		1
143		1	1
144	1	2	3
146	1	1	2
148		1	1
149	1		1
150		3	3
151	3	3	6
152	1		1
154	8	3	11

Site	Unique	Rare	Total
156	1	3	4
157		2	2
159		2	2
160	1	5	6
161	2	1	3
162	3	8	11
163		4	4
164		3	3
167		1	1
175		1	1
176	1		1
186		1	1
187	1		1
191	3		3
201		1	1
207	1		1
210		1	1
211	5	3	8

# **Chesapeake Bay Strata Species Richness**



Figure 35. Species richness in Chesapeake Bay sampling strata. Strata are arranged by region.

near the mouth of the Bay where there is a mixture of estuarine and oceanic taxa. Abundance by strata generally follows the same outline, but with greater variability between strata (Fig. 36)

Mean diversity and evenness by strata are shown in Figures 37 and 38. Strata with mean diversity values below 1 were Baltimore Harbor (stratum 7), two in the lower Potomac (strata 26 and 27) two in the deep trough (strata 11 and 14), and an eastern shore stratum (stratum 15) which abuts the deep trough on the east side of the mainstem.

#### CONCORDANCE OF SEDIMENT QUALITY TRIAD METRICS

Correlation of the toxicity results with individual chemical contaminants yielded different results between the toxicity bioassays. Amphipod toxicity did have statistically significant correlation with several of the trace elements (Table 16) although the coefficients were relatively low. Many of the chlorinated pesticides and PCBs showed significant correlation with toxicity, but most of these correlations were negative, indicating little cause and effect interaction. Only a few of the PAHs were correlated with amphipod toxicity (Table 17), and again, some of these were negative. In contrast, the sea urchin and P450 bioassays demonstrated highly significant positive correlation with almost every compound and trace element.

The community parameters of species richness, abundance and diversity were negatively correlated with virtually every chemical constituent (Table 18 and 19). Most of the correlations were highly significant. In contrast, evenness demonstrated almost no significant correlations with the contaminants.

Condensing the contaminant data into chemical groups and classes yields a similar, but simpler, view of the correlations (Table 20). The amphipod bioassay results were correlated with pesticide concentrations, but the correlations were negative. The correlation with total metals was positive, but not significant, at the 0.05 level. The P450 and sea urchin results were highly significantly correlated with every contaminant group, as was the overall toxicity response index. The community attributes of species richness, abundance, and diversity were significantly, and negatively correlated with all but one of the contaminant groups. Evenness was only significantly correlated with HCH, and this was a positive correlation.

# 700 Northern Bay Western Tributaries Western Eastern Shore Mouth Norfolk Central/ Shore Deep 4,418 850 600 500 Number of Organisms **400** 300 200 100 0

#### **Chesapeake Bay Strata Abundance**

Figure 36. Species abundance in Chesapeake Bay sampling strata. Strata are arranged by region.



# **Chesapeake Bay Strata Species Diversity**

Figure 37. Species diversity in Chesapeake Bay sampling strata. Strata are arranged by region.



# **Chesapeake Bay Strata Species Evenness**

Figure 38. Species evenness in Chesapeake Bay sampling strata. Strata are arranged by region.

Contaminant	Amphipod Toxicity	HRGS B[a]P Equivalents	Sea Urchin Fertilization	Toxicity Response
Ag	0.12133	0.65765**	0.56414**	0.6435**
Al	0.03431	0.51952**	0.59111**	0.60377**
As	0.09329	0.6038**	0.53776**	0.58335**
Cd	0.141*	0.72213**	0.62723**	0.71361**
Cr	0.16979*	0.59209**	0.55509**	0.63601**
Cu	0.15628*	0.66756**	0.56851**	0.66492**
Fe	0.10508	0.52812**	0.5223**	0.57752**
Hg	0.13797	0.6282**	0.52232**	0.62899**
Mn	0.1531*	0.55814**	0.46045**	0.54877**
Ni	0.1882**	0.66679**	0.53507**	0.6425**
Pb	0.08326	0.67297**	0.52528**	0.59582**
Sb	0.17589*	0.63256**	0.38728**	0.49877**
Sn	0.08084	0.69282**	0.52067**	0.62305**
Tl	0.05522	0.51843**	0.59748**	0.59629**
Zn	0.16681*	0.64878**	0.52658**	0.63023**
Alpha HCH	-0.32763	0.23202**	0.23661**	0.15669*
Beta HCH	-0.15229*	0.00844	0.19388**	0.10355
Delta HCH	-0.07296	0.21969**	0.26705**	0.26856**
Gamma HCH	-0.11496	0.1803**	0.03551	0.02895
Heptachlor	-0.02704	0.0299	0.06753	0.06099
Heptachlor epoxide	-0.15778*	-0.07952	0.05598	-0.03639
Oxychlordane	-0.03127	0.00082	0.18251**	0.16301*
Alphachlordane	-0.22003**	0.31958**	0.26876**	0.28781**
Gamma Cholrdane	-0.09767	0.29379**	0.21044**	0.23179**
Cis-Nonachlor	-0.11286	0.33482**	0.38004**	0.39606**
Trans-Nonachlor	-0.1451*	0.36733**	0.38446**	0.38771**
Aldrin	0.09528	0.24758**	0.09349	0.1402*
Dieldrin	-0.09887	0.23382**	0.33947**	0.3301**
Endrin	0.06563	0.09891	0.14131*	0.19402**

Table 16. Spearman-rank correlation coefficients and significance level between sediment toxicity tests and trace elements, chlorinated pesticides, butyl tins, and PCBs.

Mirex	-0.08857	0.02654	0.2083**	0.1568*
Endosulfan	0.0109	0.24623**	0.09084	0.16549*
Chlorpyrofos	-0.18154*	0.14385*	0.25728**	0.20608**
2,4' DDD	-0.21631**	0.1238	0.23551**	0.19007**
2,4' DDE	-0.2366**	0.25095**	0.23946**	0.20454**
2,4' DDT	-0.23015**	0.13464	0.32**	0.25522**
4,4' DDD	-0.1604*	0.50597**	0.36062**	0.39457**
4,4' DDE	-0.14844*	0.58575**	0.48264**	0.51034**
4,4' DDT	-0.18803**	0.38109**	0.33197**	0.34506**
Tetrachlorobenzene 1,2,3,4	-0.13264	0.43496**	0.28727**	0.3034**
Tetrachlorobenzene 1,2,4,5	-0.05126	0.39232**	0.20374**	0.24485**
Pentachlorobenzene	0.00388	0.65179**	0.40169**	0.47562**
Hexachlorobenzene	-0.15715*	0.28483**	0.2542**	0.27935**
Total Butyl Tins	0.11662	0.6824**	0.52246**	0.59285**
DCD29	0.17946*	0.46024**	0.26507**	0.20008**
PCD28	-0.17840**	0.40934**	0.20397**	0.30008***
PCB44	-0.11565	0.59678**	0.2854**	0.37219**
PCB52	-0.23253**	0.49765**	0.319//**	0.33612**
PCB66	-0.25114**	0.47548**	0.24975**	0.29/91**
PCB105	-0.21901**	0.503**	0.30075**	0.34271**
PCB118	-0.20585**	0.56964**	0.35121**	0.39782**
PCB128	-0.23617**	0.34464**	0.34801**	0.32843**
PCB180	-0.15198*	0.64753**	0.41802**	0.46084**
PCB187	-0.31372	0.46665**	0.30087**	0.31619**
PCB206	0.08846	0.78678**	0.34702**	0.49849**
PCB209	0.05831	0.72908**	0.39292**	0.48834**
PCB101_90	-0.22668**	0.4814**	0.34213**	0.3653**
PCB138_160	0.02563	0.63408**	0.45615**	0.51604**
PCB153_132	-0.17076*	0.58248**	0.41552**	0.4512**
PCB170_190	-0.28025**	0.3576**	0.15436*	0.1518*
PCB18_17	-0.33539	-0.08781	0.18342*	0.05396
PCB195_208	-0.09271	0.68065**	0.30435**	0.39907**
PCB8_5	-0.13186	0.35409**	0.20897**	0.21914**

Table 16 (cont.)

 $\label{eq:posterior} \begin{array}{l} *=0.5 \leq p \geq 0.01 \\ **=p \leq 0.01 \end{array}$ 

Table 17. Spearman-rank correlation coefficients and significance level between sediment toxicity tests and PAHs.

Contaminant	Amphipod Toxicity	HRGS B[a]P Equivalents	Sea Urchin Fertilization	Toxicity Response
Naphthalene	0.18459**	0.74789**	0.49123**	0.63081**
C1-Naphthalenes	0.18189**	0.7577**	0.49625**	0.63904**
C2-Naphthalenes	0.05304	0.7038**	0.52779**	0.61395**
C3-Naphthalenes	0.04144	0.70127**	0.51617**	0.60008**
C4-Naphthalenes	0.01802	0.7145**	0.49914**	0.57536**
Biphenyl	0.10629	0.66728**	0.48569**	0.57875**
Acenaphthylene	-0.00404	0.68388**	0.45691**	0.53572**
Acenaphthene	0.09415	0.73719**	0.52005**	0.63383**
Fluorene	0.04228	0.71616**	0.51409**	0.60821**
C1-Fluorenes	0.01737	0.73334**	0.51933**	0.60504**
C2-Fluorenes	-0.08643	0.65792**	0.53109**	0.56956**
C3-Fluorenes	-0.09009	0.66374**	0.484**	0.52442**
Anthracene	-0.042	0.69216**	0.48355**	0.54798**
Phenanthrene	0.05094	0.71675**	0.48622**	0.58265**
C1-Phenanthrenes/Anthracenes	-0.00359	0.69109**	0.50756**	0.58133**
C2-Phenanthrenes/Anthracenes	-0.04693	0.67044**	0.50851**	0.56742**
C3-Phenanthrenes/Anthracenes	-0.087	0.65521**	0.49667**	0.54157**
C4-Phenanthrenes/Anthracenes	-0.26106**	0.44864**	0.38736**	0.34995**
Dibenzothiophene	-0.00575	0.71343**	0.48965**	0.57316**
C1-Dibenzothiophenes	-0.00208	0.69805**	0.51807**	0.58965**
C2-Dibenzothiophenes	-0.02713	0.69843**	0.51754**	0.57991**
C3-Dibenzothiophenes	-0.02896	0.70922**	0.51274**	0.58096**
Fluoranthene	-0.06358	0.65212**	0.48357**	0.53556**
C1-Fluoranthenes/Pyrenes	-0.08565	0.62292**	0.47668**	0.516**
C2-Fluoranthenes/Pyrenes	0.02144	0.6335**	0.42138**	0.5028**
C3-Fluoranthenes/Pyrenes	-0.01261	0.62213**	0.42278**	0.50434**
Pyrene	-0.05993	0.65483**	0.4865**	0.5387**
Benz(a)anthracene	-0.07396	0.66065**	0.47216**	0.52371**
Chrysene	-0.06546	0.66463**	0.47957**	0.53275**
C1-Chrysenes	-0.07869	0.63355**	0.48746**	0.53637**
C2-Chrysenes	-0.1064	0.649**	0.49502**	0.53845**
C3-Chrysenes	-0.17211*	0.52124**	0.33532**	0.34452**
C4-Chrysenes	-0.11107	0.65548**	0.36763**	0.44053**
Benzo(b)fluoranthene	-0.07145	0.68196**	0.48645**	0.54512**
Benzo(k)fluoranthene	-0.12202	0.58372**	0.48066**	0.49787**
Benzo(e)pyrene	-0.07992	0.65926**	0.48398**	0.53478**

#### Table 17 (cont.)

Benzo(a)pyrene	-0.08103	0.65707**	0.48128**	0.52932**
Perylene	-0.15379*	0.55064**	0.46599**	0.48065**
Indeno(1,2,3-c,d)pyrene	-0.12451	0.59928**	0.48982**	0.51326**
Dibenzo(a,h)anthracene	-0.11545	0.65538**	0.46712**	0.51449**
Benzo(g,h,i)perylene	-0.09659	0.65316**	0.48224**	0.52546**
Additional PAHs				
2,6-Dimethylnaphthalene	0.00531	0.68542**	0.54612**	0.61223**
1-Methylphenanthrene	-0.01365	0.69955**	0.48059**	0.55778**
1-Methylnaphthalene	0.15293*	0.73221**	0.51476**	0.64036**
2-Methylnaphthalene	0.16008*	0.72663**	0.51562**	0.64159**
1,6,7-Trimethylnaphthalene	0.06714	0.76201**	0.5166**	0.6248**

 $\label{eq:point_states} \begin{array}{l} * = 0.5 \leq p \geq 0.01 \\ ** = p \leq 0.01 \end{array}$ 

	Species			
Contaminant	Richness	Abundance	Diversity	Evenness
Ag	-0.53571**	-0.36501**	-0.44885**	-0.12112
Al	-0.51935**	-0.4285**	-0.41716**	-0.09544
As	-0.53311**	-0.38611**	-0.46438**	-0.14205*
Cd	-0.62099**	-0.46581**	-0.51165**	-0.10604
Cr	-0.57429**	-0.44622**	-0.47532**	-0.11514
Cu	-0.57839**	-0.40964**	-0.48486**	-0.13105
Fe	-0.5205**	-0.37824**	-0.43438**	-0.12397
Hg	-0.50457**	-0.34168**	-0.41588**	-0.11268
Mn	-0.46579**	-0.3253**	-0.39735**	-0.10202
Ni	-0.55781**	-0.39306**	-0.46657**	-0.11667
Pb	-0.53428**	-0.3719**	-0.46027**	-0.13347
Sb	-0.48561**	-0.28408**	-0.42139**	-0.12268
Sn	-0.52365**	-0.34748**	-0.45882**	-0.15798*
Tl	-0.52862**	-0.39186**	-0.44688**	-0.14289*
Zn	-0.53707**	-0.38876**	-0.44961**	-0.12229
Alpha HCH	-0.19079**	-0.22154**	-0.11849	-0.0105
Beta HCH	0.03414	0.05179	0.00464	0.01617
Delta HCH	-0.21788**	-0.06458	-0.2311**	-0.13108
Gamma HCH	-0.11765	-0.23838**	-0.01975	0.20079**
Heptachlor	0.08774	0.15739*	0.02196	-0.12867
Heptachlor epoxide	-0.00313	0.08995	-0.03012	-0.03032
Oxychlordane	-0.06145	0.04311	-0.11619	-0.12597
Alpha Chlordane	-0.13564*	-0.01145	-0.1652*	-0.10887
Gamma Cholrdane	-0.27076**	-0.07184	-0.2985**	-0.18146**
Cis-Nonachlor	-0.18615**	-0.01992	-0.22081**	-0.17895**
Trans-Nonachlor	-0.25897**	-0.14208*	-0.23169**	-0.10286
Aldrin	-0.0664	0.07482	-0.08568	-0.08064
Dieldrin	-0.13914	0.00805	-0.1614*	-0.15895*
Endrin	-0.09896	-0.02985	-0.0718	-0.04379

Table 18. Spearman-rank correlation coefficients and significance levels between sediment community attributes and trace elements, chlorinated pesticides, butyl tins, and PCBs.

Mirex	0.06848	0.02899	0.04584	-0.06708
Endosulfan	-0.1397*	-0.00033	-0.17641*	-0.06381
Chlorpyrofos	0.02079	0.12362	-0.04096	-0.13661*
2,4' DDD	-0.05865	0.03489	-0.07216	-0.08667
2,4' DDE	-0.09958	-0.06346	-0.0276	0.08138
2,4' DDT	-0.09726	-0.01675	-0.12155	-0.09154
4,4' DDD	-0.23334**	-0.14817*	-0.16954*	-0.0453
4,4' DDE	-0.36981**	-0.27751**	-0.26835**	-0.01935
4,4' DDT	-0.109	-0.02506	-0.10396	-0.05357
Tetrachlorobenzene 1,2,3,4	-0.31483**	-0.17665*	-0.2705**	-0.05074
Tetrachlorobenzene 1,2,4,5	-0.27676**	-0.17713*	-0.23418**	-0.01142
Pentachlorobenzene	-0.40047**	-0.27929**	-0.34346**	-0.02602
Hexachlorobenzene	-0.10402	0.04162	-0.10257	-0.07669
Total Butyl Lins	-0.51046**	-0.37286**	-0.39528**	-0.1014
PCB28	-0.20498**	-0.18216*	-0.15491*	0.00484
PCB44	-0.36833**	-0.26143**	-0.31721**	-0.03362
PCB52	-0.22899**	-0.16134*	-0.16442*	-0.03444
PCB66	-0.15685	-0.1313	-0.11804	0.02322
PCB105	-0.26905**	-0.2461**	-0.18493*	0.01293
PCB118	-0.2762**	-0.20277**	-0.20952**	-0.03391
PCB128	-0.2056**	-0.11711	-0.22639**	-0.13351
PCB180	-0.357**	-0.2577**	-0.27899**	-0.07144
PCB187	-0.15854*	-0.14108	-0.12254	-0.01188
PCB206	-0.39941**	-0.28262**	-0.3211**	-0.07474
PCB209	-0.47233**	-0.33639**	-0.36888**	-0.05051
PCB101_90	-0.22255**	-0.17374*	-0.17327*	-0.01174
PCB138_160	-0.46197**	-0.26647**	-0.40697**	-0.12042
PCB153_132	-0.31918**	-0.22881**	-0.25137**	-0.04215
PCB170_190	-0.10825	-0.08976	-0.102	-0.01995
PCB18_17	-0.04702	-0.10272	0.01035	0.02369
PCB195_208	-0.31498**	-0.2444**	-0.23827**	-0.00241
PCB8_5	-0.2382**	-0.24455**	-0.13666	0.0367

Table 18 (cont.)

 $\label{eq:product} \begin{array}{l} * = 0.5 \leq p \geq 0.01 \\ * * = p \leq 0.01 \end{array}$ 

Contominant	Species	Abundanca	Diversity	Evenness
Naphthalana	0.55267**	0 27772**	0.46602**	0.11841
C1 Northelenes	-0.33207**	-0.37773**	-0.40002**	-0.11841
C1-Naphthalenes	-0.57031**	-0.39397**	-0.400//**	-0.09039
C2-Naphthalenes	-0.30913***	-0.30014**	-0.40505***	-0.06882
C3-Naphthalenes	-0.48484***	-0.34534***	-0.38238***	-0.07454
C4-Naphthalenes	-0.40143***	-0.33200***	-0.36285***	-0.05834
Accessibility	-0.481/4***	-0.33873***	-0.40076***	-0.09404
Acenaphthylene	-0.43761**	-0.31181**	-0.33862**	-0.03215
Acenaphthene	-0.5353/**	-0.36968**	-0.4430**	-0.09873
Fluorene	-0.51202**	-0.36612**	-0.408/1**	-0.06636
CI-Fluorenes	-0.48645**	-0.35793**	-0.38119**	-0.05046
C2-Fluorenes	-0.44443**	-0.32329**	-0.34408**	-0.03494
C3-Fluorenes	-0.40583**	-0.3086**	-0.31366**	-0.01381
Anthracene	-0.45741**	-0.34017**	-0.35754**	-0.04077
Phenanthrene	-0.48549**	-0.33731**	-0.39449**	-0.07474
C1-Phenanthrenes/Anthracenes	-0.46117**	-0.33609**	-0.36549**	-0.05604
C2-Phenanthrenes/Anthracenes	-0.43201**	-0.32492**	-0.3379**	-0.03951
C3-Phenanthrenes/Anthracenes	-0.39612**	-0.30127**	-0.30388**	-0.02979
C4-Phenanthrenes/Anthracenes	-0.2375**	-0.20492**	-0.14865*	0.04058
Dibenzothiophene	-0.50453**	-0.37352**	-0.3999**	-0.06584
C1-Dibenzothiophenes	-0.48284**	-0.36932**	-0.37651**	-0.05051
C2-Dibenzothiophenes	-0.4591**	-0.35129**	-0.35245**	-0.03701
C3-Dibenzothiophenes	-0.4383**	-0.33697**	-0.3346**	-0.03926
Fluoranthene	-0.41719**	-0.30243**	-0.31834**	-0.03259
C1-Fluoranthenes/Pyrenes	-0.40128**	-0.30143**	-0.30461**	-0.02566
C2-Fluoranthenes/Pyrenes	-0.57592**	-0.39246**	-0.47101**	-0.16475
C3-Fluoranthenes/Pyrenes	-0.5907**	-0.39871**	-0.47055**	-0.15509
Pyrene	-0.41039**	-0.29907**	-0.31207**	-0.03621
Benz(a)anthracene	-0.41161**	-0.31044**	-0.3052**	-0.01639
Chrysene	-0.40766**	-0.30386**	-0.3048**	-0.02433
C1-Chrysenes	-0.40888**	-0.29369**	-0.31836**	-0.04744
C2-Chrysenes	-0.40711**	-0.3184**	-0.31427**	-0.036
C3-Chrysenes	-0.38304**	-0.3387**	-0.28495**	0.02518
C4-Chrysenes	-0.41412**	-0.32435**	-0.33726**	-0.03793
Benzo(b)fluoranthene	-0.42049**	-0.31245**	-0.31908**	-0.02619
Benzo(k)fluoranthene	-0.39495**	-0.29344**	-0.29079**	-0.01612
Benzo(e)pyrene	-0.41169**	-0.30042**	-0.31319**	-0.03333

Table 19. Spearman-rank correlation coefficients and significance levels between sediment community attributes and PAHs.

#### Table 19 (cont.)

Benzo(a)pyrene	-0.41681**	-0.31235**	-0.31404**	-0.02318
Perylene	-0.32999**	-0.22966**	-0.25051**	-0.03201
Indeno(1,2,3-c,d)pyrene	-0.39815**	-0.29174**	-0.31091**	-0.04314
Dibenzo(a,h)anthracene	-0.40542**	-0.29454**	-0.31244**	-0.03011
Benzo(g,h,i)perylene	-0.40894**	-0.30282**	-0.30803**	-0.02227
Additional PAHs				
1-Methylnaphthalene	-0.55087**	-0.37859**	-0.45393**	-0.10564
2-Methylnaphthalene	-0.55259**	-0.3784**	-0.45988**	-0.11255
2,6-Dimethylnaphthalene	-0.48281**	-0.3547**	-0.38163**	-0.06865
1,6,7-Trimethylnaphthalene	-0.52625**	-0.39135**	-0.4097**	-0.05442
1-Methylphenanthrene	-0.46448**	-0.34928**	-0.35641**	-0.03858
Total Normalized Contaminants	-0.46342**	-0.32325**	-0.36729**	-0.07755

 $\label{eq:posterior} \begin{array}{l} *=0.5 \leq p \geq 0.01 \\ **=p \leq 0.01 \end{array}$ 

	Amphipod Toxicity	HRGS B[a]P Equivalents	Sea Urchin Fertilization	Toxicity Response	Species Richness	Abundance	Diversity	Evenness
Normalized Metals	0.11733	0.64778**	0.55315**	0.63172**	-0.53319**	-0.37274**	-0.45435**	-0.13197
Total HCH	-0.25668**	0.27111**	0.18192**	0.12425	-0.18121**	-0.24942**	-0.09822	0.13722*
Total Cyclodienes	-0.13787	0.53728**	0.50379**	0.52765**	-0.3585**	-0.194**	-0.28792**	-0.07989
Total DDTs	-0.2426**	0.46984**	0.42697**	0.41362**	-0.26506**	-0.18323**	-0.19383**	-0.02907
Total Chlorinated Benzene	-0.09806	0.54743**	0.34149**	0.38451**	-0.37198**	-0.23865**	-0.30736**	-0.02008
<b>Total Pesticides</b>	-0.23458**	0.57722**	0.43646**	0.44392**	-0.34224**	-0.23983**	-0.25671**	0.00454
Normalized Pesticides	-0.16942*	0.58807**	0.44826**	0.46624**	-0.34598**	-0.2382**	-0.28058**	-0.02635
Total Butyl Tins	0.11662	0.6824**	0.52246**	0.59285**	-0.51046**	-0.37286**	-0.39528**	-0.1014
Total PCBs	-0.0907	0.67439**	0.46647**	0.5237**	-0.44806**	-0.28316**	-0.37189**	-0.07204
total PAHs	-0.03385	0.68425**	0.49783**	0.56228**	-0.44329**	-0.32028**	-0.34689**	-0.04711
Low Weight Base PAHs	0.08539	0.73816**	0.4889**	0.59757**	-0.50482**	-0.35213**	-0.41273**	-0.07821
Low Weight Substituted PAHs	0.01763	0.72192**	0.51094**	0.5933**	-0.48268**	-0.35899**	-0.37563**	-0.04852
Low Weight PAHs	0.05155	0.73412**	0.50083**	0.59731**	-0.49417**	-0.35616**	-0.39486**	-0.06198
High Weight Base PAHs	-0.08557	0.64334**	0.4825**	0.52786**	-0.40114**	-0.29095**	-0.304**	-0.02971
High Weight Substituted PAHs	-0.09837	0.6329**	0.48316**	0.52203**	-0.40705**	-0.3072**	-0.3111**	-0.03167
High Weight PAHs	-0.08594	0.64505**	0.48297**	0.52896**	-0.4027**	-0.29385**	-0.30601**	-0.03059
Total Normalized Contaminants	-0.06816	0.68833**	0.55858**	0.59737**	-0.46342**	-0.32325**	-0.36729**	-0.07755

Table 20. Spearman-rank correlation coefficients and significance level between contaminant classes vs toxicity bioassay results and community characteristics. Normalized chemicals were mean normalized.

 $\label{eq:posterior} \begin{array}{l} *=0.5 \leq p \geq 0.01 \\ **=p \leq 0.01 \end{array}$ 

Toxicity results showed significant correlations with community attributes (Table 21). Species richness, abundance and diversity were consistently negatively correlated with all the bioassay results. All but one relationship was highly significant. Evenness was negatively correlated with the bioassay results, but was only significantly correlated with the amphipod bioassay results. The P450 results correlated with the amphipod and sea urchin bioassays, but the latter two did not correlate with each other. All the community attributes were significantly correlated with each other. Evenness and abundance were negatively correlated however.

Slope estimates and regression coefficients (%) were calculated using condensed parameters and indices, including log transformation of highly variable parameters (Table 22). Many of the resulting slopes are deceptively small due to the log transformations. Regressions were significant for all community parameters (except evenness) on the contaminant and toxicity parameters. All significant regression slopes were negative except between log abundance and log normalized concentration. The toxicity index and the contaminant parameters showed positive and highly significant regression relationship. Variability was still high, but regression correlation coefficients were greater than with the biological parameters. The relationship between log normalized concentrations and the log mean ERMq was quite strong as would be expected. Salinity regressions generally yielded very low slope relationships with low correlation coefficients. Regressions with % silt/clay were highly significant for all parameters. All the community attributes had negative slopes, and all the chemical and toxicological parameters had positive slopes with % silt/clay. The % silt/clay, TOC and chemical concentrations all demonstrated relatively high correlation coefficients. Using quadratic regression equations yielded marginally better fits in most cases, indicating slightly non-linear relationships, but the differences between linear and quadratic results was minor and are not shown here. Using the residuals from regression of the community, toxicity and contaminant parameters on %silt/clay, regressions between the community attributes and chemical/toxicity data were again calculated (Table 23). In the absence of the influence of grain size, none of the community attributes demonstrated significant regressions with the chemical contaminant indices. In contrast, species number, abundance and diversity still show significant negative regression relationship with toxicity score, albeit with high variability as reflected by the correlation coefficients.

Table 21. Spearman-rank correlation coefficients and significance level between toxicity bioassay responses and benthic community attributes.

	Amphipod Toxicity	HRGS B[a]P Equivalents	Sea Urchin Fertilization	Toxicity Response	Species Richness	Abundance	Diversity	Evenness
Amphipod Toxicity	/							
HRGS B[a]P Equivalents	0.1419*	/						
Sea Urchin Fertilization	0.0236	0.3855**	/					
Toxicity Response	0.3592**	0.5861**	0.8562**	/				
Species Richness	-0.2758**	-0.4530**	-0.4462**	-0.5286**	/			
Abundance	-0.1274	-0.3734**	-0.3760**	-0.4041**	0.7636**	/		
Diversity	-0.3104**	-0.3314**	-0.3379**	-0.4352**	0.8236**	0.3933**	/	
Evenness	-0.1449*	-0.0281	-0.0778	-0.1311	0.1773*	-0.2450**	0.6023**	/

 $\label{eq:product} \begin{array}{l} * = 0.5 \leq p \geq 0.01 \\ * * = p \leq 0.01 \end{array}$ 

	#	Log	Diversity	Evenness	Log	Log	Log	Bottom	%	TOC
Dependent Independent	Species	Abundance			Normalized Concentration	Mean ERMq	Response	Salinity	Silt/Clay	
# Species	/									
Log	8.02**	/								
Abundance	45.6									
Diversity	8.00**	0.43**	/							
	65.5	26.67								
Evenness	9.32**	0.42*								
	10.28	2.89								
Log	-5.54**	0.32**	-0.45**	-0.05	/					
Normalized	16.3	7.7	10.7	1.5						
Concentration										
Log Mean	-6.59**	-0.42**	-70.57**	-0.08	0.88**	/				
ERMq	23.3	13.1	17.23	2.8	77.8					
Log Toxicity	-3.82**	-0.30**	-0.38**	-0.06**	0.34**	0.38**	/			
Response	19.3	16.2	18.2	4.2	28.5	37.0				
Bottom	0.43**	0.01	0.03**	0.004	-0.02**	-0.03**	-0.03**	/		
Salinity	14.9	0.6	8.7	1.3	7.5	11.8	6.5			
% Silt/Clay	-0.10**	-0.01**	-0.01**	-0.001**	0.001**	0.01**	0.01**	-1.66**	/	
	31.0	21.1	22.5	3.2	53.0	68.4	34.27	6.43		
TOC	-2.18**	-0.11**	-0.19**	-0.03*	0.27**	0.29**	0.29**	-0.09**	0.02**	/
	17.63	6.3	12.9	2.2	52.0	57.3	23.0	17.88	52.8	

Table 22. Slope estimates and regression coefficients (%) for toxicity, community, contaminant and selected habitat indices.

 $\substack{*=0.5 \leq p \geq 0.01 \\ **=p \leq 0.01}$ 

Table 23. Slope estimates and regression coefficients (%) for toxicity, community, contaminant and habitat indices using data normalized for grain size (%silt clay).

Dependent	#	Log	Diversity	Evenness	Log
	Species	Abundance			Toxicity
Independent					Response
Log	0.03	0.14	0.05	0.008	0.36**
Normalized	0.00	0.9	0.1	0.01	3.7
Concentration					
Log Mean	-0.95	0.06	-0.10	-0.03	0.62**
ERMq	0.2	0.1	0.2	0.1	7.5
Log Toxicity	-1.50*	-0.15**	-0.20**	-0.05	/
Response	2.8	3.5	4.3	1.6	
Bottom	0.29**	-0.004	0.02*	0.003	-0.01*
Salinity	9.3	0.2	4.2	0.5	1.9
TOC	-0.17	0.08	-0.02	-0.01	0.07
	0.1	1.8	0.1	0.1	0.9

 $\label{eq:product} \begin{array}{l} * = 0.5 \leq p \geq 0.01 \\ * * = p \leq 0.01 \end{array}$ 

Examination of the data shows some of this is due to a subset of stations where toxicity response was elevated even though the sediment was sandy and species numbers were relatively high, resulting in high residuals (Fig. 39).

#### NODAL ANALYSIS

The cluster analysis divided the sites into five major clusters and several smaller groups. Similarly, the species divided into six major clusters and some smaller groups. When combined (Fig. 40), the clusters resolved into nodes for 1-Susquehanna Flats, 2- the upper Bay between Baltimore and the Choptank River plus the upper reaches of the major western tributaries, 3-Tangier Sound and the lower reaches of the western tributaries, 4- sandy sites distributed throughout the lower Bay, 5- the mouth of the Bay, plus two sites in the lower Bay. In addition, there were four small groups of sites without as distinctive a spatial association as the others. These were #7 and #8 in which the species composition and abundance were low, but consistently included one of two species (P. pinnatao or N. succinea), and two clusters (#6 and #9), one with relatively low species richness and abundance but with no dominant species. Sites in the Tangier Sound node that were physically located in the open Bay (Fig. 41) tended to have finer grained sediments than the surrounding open Bay sites. Both of the lower Bay nodes (Sand and Mouth) were comprised of coarse grained sandy sites. All three had the group of species found in the Tangier Sound/Lower tributaries node. However, the Sand node sites also contained an additional subset of species seldom found in the Tangier Sound node. The node at the Mouth contained species found in the Tangier Sound node, and another subset of species seldom found in the Sand sites or Tangier Sound. Thus there were three overlapping, but distinct community nodes in the lower Chesapeake Bay (Fig. 40). The last large cluster of species (#4 in Fig. 40) was primarily associated with the sites in the Mouth node, but were also present in the open Bay sites associated with the Tangier Sound node. In contrast, the Susquehanna Flats node and upper Bay/upper tributary node shared fewer species, and these tended to be cosmopolitan taxa, such as Tubificids and *Cyathuria polita*. The nodes that were distinguished by single dominant species were generally locations that contained very fine grained sediments. The P. pinnatao sites (node #7) were primarily located in deep areas on the shoulders of the deep trough. Node #8 was populated primarily by *N. succinea* at sites scattered in the upper Bay region and or tributaries. The two stations in node #6 were adjacent to open shorelines and were sandy. The sites in node



# **Regression Residuals - Species and Toxicity**

Figure 39. Plot of residuals from regression of number of species on toxicity score data normalized for %silt/clay in Chesapeake Bay sediment samples.

Species Clusters



Figure 40. Nodal analysis of Chesapeake Bay. Dots indicate species occurrence in the sites. Red dots indicate a value in the upper third of each species' abundance.



Figure 41. Distribution of species association nodes in Chesapeake Bay.

#9 were also scattered in the upper Bay. Unlike the other three small nodes, they were not depauperate in species but contained two groups of species which were widely separated in the species clusters. Six remaining sites were separated from all other nodes in that they contained no organisms at all. These were located primarily in the deep trough.

The nodal analysis, excluding the contaminated sites, yielded essentially the same pattern (Fig. 42). The Susquehanna Flats node sites were unchanged. Exclusion of the contaminated sites did not induce any mixing with sites from another node. The upper Bay and Tangier Sound nodes were largely unchanged, with five of the 43 upper Bay sites clustering with the Tangier Sound node. There were no contaminated sites in the sand or mouth nodes and these groups were unchanged. The single species dominated nodes were also unchanged.

#### PRINCIPAL COMPONENT ANALYSIS

All sites were included in a PCA analysis except the deep trough sites where no macrofauna were present. The percent of variation explained by the first five factors was 68.1% (Table 24). Many of the PCA loadings for individual metrics approached 1.0 This was true for the entire data set and several of the individual nodes. The first component clearly separated the most contaminated sites in the Elizabeth River and Baltimore Harbor from all other sites (Fig. 43). The loadings for PCBs, PAHs, pesticides, ERMq, and DDT were all above 0.8 in the first component. The highest biological metric was percent Capitellids, a well known indicator species for polluted conditions. The highest loadings for component 2 were for abundance, number of species, and diversity. The patterns in Figure 43 are typical of all the results, with a small group of sites separated from the main assemblage, and the bulk of sites being spread along one of the components in a gradient.

For node-specific analyses, two different nodal associations were combined based on the salinity and grain size characteristics of the sites. The first included the Upper Bay/tributary node and species cluster #9, one of the clusters with no discernable dominant species. The second was the Tangier Sound/lower tributary node and the single species dominated clusters #7 and #8 (*P. pinnatao* and *N. succinea*), plus the remaining low species/abundance cluster (#6, two sites)

154



Figure 42. Distribution of species association nodes in Chesapeake Bay, excluding contaminated sites

Table 24. Principal component analysis factor loadings on chemical, community, and toxicity metrics. High loadings for each metric are highlighted. Stations with the 10 highest scores are listed below each factor.

Metric	Factor1	Factor2	Factor3	Factor4	Factor5
Normalized PAH	0.8955	-0.0422	0.0371	-0.0031	-0.0254
Normalized PCB	0.9343	-0.0296	0.0559	0.0116	0.0333
Normalized DDT	0.8532	0.0582	-0.0393	0.0327	-0.0087
Normalized Metals	0.5963	-0.5413	0.3092	0.0902	0.1404
Normalized Pesticides	0.8943	-0.0705	0.0807	0.0508	-0.0498
Normalized Butly-tins	0.2029	-0.1424	-0.0784	-0.0503	0.3481
Mean ERMq	0.8576	-0.3634	0.2228	0.0875	0.0724
% Tolerant	0.1418	-0.2993	0.8356	-0.0023	-0.0144
% Tubificids	0.0943	0.0196	0.8992	0.0176	-0.0993
% Limnodrilus sp.	0.0561	0.1231	0.6905	0.0687	-0.0487
% Spinoids	-0.0205	-0.8204	-0.1155	-0.1995	0.0605
% Capitellids	0.4572	0.1971	-0.2594	-0.2754	-0.5265
% Sensitive	0.2412	0.3540	-0.4510	0.1089	-0.4397
% Amphipods	-0.0129	0.2070	-0.1347	-0.0447	0.7154
% Ampelisca sp.	-0.0785	0.2433	-0.1881	-0.4787	0.2328
% Bivalves	-0.0517	0.2491	-0.1172	0.8134	0.1473
# Species	-0.1317	0.6825	-0.1065	-0.5156	0.1318
Diversity	-0.1517	0.5923	-0.0501	-0.6097	0.0885
Log Abundance	0.0251	0.7705	-0.0463	-0.1008	0.0978
Toxicity Score	0.2430	-0.5748	0.0996	0.0083	0.2217
% Variance Explained	28.1	16.1	10.2	7.6	6.1
	Sites	Sites	Sites	Sites	Sites
	206	162	1	18	202
	203	153	5	37	176
	205	3	3	100	153
	204	135	4	14	59
	23	205	40	57	20
	207	163	7	16	106
	15	160	52	161	180
	81	152	194	30	63
	10	90	35	90	81
	6	157	26	21	60


Figure 43. Principal component analysis results for all Chesapeake Bay stations (excluding the deep trough). Data are plotted as station scores on the component axes. Numbers are station designations.

The other nodal groupings were unchanged. The PCA results for Susquehanna Flats stations did not reveal any pattern (Fig. 44). The only station that was distinctly different from the others was #20, which had an extremely elevated TBT concentration. The Upper Bay/Tributary plus node #9 analyses consistently separated the East Branch Elizabeth River stations from all others (Fig. 45). These were among the most contaminated stations in the entire study area. Sites which scored higher on component 5 were stations with high percentages of Amphipods present. Sites appearing elevated on component #4 were either above average contamination or were oxygen stressed, and contained high percentages of Tubificid worms. Results from the Tangier Sound/Lower tributaries node, including the remaining low species node sites, was dominated by the separation of the badly contaminated site #206 in the lower Elizabeth River (Fig. 46). Plotting components 2-5 against each other did not reveal obvious groupings. Site 81, at the mouth of the Patuxent River is also contaminated. Site 90 is an anomalous station on component 5 due to the presence of an astonishing number of clams (Gemma gemma), over 77,000/m<sup>2</sup>, and over 31,000/m<sup>2</sup> snails of the genus *Odostomia*. Calculating the PCA without stations 90 and 206 did not reveal any obvious groupings in this node. Figure 47 shows PCA results from the Bay Mouth node sites. This node did not contain any contaminated sites, and no patterns are evident in the results. In contrast, the results from the sandy areas shows some spread of the sites, with one station in particular (#72) separating from all others (Fig. 48). This appears to be due to contaminant concentrations at the site. While the concentrations found at site 72 are relatively low on a Bay-wide basis, compared to the other sandy sites in the group, the concentrations are relatively high.

#### SEDIMENT QUALITY TRIAD

Four example SQT tri-axial plots are illustrated in Figure 49. These examples demonstrate divergent forms of the triangles. A variety of parameters from the data set were contrasted with the areas of the triangles. Most parameters appear to co-vary with the calculated areas over the range of values. For example, percent TOC and normalized contaminant concentrations show an increasing trend with SQT area (Fig. 50). Total organic carbon, which is confounded with contaminant concentrations, appeared to increase with triangular area, but only up to a certain threshold, above which the relationship was flat. The % silt/clay content of the sediment was much more variable, indicating that the physical makeup of the sediment was of secondary



Figure 44. Principal component analysis results for Susquehanna Flats stations. Data are plotted as station scores on the component axes. Numbers are station designations.



Figure 45. Principal component analysis results for the combined Upper Bay/Tributaries and node #9 stations. Data are plotted as station scores on the component axes. Numbers are station designations.



Figure 46. Principal component analysis results for the combined Tangier Sound/Lower tributaries and node 6, 7, and 8 stations. Data are plotted as station scores on the component axes. Numbers are station designations.



Figure 47. Principal component analysis results for stations in the Bay Mouth node. Data are plotted as station scores on the component axes. Numbers are station designations.



Figure 48. Principal component analysis results for stations in the Sand node. Data are plotted as station scores on the component axes. Numbers are station designations.



Figure 49. Example tri-axial plots of Sediment Quality Triad data from Chesapeake Bay sediment samples.



**SQT Triangular Areas vs Habitat Parameters** 

Figure 50. Values of example habitat parameters plotted as a function of calculated areas of SQT triangles from Chesapeake Bay sediment samples

importance to organic carbon content with respect to observed impact. Organism abundance declined with increasing SQT area (Fig. 50). These relationships are consistent with the regression results of chemical and biological indices (Table 22). A plot of the standard deviation of the SQT triangle angles and the calculated areas of the triangles are shown in Figure 51. At stations with a small triangular area, there is a high degree of scatter. At higher values the standard deviations show a more direct relationship with area. Relationships between triangle area and contamination is probably irrelevant below 1000 because there is low contamination present and triangle shapes vary randomly. These stations are located primarily in the Mouth, Sand, and Tangier Sound/Lower Trib. nodes, with a portion of the Upper Bay/Upper Trib. sites. At progressively larger triangle areas, the standard deviation decreases, indicating a more uniform distribution of SQT parameters. Plotting the relationship between ERMq and area reveals a log/linear relationship (Fig. 52) at areas above 1000. This would be expected as ERMq represents one the three axes from which the triangular areas are calculated. Examination of specific sampling site locations and their position on the plot reveals that sites located in areas with known hypoxic impacts (e.g. deep trough) are below the ERMq prediction line and known contaminated harbor sites (Baltimore Harbor and Elizabeth River) are above the prediction line. Locations which demonstrate lower ERMq than predicted by the regression may be impacted by factors in addition to contamination i.e. hypoxia. Locations which demonstrate higher ERMq than predicted by ERMq - Area regression are primarily impacted by chemical contamination.

## **Chesapeake Bay Triad Areas**



Figure 51. Relationship between the area of triad plots and the standard deviation of the internal angles of the triangles.

# Chesapeake Bay SQT Triangle Areas and ERMq



Figure 52. Plot of Effects Range-Median quotient (ERMq) and surface area of Sediment Quality Triad triangles greater than 1000.

### DISCUSSION

Salinity and grain size are the primary factors which determine benthic community distributions in the Chesapeake Bay mainstem. Similar findings were noted in Delaware Bay (Hartwell and Hameedi, 2006) and other systems (SCBW, 1959). In Delaware Bay, benthic community species structure transforms from fresh to marine as one proceeds from north to south, with grain size characteristics determining site specific assemblages within a salinity zone. In the Chesapeake however, similar benthic communities were not always contiguous. Each of the major western tributaries contained distinct mesohaline and polyhaline communities that mimick the distribution in the mainstem, although they were not physically connected and maintain themselves independently in each subsystem (Fig. 41).

Toxicity bioassay results and chemical contamination are clearly related. The concordance for the toxicity response index and the mean ERMq is illustrated in Figure 53 for the entire data set. This result is remarkably similar to results from the NS&T study of Delaware Bay, using a different set of bioassays and samples collected in different years (Fig. 54). On a gross scale, chemical contamination and toxicity responses are more closely correlated to each other than either of these two parameters are with benthic community metrics. When viewed in detail, the benthic community does respond to contamination in measurable fashion, however, certain patterns need to be illuminated to clarify the relationships.

For example, there is a relationship between the ERMq and community diversity. A mean ERMq value of 0.1 has been invoked by some researchers as a threshold where degraded communities begin to be seen (Hyland *et al.*, 1999) in the southeast US. Examination of the Chesapeake Bay data indicates this may be an artifact. Diversity, abundance, and number of species do decline with increasing mean ERMq. Diversity is plotted against mean ERMq in Figure 55 as an example. Examination of the relationship between diversity and mean ERMq above and below a threshold quotient of 0.1 reveals a discontinuity in the trend (Fig. 56). The reason for this apparent paradox lies in the confounded relationships between grain size, contaminant concentration, and diversity. The following observations explain why this is so;

 Mean ERMq is related to the percent fines in the sediment (Fig. 57). Few samples below 50% silt/clay had a mean ERMq above 0.1.

**Toxicity Score vs ERMq** 



Figure 53. Relationship between observed toxicity response index and mean ERM quotient values in Chesapeake Bay sediments.

**Toxicity Score vs ERMq** 



Figure 54. Relationship between observed toxicity response index and mean ERM quotient in independent studies of Delaware and Chesapeake Bays.



**Diversity vs Mean ERM quotient** 

Figure 55. Relationship between species diversity and mean ERM quotient values in sediment samples from Chesapeake Bay.





Figure 56. Relationship between species diversity and mean ERM quotient above and below a value of 0.1.

Grainsize and Mean ERM quotient



Figure 57. Relationship between mean ERM quotient and grain size in Chesapeake Bay sediments.

- 2) The distribution of silt/clay proportions in the Bay are shown in Figure 6. Fine grained sediments are primarily found in the Susquehanna Flats, upper Bay, deep trough, and in the tributaries. Figure 25 illustrates that mean ERMq values above 0.1 are also found in those locations.
- 3) The distribution of silt/clay proportions in the Bay are shown in Figure 6. Fine grained sediments are primarily found in the Susquehanna Flats, upper Bay, deep trough, and in the tributaries. Figure 25 illustrates that mean ERMq values above 0.1 are also found in those locations.
- 4) The Nodal analysis (Fig. 41) clearly demonstrates that the resident community found in those areas are inherently different from the areas with coarser grained sediments and low mean ERMq values in the mainstem.
- 5) Figure 58 illustrates the distribution of diversity values throughout the Bay. The apparent break in the relationship between diversity and a mean ERMq above 0.1 is a consequence of comparing fundamentally different benthic communities.

However, the fact remains that observed toxicity does increase with increasing ERM values (Fig. 53), and that impact cannot be ignored when evaluating community impact patterns. The aerial extent of observed toxicity and elevated ERMq values were consistently seen in the upper Bay, urban harbor areas, and the major western tributaries. Significant pore water toxicity was seen in over 30% of the Bay area. Elevated response to the P450 bioassay was seen in over 20% of the Bay. These are substantial proportions of the system. It is particularly important when considering the great size of Chesapeake Bay. Management of a system in which up to 3,000 km<sup>2</sup> appears degraded is a considerable challenge for regulatory agencies.

When viewed in terms of a consistent community assemblage, as derived from the nodal analysis, biological indices do indicate detectable impact of contaminants. Contrary to expectation, the nodal analysis excluding highly contaminated sites yielded a more complicated set of community associations than what was seen using all the data (Fig. 42). However, the basic pattern of two primary community types in the northern Bay and



Figure 58. Distribution of diversity index values in Chesapeake Bay sediments. Color scale represents percentile rank.

upper tributaries, a set of lower tributary and Tangier Sound stations, and an overlapping series of open Bay communities extending down to the mouth of the Bay remained. Within those community types it is appropriate to examine patterns of impact on the biological community. This is most revealing in the Susquehanna Flats and upper Bay/upper tributary areas where there are an adequate number of stations to contrast contaminated and uncontaminated stations within similar physical habitats.

A further question to be addressed is whether or not to include stations with matching physical characteristics and geographic proximity but with extremely limited species assemblages, such as the sites dominated by *P. pinnata* and *N. succinea*. Most of these sites had very fine grained sediment. Most of the sites dominated by *P. pinnata* are along the shoulders of the deep trough where oxygen stress is clearly a driving factor (Dauer at al., 2000). This species is considered a pollution tolerant indicator species (Llanso *et al*, 2002). Inclusion of these sites in the larger nodes would definitely influence the apparent relationships between community indices and chemical contamination. To do a more indepth analysis of community indicators by looking at individual species and community metrics, as is done in IBI development, is the next step but is beyond the scope of the present report. It may also be possible to address specific causes of stress such as a distinction between hypoxia and toxic contaminants (Christman and Dauer, 2003).

The Susquehanna Flats area is straightforward because dropping contaminated sites from the entire data set did not alter the stations included in that node. None were included that hadn't been included before, and none were lost to a different node. The physical characteristics (depth, salinity, etc.) of the clean and contaminated sites in the Susquehanna Flats node all overlap except for grain size. The contaminated sites tended to have finer grain size. Normalizing community indices for grain size yields a relationship between them and the ERMq. Figure 59 illustrates a declining diversity index with increasing ERMq. A similar relationship exists for species richness, but the relationship with abundance is less distinct. This probably indicates that tolerant species can reproduce to high abundance in contaminated sites either due to lack of competition or predation, or some indirect effect on productivity (Fleeger *et al.*, 2003).



## Susquehanna Flats Normalized Diversity vs ERM Quotient

Mean ERMq

Figure 59. Diversity, normalized by % silt/clay content, plotted as a function of the mean ERM quotient for Susquehanna Flats stations.

The upper Bay/upper tributary areas show a very distinct relationship between normalized diversity and mean ERMq (Fig. 60). In part this is due to a larger number of sandy sites than in Susquehanna Flats, which generates very high normalized values, and a higher range of ERM values. Again, the same relationship holds for species richness. In the figure, the triangles are the original stations that were in the node. The circles were the sites in the undefined node #9 that were included in the upper Bay/upper tributary node. The one exception of a contaminated site with high normalized diversity was station 170, which was located far up a tributary to the Rappahannock River. That station had obviously been recently dredged. It was the only station in the entire three year data set that exceeded the ERM for 4,4- DDE. Other than DDE, the site was not highly contaminated (Table 8).

The Tangier Sound node sites also show a distinct relationship between normalized diversity and mean ERMq (Fig. 61). This group included several sites in the Elizabeth River. Site 207 was located at the mouth of a small drainage creek entering the Elizabeth River, and the site was much more sandy than the surrounding area. Also shown are the sites dominated by *P. pinnatao* and *N. succinea* and the undefined node #6 (circles). The very lowest normalized diversity values are from the sites dominated by *P. pinnatao* and *N. succinea*. They have very low values because they are primarily fine grained sediment and they occur in stressed hypoxic areas on the shoulders of the deep trough or deep spots in the Potomac River, thus the low diversity. These sites are marginally contaminated because these tend to be depositional zones. The two sites in node #6 were sandier, uncontaminated, had much higher number of taxa, and their normalized diversity values were in the vicinity of 10. Thus, low values of diversity normalized for grain size is a consistent indicator of stressed conditions in all areas, but distinguishing contaminant stress responses from other stressors (e.g. hypoxia) may not be possible with this approach.

Grain size distribution also explains the distinct variation in the distribution of contaminated and uncontaminated areas in Baltimore Harbor and the Elizabeth River. Within those systems, sandy sites do not contain contaminants at concentrations as high



## Upper Chesapeake Bay Normalized Diversity vs Mean ERM Quotient

Figure 60. Diversity, normalized by % silt/clay content, plotted as a function of the mean ERM quotient for upper Chesapeake Bay stations.

### Tangier Sound/Lower Tributaries Normalized Diversity vs Mean ERM Quotient



Figure 61. Diversity, normalized by % silt/clay content, plotted as a function of the mean ERM quotient for Tangier Sound/lower tributary stations.

as those found at the muddy sites. TOC normalized PAH data (Fig. 62) illustrates that all Elizabeth River and the Baltimore Harbor sites have elevated PAH concentrations relative to most other areas. Note also that based on this transformation, the concentrations in the deep trough are relatively low away from the mouths of tributaries, but Susquehanna Flats is not. Normalization for grain size yields a similar picture for metals. Thus, loading rates (and/or residual deposits) in the Elizabeth and Susquehanna Rivers, and in the vicinity of Baltimore Harbor remain elevated.

Previous studies in Baltimore Harbor demonstrate strong gradients in contaminant concentrations from the heads of the various tributaries down into the Patapsco River (Baker *et al.*, 1997). With one exception they generally found higher concentrations of PAHs, PCBs, pesticides and metals because their sampling sites were further up the tributaries. The NS&T station #23 showed very similar values to their station # 37 in the middle of the harbor. The other three NS&T stations in the vicinity contained sediment with a much lower proportion of fine grained material, and lower TOC concentrations than stations in the Baker *et al.* study. This highlights the importance of grain size characteristics to contaminant assessments, even on a very small scale, in heavily contaminated harbors.

In previous studies of the Elizabeth River (Winfield, 1998), contaminant concentrations were also seen to be highly variable on a site specific basis due to a combination of historical sources of pollution and sediment characteristics. The range of metals concentrations in the South Branch and mainstem were similar to the NS&T values. PAH concentrations were generally lower, but the suite of measured constituents was smaller than the NS&T list. PCBs were measured as Aroclors and are not comparable with the NS&T data. Chlordane, HCH, and DDT values were similar within the Elizabeth River although a very high value for HCH was seen in the Lafayette River in the 1998 report. The NS&T sampling scheme also included the Eastern Branch of the Elizabeth River system. The Eastern Branch contaminant concentrations are as high, if not higher, than the Southern Branch even though the Eastern Branch is primarily residential along the shoreline of the upper reaches. Residential areas on the eastern branch of the Elizabeth



Figure 62. Distribution of PAHs, normalized for TOC, in Chesapeake Bay sediments. Color scale represents percentile rank.

river have PAH and PCB concentrations in the same order of magnitude as the industrial areas, and have higher concentrations of pesticide residues. Some stations exceeded the ERM for DDT. Contaminants from industrial areas have been transported into non-industrial areas, either through sediment transport or runoff from watershed sources.

The Hart Miller Island containment facility is the repository for dredge spoil from Baltimore Harbor and the approach channels. Sediment derived from those areas is finegrained and enriched in trace metals and organic constituents (Hill and Van Ryswick, 2004). Oxidation of the sediment placed in the facility during dewatering and crust management produces an effluent enriched in metals. The single NS&T station in the Hart Miller Island area showed elevated metals concentrations relative to the surrounding area (Fig. 18a). Even after grain size normalization, station 20 demonstrates higher concentrations of metals relative to other stations with similar grain size (Table 25). Concentrations of As, Cd, Cr, Cu, Hg, and Pb matched or exceeded the ERLs and Ni and Zn exceeded the ERMs. These data are consistent with monitoring in the vicinity conducted by the State of Maryland (Hill and Van Ryswick, 2004). The Hart Miller Island area has elevated trace metals, but not PAHs or PCBs.

With respect to the SQT triangles, the distribution of points above and below the regression line in Figure 52 may be interpreted as an indication of the relative impact of contaminants on the community. Those above the line have chemical contaminant concentrations higher than predicted by the regression. Those below the line have lower contaminant concentrations and may indicate impacts in addition to chemical contaminants. Ignoring all sites with an area below 1000 (triaxial lengths of 34 on a scale of 1 to 100), a plot of the sites above and below the regression line reveals the distribution within the Bay system (Fig. 63). Virtually all of the sites above the line are found in the tributaries and/or Susquehanna Flats. The sites from below the line are distributed between the tributaries and the mainstem. Significantly, most of the stations in the vicinity of the deep trough are in this group, where hypoxia is a well documented stressor. These are the same stations that fall below the curve of normalized diversity and ERMq that are represented by the circles in Figures 60 and 61. These results are

Site	Mean Normalized Metals	%SiltClay	Metals/%SiltClay	Stratum	Zone
20	59.57	78.17	76.20	6	М
203	41.91	80.67	51.95	63	Т
12	36.95	72.31	51.10	4	Т
29	41.92	86.00	48.75	8	М
39	34.00	78.74	43.19	11	М
9	34.26	78.71	43.52	3	Т
166	26.74	70.96	37.68	50	Т
27	32.99	88.54	37.26	8	М
85	30.66	76.81	39.92	25	Т
14	26.26	78.54	33.43	5	М
40	22.94	77.09	29.76	11	М
197	24.42	85.45	28.58	61	Т
16	25.78	88.73	29.05	5	М
88	18.01	73.38	24.55	26	Т
76	21.24	81.98	25.92	22	Т
168	19.02	74.66	25.47	51	Т
186	17.31	69.22	25.00	57	Т
188	21.15	84.08	25.15	58	Т
44	19.45	82.15	23.68	12	E
192	20.68	85.78	24.11	59	Т
45	17.35	75.98	22.84	12	М
199	19.76	85.96	22.98	61	Т
132	14.40	83.71	17.20	40	E
131	13.96	84.42	16.54	40	E
170	13.35	81.77	16.33	52	Т
55	13.16	78.44	16.78	15	М
119	12.04	79.01	15.24	36	Т

Table 25. Mean-normalized metals concentrations adjusted for grain size. Selected stations are within  $\pm$  5% of the silt clay content of station 20.



Figure 63. Locations of stations with Effects Range-Median quotients (ERMq) above and below the regression line of Sediment Quality Triad triangular areas and mean ERMq.

consistent with an analysis of degraded benthic communities by Dauer and Llanso (2003). They concluded that between 40-68% of the area in the Maryland portion of the mainstem were in a degraded condition and the major western tributaries had larger proportions of degraded benthos than the Virginia mainstem. That analysis did not distinguish between contaminant impacts and hypoxia. The stations in the lower Bay are anomalous. None of them have impacted community characteristics. The elevated SQT triangular surface areas are primarily a consequence of elevated pore water toxicity.

The Chesapeake Bay Program, in conjunction with the States of Maryland and Virginia, have established sampling sites throughout the Bay to monitor the condition of the benthic community (Llanso et al., 2004). While the prime focus of the Bay Program is eutrophication and the condition of the tributaries, the benthic assessment program has included permanent sites in the mainstem and the tidal tributaries for trend analysis since 1985, and randomly chosen sites in a stratified sampling pattern, similar to the NS&T approach. Since 1996, the condition of the benthos has been considered to be degraded or marginally degraded in more than 50% of the areal extent of the Bay (Llanso et al. 2004). Most of the locations considered to be degraded are in tidal tributary areas or the deep trough. Most of the fixed sites do not demonstrate any long term trends, either improving or degrading. Hypoxia and anoxia have continued to be increasing problems in the Bay over several decades. During summer, the deep trough and lower parts of some tributaries like the Patuxent, Potomac, and Rappahannock rivers become anoxic. The benthic community in these areas have become progressively depauperate. The CBP B\_IBI results from the NOAA benthic infaunal replicate samples are shown in Figure 64 (Llanso et al., 2006). Virtually all sites in the deep trough region are classified as degraded, as are most of the tributary sites to some degree. A surprising number of mainstem sites in the lower Bay are considered degraded, including locations at the mouth of the Bay. Conversely, most of the sites in the Susquehanna Flats area, where a large proportion of contaminated sites are found, are classified as being in good condition. Spearman-rank correlations between the B\_IBI and other indices used here are shown in Table 26. The B\_IBI is significantly, negatively correlated with contaminants,



Figure 64. Benthic Index of Biotic Integrity (B\_IBI) classification of benthic community condition in Chesapeake Bay.

Table 26. Spearman-rank correlation coefficients and significance level between B\_IBI and related sediment quality triad attributes. (Normalized No. Species refers to species richness normalized for grain size, see text.)

	B_IBI	Triad Area	Normalized No. Species	Toxicity Response	Mean ERMq	% Silt+Clay
B_IBI	/					
Triad Area	-0.4355**	/				
Normalized No. Species	0.4063**	-0.7845**	/			
Toxicity Response	-0.3765**	0.9037**	-0.6022**	/		
Mean ERMq	-0.3414**	0.8229**	-0.7315**	0.6394**	/	
% Silt+Clay	-0.3061**	0.6481**	-0.8993**	0.5040**	0.6799**	/

\*\* =  $p \leq 0.01$ 

observed toxicity and the derived triad area values. There is a positive correlation with number of species, as would be expected. However, species richness is more strongly correlated with contaminant and toxicity measures than the B\_IBI. (The triad area measure is naturally highly correlated with the contaminant, toxicity and species values, as these are all confounded with the area calculations.) While the trends between the B\_IBI and contaminant-related indices are coherent, there is a great deal of variability (Fig. 65). This indicates the B\_IBI is responding to a variety of potential stressors, especially hypoxia (as it was designed to do) (Llanso, 2002), but this reduces predictive power with respect to cause and effect. Response to a toxicity signal is overwhelmed by other metrics used in the index. For example, classification of what are essentially coastal conditions at the mouth of the Bay as degraded, is more likely reflective of a community existing in a physically taxing habitat of strong currents and limited food resources (Hartwell and Hameedi, 2006). It is doubtful these stations will ever be classified as being in good condition by this sort of index, even if the Bay is restored to 'pristine conditions'. The predominantly 'good' classification of the Susquehanna Flats stations is more problematic, and may reflect the reduced effectiveness of the B\_IBI in fresher waters (Llanso *et al.*, 2002). While this area contained the largest proportion of contaminated sites, the toxicity response values for the Susquehanna Flats area were also highly variable in this area.

Loading estimates of various chemicals to the Bay system are inconsistent. The major sources are point sources, urban runoff, atmospheric deposition, spills, and watershed input, based on measurements at the fall line of the major western tributaries. Some watershed data is also available from tributaries on the Eastern Shore (CBP, 1999a). Given the uncertainties in the analytical data only generalizations can be made. However, there is no one source type that stands out. Point sources in the Bay proper and the watershed contribute large quantities of contaminants including metals, PAHs and PCBs. Depending on the specific metal, point sources and tributary input appear to contribute the most to the Bay. Based on 1990 discharge permits in Baltimore Harbor, 667,000 kg of heavy metals (excluding Al and Fe) are discharged into the Bay annually (Warner *et al.*, 1992). Over 450,000 kg of heavy metals were estimated to flow into the harbor from



Figure 65. Relationship between Benthic Index of Biotic Integrity (B\_IBI) and sediment contaminant indicators in Chesapeake Bay.



**Toxicity Response Score** 

Figure 65 (cont.). Relationship between Benthic Index of Biotic Integrity (B\_IBI) and sediment contaminant indicators in Chesapeake Bay.
urban non-point sources. Approximately 64,000 kg of cyanide, 3,300 kg of PAHs, and 10,600 metric tons of ammonia were also annually discharged to the water from point sources in Baltimore. Urban runoff contributes considerable quantities of PAHs and PCBs, but estimates range over three orders of magnitude depending on what assumptions are used (CBP, 1999b). Spill data is very limited, and primarily includes only reported accidents. The magnitude of contaminants from the myriads of small spills from large and small boats that happen every day are virtually unknown. Furthermore, spills are generally reported in volume measures of released material, rather than mass data, so comparison with other sources is not possible. Contaminant contributions from groundwater sources are basically unknown. Atmospheric deposition has been assessed in selected locations, both urban and rural, but an atmospheric loading budget is still preliminary. Pesticide inputs to the Bay have not been quantified. Nearly 14 million kg of pesticide active ingredient (excluding wood preservatives) was applied to the watershed in Maryland alone in 2000 by certified applicators (MDA, 2002). This does not include unregulated application by private citizens. A survey of surface water in the vicinity of POTWs detected a variety of human use pharmaceuticals including antidepressants, antibiotics, pain relievers and antianginal medications and/or their metabolites (Pait et al., 2006), in addition to other compounds from human consumption (e.g. caffeine, nicotine). It is unknown to what extent the low level, but continuous release of these compounds has on resident organisms.

In the mainstem and embayments, PAHs were evenly split between high weight ( $\geq 4$  rings) and low weight ( $\leq 3$  rings). Alkyl-substituted PAHs were more prevalent in the low weight category (Fig. 15) than in the high weight category (Fig. 16). This indicates a pyrogenic source for the high weight PAHs, whereas the low weight PAHs are likely a mixture of pyrogenic sources and fuel spills. This may be influenced by the analytical scheme which emphasizes the lower weight substituted compounds. The median concentration of PAHs in the tributaries is five times what is found in the mainstem or embayments. It is certain that concentrations would be shown to be even higher if all forms (other than just alkyl substitutions) were considered. Also, the tributaries contained higher concentrations of high molecular weight PAHs than low molecular weight PAHs

by a factor of 2X (Fig. 14). The difference is most dramatic in the more heavily contaminated areas.

The mass of reservoirs of contaminants can be calculated based on the observed concentrations and the areal extent of the sampling strata. The mass of material contained in a given area is the product of the deposition rate and the concentration. What is retained in an area will be influenced by the physical stability of the location, sediment/chemical reactions with the compounds of interest, contaminant persistence, and physical disturbance which may move contaminated sediment away, or expose it to dissolution into the water column. In areas with high deposition rates or areas which are seldom disturbed, contaminants in the sediments will ultimately be buried beyond the depth subject to normal storm activity and reworking by benthic infauna, and therefore become unavailable to the system. For example, Kepone was not detected in surface sediments in the James River below Richmond, Va. following Hurricane Isabel in 2003 (Dr. Mike Unger, personal communication). Other contaminants may be more mobile in the environment or may be recycled between the sediment, the water column, and the biota, and remain in the active portion of the system for long time spans. The mass of various contaminants in the upper 10 cm of sediment for different depositional compartments of the Chesapeake Bay mainstem are shown in Table 27. These calculations are based on an assumed sediment density of 1.35 gm/cm<sup>3</sup> and the average concentration of contaminants seen in the entire area. For more refined accountings or for modeling purposes, these values would have to be modified for site specific grain size and/or TOC but they are revealing. For example, the chlorinated compounds had highly variable distributions and median values were frequently half or less of the average. The northern portion of the Bay, including Susquehanna Flats, the Patapsco, and Chester Rivers contains a much higher reservoir of contaminants than other areas. On an areal basis however, the concentrations found in the deep trough are comparable. In contrast, Tangier Sound which is similar in size, contains vastly less contamination. The Elizabeth River, although relatively small in size contains significant quantities of contaminants. PAH concentrations are an order of magnitude higher than other regions. Metals are found at concentrations comparable to those in the northern region. The areas in Hampton

Region	gion Northern Bay		Deep Trough		Tangier S	Sound	Elizabeth River		
Strata	1-9		11,14,	11,14,19		0	62-64		
Area (km <sup>2</sup> )	1135.	.0	333.5		1174.	1	14.9		
	kg	kg/km <sup>2</sup>	kg	kg/km <sup>2</sup>	kg	kg/km <sup>2</sup>	kg	kg/km <sup>2</sup>	
PAH	219,415	193	44,845	134	50,017	43	16,420	1,100	
PCB	1,667	1	326	1	716	1	89	6	
DDT	454	0.4	35	0.1	145	0.1	42	3	
Chlordanes	113	0.1	14	0.04	77	0.07	12	1	
As	1,738,872	1,532	642,942	1,928	758,368	646	21,283	1,426	
Cd	82,798	73	25,243	76	23,106	20	1,047	70	
Cr	12,006,975	10,579	3,850,546	11,545	5,341,199	4,549	115,201	7,717	
Cu	5,579,045	4,915	1,580,890	4,740	1,456,042	1,240	126,507	8,474	
Pb	6,599,546	5,814	1,887,153	5,658	2,300,265	1,959	102,645	6,876	
Hg	23,165	20	5,063	15	3,661	3	560	38	
Ag	58,803	52	13,067	39	6,295	5	620	42	
Ni	7,555,691	6,657	1,910,015	5,727	2,232,902	1,902	46,254	3,098	
Se	128,775	113	48,571	146	56,465	48	2,605	174	
Zn	32,824,582	28,920	9,613,109	28,824	9,056,296	7,713	502,461	33,657	

Table 27. Total mass and mass/km<sup>2</sup> of contaminants in sediments in selected regions of Chesapeake Bay.

Roads and Norfolk cannot be compared in the same way because the sediments are sandy. While industrial, and shipping-related activity is intense, Hampton Roads is not as contaminated as one might presume because it is not a depositional environment and it is well flushed.

Unlike synthetic chemicals, trace elements occur naturally in watershed rocks and soils, and are delivered to the Bay by normal erosion and weathering processes. Assessment of the magnitude of anthropogenic input of trace elements present in the sediments requires comparison to the background ratios found in the watershed. Numbers specific to the Chesapeake Bay watershed are not available, so comparisons have been made to more generic values from Turekian and Wedepohl (1961). Table 28 shows the relative enrichment of several trace elements from depositional zones and specific sampling sites in Chesapeake Bay. These values were calculated by comparing the iron:element ratio of the samples to the background ratio for shale from Turekian and Wedepohl (1961). Relative to the shale values, the Chesapeake is enriched for most elements even in the relatively clean area of Tangier sound. This is due to the depositional nature of an estuary. Enrichment in the Susquehanna Flats exceeds Tangier Sound for every element except Cr. Enrichment levels in Elizabeth River are lower for As, Cr, and Ni, but higher for all the others. Enrichment of Se and Hg were especially high. The single muddy site in Baltimore Harbor (# 23) showed the highest enrichment rates of any location in the Bay, except for Hg. The Patapsco River is highly polluted with metals and other trace elements. The Elizabeth River is also contaminated with metals, but not to the same levels as the Patapsco. The Magothy River below Baltimore and Broad Bay in Virginia Beach are heavily developed areas that demonstrate elevated metals enrichment.

Location	Silver	Arsenic	Cadmium	Chromium	Copper	Nickel	Lead	Selenium	Zinc	Mercury
Strata 33-40 Tangier Sound	2.5	11.2	3.2	1.4	0.7	0.7	4.5	28.9	3.5	1.4
Strata 1-9 Susquehanna										
Flats	10.6	11.2	5.3	1.4	1.2	1.2	6.4	32.4	5.7	3.2
Strata 62-64 Elizabeth										
River	8.0	9.7	4.2	1.0	2.1	0.5	6.6	42.2	6.3	6.8
Site 23 Baltimore Harbor	14.5	16.6	9.6	3.4	2.9	0.8	11.4	66.4	7.5	5.3
Site 28 Magothy River	9.7	9.9	4.1	1.4	1.5	1.1	8.1	39.9	7.9	3.7
Site 166 Broad Bay	9.7	11.8	4.9	1.1	2.3	0.6	3.4	58.0	5.0	7.8

Table 28. Enrichment values for trace elements in selected regions and specific locations in Chesapeake Bay.

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Baltimore power plant

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## **APPENDIX** A

## Sample Site Locations

Year	Stratum	Site	Zone	Latitude DD	Longitude DD	Depth m
1	1	1	Т	39.4900	-76.1241	0.5
1	1	2	М	39.5261	-76.0068	1.2
1	1	3	М	39.4645	-76.0535	4.0
1	2	4	Т	39.5817	-75.9531	3.0
1	2	5	М	39.4639	-76.0215	1.8
1	2	6	М	39.3989	-76.1406	5.1
1	3	7	Т	39.5532	-75.8698	1.1
1	3	8	Т	39.5067	-75.9004	3.0
1	3	9	Т	39.4729	-75.9760	1.2
1	4	10	Т	39.3809	-76.0577	3.4
1	4	11	Т	39.3810	-75.9952	3.4
1	4	12	Т	39.3726	-76.0813	3.4
1	5	13	М	39.4157	-76.0283	8.0
1	5	14	М	39.3724	-76.1335	6.2
1	5	15	М	39.2918	-76.2207	6.7
1	5	16	М	39.3717	-76.1384	5.2
1	5	17	М	39.3141	-76.2033	6.4
1	6	18	Е	39.3037	-76.3682	1.5
1	6	19	Е	39.2895	-76.3874	3.0
1	6	20	М	39.2076	-76.3949	4.6
1	6	21	М	39.1271	-76.3289	7.1
1	6	22	М	39.1025	-76.3591	6.7
1	7	23	Т	39.2316	-76.5349	6.1
1	7	24	Т	39.2288	-76.5612	1.8
1	7	25	Т	39.1703	-76.4896	3.7
1	7	26	Т	39.1705	-76.5173	3.0
1	8	27	М	39.1092	-76.3878	4.2
1	8	28	Т	39.0691	-76.4697	3.0
1	8	29	М	39.0914	-76.4014	4.6
1	8	30	М	39.0068	-76.3294	1.5
1	9	31	Т	39.1084	-76.1783	1.2
1	9	32	Е	39.0479	-76.2528	6.4
1	9	33	Е	39.0477	-76.2670	7.1
1	9	34	Т	38.9850	-76.1880	1.2
1	10	35	М	38.9846	-76.4025	7.9
1	10	36	М	38.9499	-76.4634	1.2
1	10	37	М	38.9011	-76.4466	2.4
1	10	38	М	38.8342	-76.4793	4.0

Year	Stratum	Site	Zone	Latitude DD	Longitude DD	Depth m
1	11	39	М	39.0052	-76.3488	14.6
1	11	40	М	38.9829	-76.3759	17.1
1	11	41	М	38.8759	-76.4026	25.9
1	12	42	Е	38.8852	-76.2030	1.8
1	12	43	Е	38.8992	-76.2420	0.6
1	12	44	Е	38.8290	-76.2134	8.4
1	12	45	М	38.8180	-76.3827	15.5
1	13	46	М	38.7930	-76.5213	4.9
1	13	47	М	38.6937	-76.4841	10.1
1	13	48	М	38.6355	-76.4996	9.1
1	13	49	М	38.5820	-76.5031	8.2
1	14	50	М	38.8364	-76.4269	12.5
1	14	51	М	38.7512	-76.4702	11.0
1	14	52	М	38.6427	-76.4715	10.0
1	15	53	М	38.7873	-76.3931	6.1
1	15	54	М	38.6794	-76.4252	25.6
1	15	55	М	38.6018	-76.3406	7.6
1	16	56	М	38.8383	-76.3110	6.1
1	16	57	М	38.7703	-76.3618	1.8
1	16	58	М	38.6670	-76.3289	2.7
1	17	59	Е	38.7306	-76.2513	5.8
1	17	60	Т	38.6855	-76.1753	2.4
1	17	61	Е	38.6808	-76.2720	4.6
1	17	62	Е	38.6642	-76.2319	6.7
1	17	63	Т	38.5990	-76.1256	5.8
2	18	64	М	38.5229	-76.5040	7.7
2	18	65	М	38.2892	-76.3605	8.3
2	18	66	М	38.0436	-76.3119	4.6
2	19	67	М	38.5658	-76.4490	13.2
2	19	68	М	38.4760	-76.3995	19.6
2	19	69	М	38.2817	-76.3538	10.9
2	20	70	М	38.5459	-76.3117	6.7
2	20	71	М	38.4479	-76.3528	22.1
2	20	72	М	38.3653	-76.3070	6.1
2	21	73	Т	38.4982	-76.6668	5.4
2	21	74	Т	38.4334	-76.6070	2.5
2	21	75	Т	38.4089	-76.5881	6.4
2	22	76	Т	38.3972	-76.5493	9.6

Year	Stratum	Site	Zone	Latitude DD	Longitude DD	Depth m
2	22	77	Т	38.3634	-76.5013	12.3
2	22	78	Т	38.3533	-76.4985	3.7
2	23	79	Т	38.3249	-76.4521	5.5
2	23	80	Т	38.3178	-76.4753	4.8
2	23	81	Т	38.2887	-76.4503	5.0
2	24	82	Т	38.2844	-76.9158	5.1
2	24	83	Т	38.2060	-76.7994	9.3
2	24	84	Т	38.2286	-76.8474	7.5
2	25	85	Т	38.3352	-77.0017	3.4
2	25	86	Т	38.1721	-76.7542	3.4
2	25	87	Т	38.1689	-76.7710	2.9
2	26	88	Т	38.1548	-76.5584	12.3
2	26	89	Т	38.1127	-76.4099	5.3
2	26	90	Т	38.0582	-76.3613	2.7
2	27	91	Т	38.1741	-76.6155	11.5
2	27	92	Т	37.9953	-76.3395	13.4
2	27	93	Т	38.0218	-76.4174	11.1
2	28	94	Т	38.1504	-76.6484	5.5
2	28	95	Т	38.1305	-76.6419	3.8
2	28	96	Т	38.0026	-76.4369	5.9
2	29	97	М	37.9647	-76.2450	12.7
2	29	98	М	37.7268	-76.0633	9.9
2	29	99	М	37.6859	-76.1736	18.8
2	30	100	М	38.1258	-76.1027	1.5
2	30	101	М	38.0412	-76.0621	5.6
2	30	102	М	37.8155	-76.0740	10.1
2	31	103	М	37.9169	-76.1390	18.4
2	31	104	М	37.7971	-76.1570	9.9
2	31	105	М	37.7416	-76.1241	9.3
2	32	106	М	37.8938	-76.2154	4.9
2	32	107	М	37.8067	-76.2701	3.5
2	32	108	М	37.7083	-76.2485	5.6
2	33	109	Е	38.2560	-76.1486	3.7
2	33	110	Е	37.8983	-75.9701	5.9
2	33	111	Е	37.8713	-75.9595	4.4
2	34	112	Е	37.9423	-75.9410	18.4
2	34	113	E	37.9051	-75.9356	4.3
2	34	114	Е	37.8534	-75.9233	7.7

Year	Stratum	Site	Zone	Latitude DD	Longitude DD	Depth m
2	35	115	Е	38.1677	-75.9605	4.4
2	35	116	Е	38.0585	-75.9262	4.6
2	35	117	Е	37.8486	-75.9025	3.5
2	36	118	Т	38.3328	-75.9029	1.7
2	36	119	Т	38.2790	-75.9306	3.7
2	36	120	Т	38.2733	-75.9259	8.1
2	37	121	Е	38.2255	-75.8858	1.7
2	37	122	Е	38.2228	-75.8402	2.0
2	37	123	Е	38.2083	-75.8606	1.8
2	38	124	Е	38.1370	-75.8185	4.1
2	38	125	Е	38.1288	-75.9040	3.4
2	38	126	Е	38.1176	-75.9291	2.4
2	39	127	Е	38.0612	-75.8065	1.8
2	39	128	Е	38.0426	-75.8484	5.1
2	39	129	Е	38.0301	-75.8429	2.7
2	40	130	Е	37.9507	-75.7206	3.8
2	40	131	Е	37.8589	-75.7409	4.2
2	40	132	Е	37.8425	-75.8106	10.6
3	41	133	М	37.7460	-75.9390	6.5
3	41	134	М	37.7426	-75.9879	6.5
3	41	135	М	37.6943	-76.0317	10.3
3	42	136	Е	37.6649	-76.3268	1.3
3	42	137	М	37.6099	-76.2158	8.1
3	42	138	М	37.5430	-76.3059	0.9
3	42	139	М	37.3327	-76.2254	10.6
3	43	140	М	37.7243	-75.9399	14.5
3	43	141	М	37.6158	-76.1026	13.0
3	43	142	М	37.5658	-76.1945	11.0
3	43	143	М	37.4635	-76.1054	10.9
3	43	144	М	37.2248	-76.0857	13.5
3	44	145	Т	37.7217	-75.7900	4.3
3	44	146	М	37.6361	-75.9253	5.2
3	44	147	М	37.4011	-76.0406	12.5
3	44	148	М	37.2243	-76.0356	7.3
3	45	149	М	37.1700	-76.0131	8.6
3	45	150	М	37.0838	-76.0800	7.0
3	45	151	М	37.0356	-75.9742	8.0
3	46	152	М	37.2153	-76.2709	5.5

Year	Stratum	Site	Zone	Latitude DD	Longitude DD	Depth m
3	46	153	М	37.0829	-76.1592	9.7
3	46	154	М	36.9591	-76.0082	20.0
3	47	155	М	37.1118	-76.2706	3.0
3	47	156	М	36.9711	-76.0582	10.0
3	47	157	М	37.0200	-76.2588	5.8
3	48	158	Т	36.9781	-76.3734	3.4
3	48	159	Т	36.9785	-76.3868	3.0
3	48	160	Т	36.9611	-76.4029	3.0
3	49	161	М	36.9986	-76.2522	4.7
3	49	162	Т	36.9814	-76.3132	5.8
3	49	163	М	36.9567	-76.0986	9.0
3	50	164	М	36.9336	-76.1913	5.0
3	50	165	Т	na	na	na
3	50	166	Т	36.8613	-75.9949	2.1
3	51	167	Т	36.9318	-76.3624	5.5
3	51	168	Т	36.9242	-76.4372	5.1
3	52	169	Т	36.9049	-76.4197	1.2
3	52	170	Т	37.7412	-76.5176	0.6
3	52	171	Т	37.6298	-76.4555	8.1
3	52	172	Т	37.6043	-76.3679	9.4
3	53	173	Т	37.7919	-76.6463	2.1
3	53	174	Т	37.7098	-76.5602	13.4
3	53	175	Т	37.6672	-76.5545	11.9
3	54	176	Т	37.8927	-76.7804	6.8
3	54	177	Т	37.8731	-76.7701	6.5
3	54	178	Т	37.8440	-76.7520	3.0
3	55	179	Т	37.9163	-76.8345	1.3
3	55	180	Т	37.8394	-76.7548	3.0
3	55	181	Т	37.8000	-76.7130	2.6
3	56	182	Т	37.4103	-76.6741	1.5
3	56	183	Т	37.3369	-76.6057	7.6
3	56	184	Т	37.3104	-76.5654	1.5
3	57	185	Т	37.3580	-76.6338	2.7
3	57	186	Т	37.3020	-76.5768	4.0
3	57	187	Т	37.2619	-76.5349	10.0
3	58	188	Т	37.3411	-76.6375	2.6
3	58	189	Т	37.3067	-76.6113	2.7
3	58	190	Т	37.3022	-76.5770	2.7

Year	Stratum	Site	Zone	Latitude DD	Longitude DD	Depth m
3	59	191	Т	37.1063	-76.6312	6.0
3	59	192	Т	37.0587	-76.5437	3.4
3	59	193	Т	37.0520	-76.5114	1.4
3	60	194	Т	37.0891	-76.6457	4.0
3	60	195	Т	37.0640	-76.6594	2.4
3	60	196	Т	37.0446	-76.6342	2.4
3	61	197	Т	37.0078	-76.5603	2.7
3	61	198	Т	36.9905	-76.5281	2.4
3	61	199	Т	36.9387	-76.4937	0.6
3	62	200	Т	36.9126	-76.3400	16.3
3	62	201	Т	36.8975	-76.3383	15.1
3	62	202	Т	36.8592	-76.3223	13.4
3	63	203	Т	36.8382	-76.2384	2.3
3	63	204	Т	36.8359	-76.2550	1.8
3	63	205	Т	36.8343	-76.2185	2.1
3	64	206	Т	36.8226	-76.2914	11.0
3	64	207	Т	36.7905	-76.3056	1.2
3	64	208	Т	36.7443	-76.2971	4.9
3	65	209	E	37.3850	-76.4005	7.0
3	65	210	Е	37.3184	-76.3604	5.5
3	65	211	Е	37.2694	-76.3681	1.6



Figure A1. Locations of sampling stations in the upper Chesapeake Bay region.



Figure A2. Map of central Chesapeake Bay showing sampling locations.



Figure A3. Map of lower Chesapeake Bay showing sampling stations. Inset details locations in the upper Rappahannock River.

United States Department of Commerce

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