Chemical Analyses of Sediment Sampling at the Massachusetts Bay Disposal Site, 5-7 June 1989

Disposal Area Monitoring System DAMOS

Contribution 91
November 1994

US Army Corps
of Engineers
New England Division

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	November 1994	Final report

4. TITLE AND SUBTITLE

Chemical Analyses of Sediment Sampling at the
Massachusetts Bay Disposal Site, 5 - 7 June 1989

5. FUNDING NUMBERS

6. AUTHOR(S)

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8. PERFORMING ORGANIZATION REPORT NUMBER

C98

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

US Army Corps of Engineers - New England Division
424 Trapelo Road
Waltham, MA 02254-9149

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

DAMOS Contribution No. 91

11. SUPPLEMENTARY NOTES

Available from DAMOS Program Manager, Regulatory Division
USACE-NED, 424 Trapelo Road, Waltham, MA 02254-9149

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

Sediment chemistry studies at the Massachusetts Bay Disposal Site (MBDS) have concentrated on the interim disposal area, established in 1977. Prior to the establishment of the interim site, materials may have been released at the site that were more contaminated than those currently being disposed. A survey conducted during June, 1989 sampled areas within the MBDS suspected to contain contaminated sediments, and identified potential areas to be capped by future disposal of sediments that are suitable for open ocean disposal.

Sediment samples were taken at 20 stations within, or adjacent to, the western half of the MBDS. This area overlaps the historical Industrial Waste Site. Samples were analyzed for both trace metal and organic contaminants. Results of samples from the June 1989 survey showed that contaminant concentrations were primarily influenced by historical dredged material and waste disposal. The spatial distribution of chemical data, especially polynuclear aromatic hydrocarbons (PAHs), indicated that contaminant concentrations were highest along the western edge of MBDS, in the center of the historical waste site. This area should be further investigated by site managers for receipt of capping material. Concentrations of all trace metals were relatively low compared to MBDS reference areas and regional Massachusetts Bay data. PCBs were undetected at stations previously reported to have concentrations of up to 1 ppm. The decrease in concentration of PCBs at the MBDS is possibly due to further disposal of sediments with low concentrations of PCBs; in this case below the detection limit of 20 ppb. Low levels (<11 ppb) of pesticides (4,4'-DDE) were detected at over half of the MBDS stations. Measured concentrations were within regional ranges reported for Massachusetts Bay.

14. SUBJECT TERMS

MBDS	contaminated sediments
dredged material	sediment chemistry

15. NUMBER OF PAGES

43

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified			

CHEMICAL ANALYSES OF SEDIMENT SAMPLING AT THE MASSACHUSETTS BAY DISPOSAL SITE, 5-7 JUNE 1989

CONTRIBUTION #91

November 1994

Report No. C98

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EXECUTIVE SUMMARY

Sediment chemistry studies at the Massachusetts Bay Disposal Site (MBDS) have concentrated on the interim disposal area, established in 1977. Prior to the establishment of the interim site, materials may have been released at the site that were more contaminated than those currently being disposed. A survey conducted during June 1989 sampled areas within the MBDS suspected to contain contaminated sediments, and identified potential areas to be capped by future disposal of sediments that are suitable for open ocean disposal.

Sediment samples were taken at twenty-six stations within, or adjacent to, the western half of the MBDS. This area overlaps the old Industrial Waste Site. Samples were analyzed for both trace metal and organic contaminants.

Results of samples from the June 1989 survey showed that contaminant concentrations were primarily influenced by historical dredged material and waste disposal. The spatial distribution of chemical data, especially polynuclear aromatic hydrocarbons (PAHs), indicated that contaminant concentrations were highest along the western edge of MBDS, in the center of the historical waste site.

Concentrations of all trace metals were relatively low compared to MBDS reference areas and regional Massachusetts Bay data. Maximum trace metal concentrations were concentrated in the center of the western half of the MBDS, north of the current disposal point. Of the metals analyzed, measured lead concentrations were highest relative to regional and national coastal data.

PCBs were undetected at stations previously reported to have concentrations of up to 1 ppm. The decrease in concentration of PCBs at the MBDS is possibly due to further disposal of sediments with low concentrations of PCBs; in this case below the detection limit of 20 ppb. Low levels (<11 ppb) of pesticides (4,4'-DDE) were detected at over half of the MBDS stations. Measured concentrations were within regional ranges measured in Massachusetts Bay.

PAHs were measured above the method detection limit at only three of the twenty-six stations. However, approximately two-thirds of the MBDS stations contained estimated concentrations of PAHs. Maximum measured PAHs (versus estimated values) were present at three stations along the far western edge of MBDS in concentrations higher than those measured in relatively contaminated coastal Massachusetts Bay sediments. PAH results (total PAHs ranging from 1.9 ppm to 5.9 ppm) indicated that the western edge of the MBDS should be further investigated by site managers for receipt of capping material.

1.0 INTRODUCTION

A sediment survey was conducted by the US Army Corps of Engineers, New England Division (NED) in June 1989 in the western half of the interim Massachusetts Bay Disposal Site (MBDS, formerly the Foul Area Disposal Site). Sediment samples were analyzed for trace metals and organic constituents to identify areas of potential contamination which should be capped with sediments (suitable for unconfined disposal) from permitted dredging projects.

MBDS is a 2 nmi circular area located approximately 18 nmi east-northeast of the entrance to Boston Harbor and 14 nmi south-southeast of Gloucester, Massachusetts (Figure 1-1). Since 1985, dredged material has been disposed near a disposal buoy located in the southwestern quadrant of MBDS. Prior to the establishment of the interim MBDS in 1977, an area known as the Industrial Waste Site, centered approximately 1 nmi west of the center of the MBDS, was used for the disposal of a wide variety of material not limited to dredged sediments, including building debris, canisters of industrial waste, and encapsulated low-level nuclear waste (SAIC 1988). After the establishment of the interim MBDS in 1977, only dredged material was disposed in the area, but it was scattered over the entire western half of the site (SAIC 1988).

Three replicate samples were collected in June 1989 at twenty-six stations randomly distributed in the western half of MBDS (Figure 1-2), and at two reference areas. Stations were concentrated in the western sector because this area overlaps the historical Industrial Waste Site, and the southwestern quadrant of MBDS currently receives dredged material approximately at the location of the "MDA" buoy (formerly the "FDA" buoy; Figure 1-2). The "A" buoy is a location which has at times been the authorized disposal point for the receipt of dredged material.

Material disposed prior to the establishment of MBDS may have contained relatively more contaminated materials because of the lower emphasis placed on testing in the 1960s and 1970s (Fredette 1990). In order to test for the presence of contaminated sediments within the MBDS boundary, collected sediments were analyzed for several trace metals, total organic carbon (TOC), and a suite of semivolatile organics including polynuclear aromatic hydrocarbons (PAHs), pesticides, and polychlorinated biphenyls (PCBs).

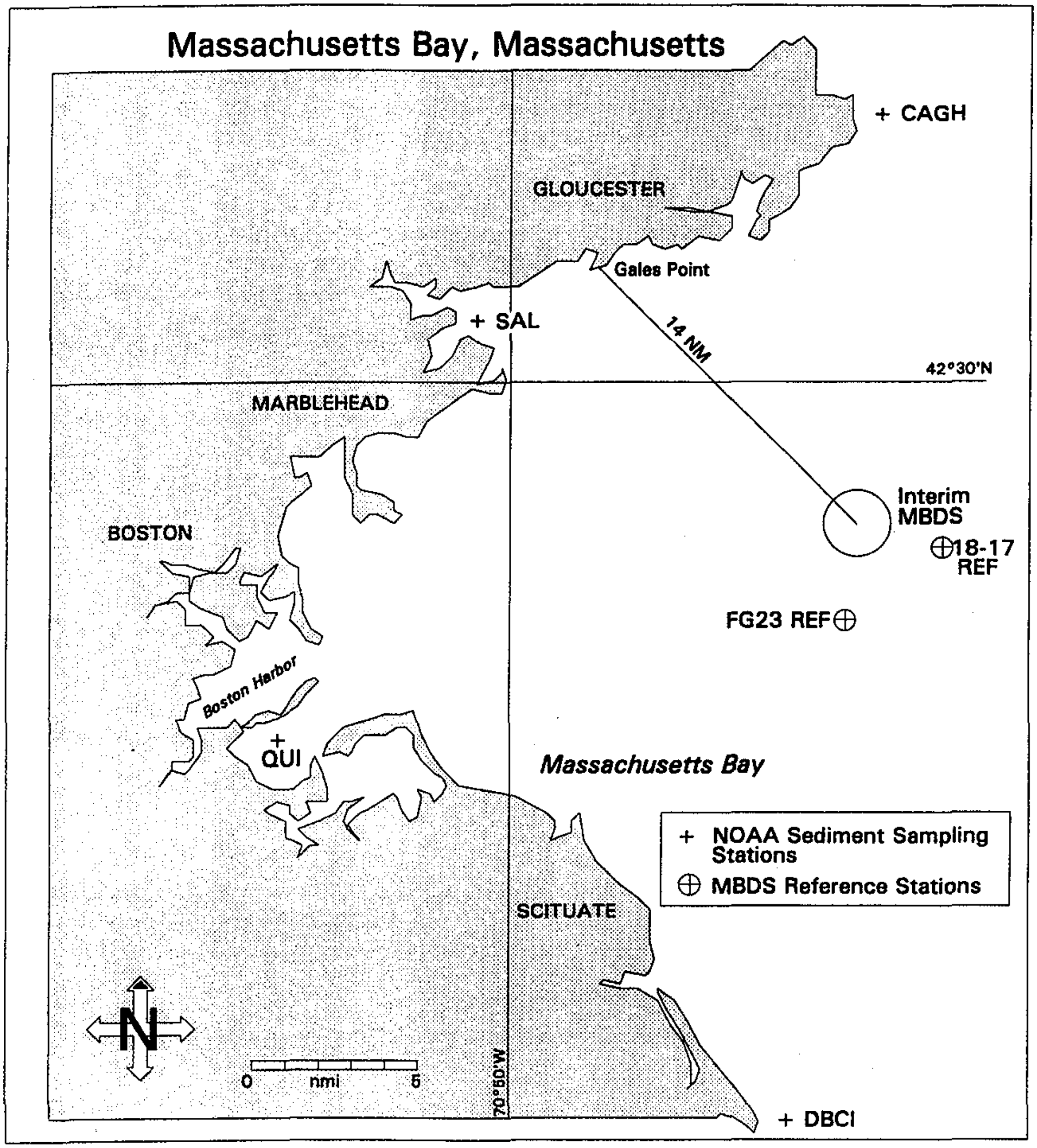

Figure 1-1. Location of MBDS and MBDS reference areas

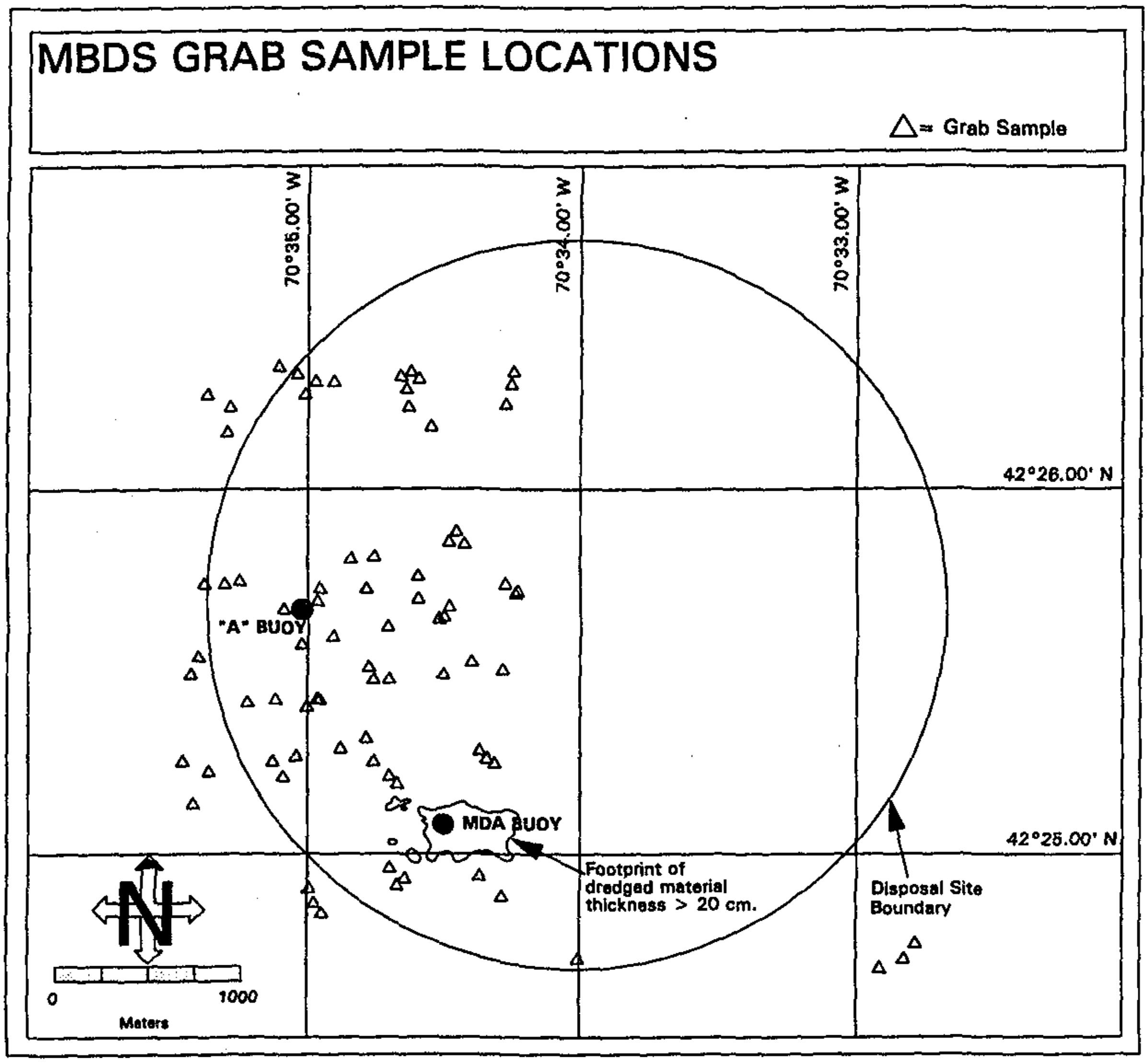

Figure 1-2. Location of grab samples taken at MBDS, June 1989. MDA buoy is the active disposal point; "A" buoy was an historic disposal location. Dredged material footprint from bathymetric survey of 1990 (Germano et al. 1994).

2.0 METHODS

2.1 Field Procedures

Samples were collected aboard the US Environmental Protection Agency's (EPA) vessel O.S.V. *Anderson* by the NED during 5-7 June 1989. LORAN-C, calibrated to a fixed reference point, was used for navigational control. Water depths at the sample stations ranged from approximately 60 to 90 meters.

Three replicate grab samples were taken at twenty-six stations located within or adjacent to the western half of the MBDS (Figure 1-2). Replicate grabs are collected in order to average out local sediment variation. Contaminant concentrations are, in general, highly dependent upon local sediment redox conditions, and dredged materials are characterized by high variability (Morton and Karp 1980). Results are presented for each approximate station location rather than for each replicate (Figure 2-1).

Two reference areas (18-17 and FG-23), located south of the site (Figure 1-1), were also sampled in triplicate. Two additional replicates were collected from 18-17 from the same grab sample as a measure of field sampling replicability. Each station sample replicate was analyzed for a suite of metals and total organic carbon (TOC) by the NED laboratory. Samples from the three replicate grabs were composited at each station for analysis of a suite of semivolatiles. Replicate samples from station 18-17 were analyzed individually for semivolatile compounds.

Grab samples were taken at each station using a Smith-McIntyre grab sampler. One core was taken from each grab sample using polycarbonate tubes which had been rinsed with seawater by the NED laboratory prior to the cruise; stainless steel spoons were used to stabilize lifting the core from the grab sampler. The grab sampler and the stainless steel spoons were thoroughly rinsed with seawater between each station. The replicate samples at reference station 18-17 were taken without the use of stainless steel spoons. Cores were taken from the center of each grab to avoid contamination. Samples were stored at approximately 4° C in plastic sample bags and then transported to the NED laboratory where they were stored again at approximately 4° C until analysis.

2.2 Laboratory Procedures

Samples were analyzed for both metal and organic constituents (Table 2-1). Metals, including chromium (Cr), nickel (Ni), copper (Cu), zinc (Zn), cadmium (Cd), mercury (Hg), and lead (Pb), were analyzed using the EPA's Test Methods for Evaluating Solid Waste (SW-846) procedures (Table 2-1; EPA 1986). Sediment samples were acid digested (Method 3050) and analyzed using direct aspiration atomic absorption (AA) except for mercury (Hg) analysis (Method 7471). Mercury was analyzed using cold vapor atomic absorption

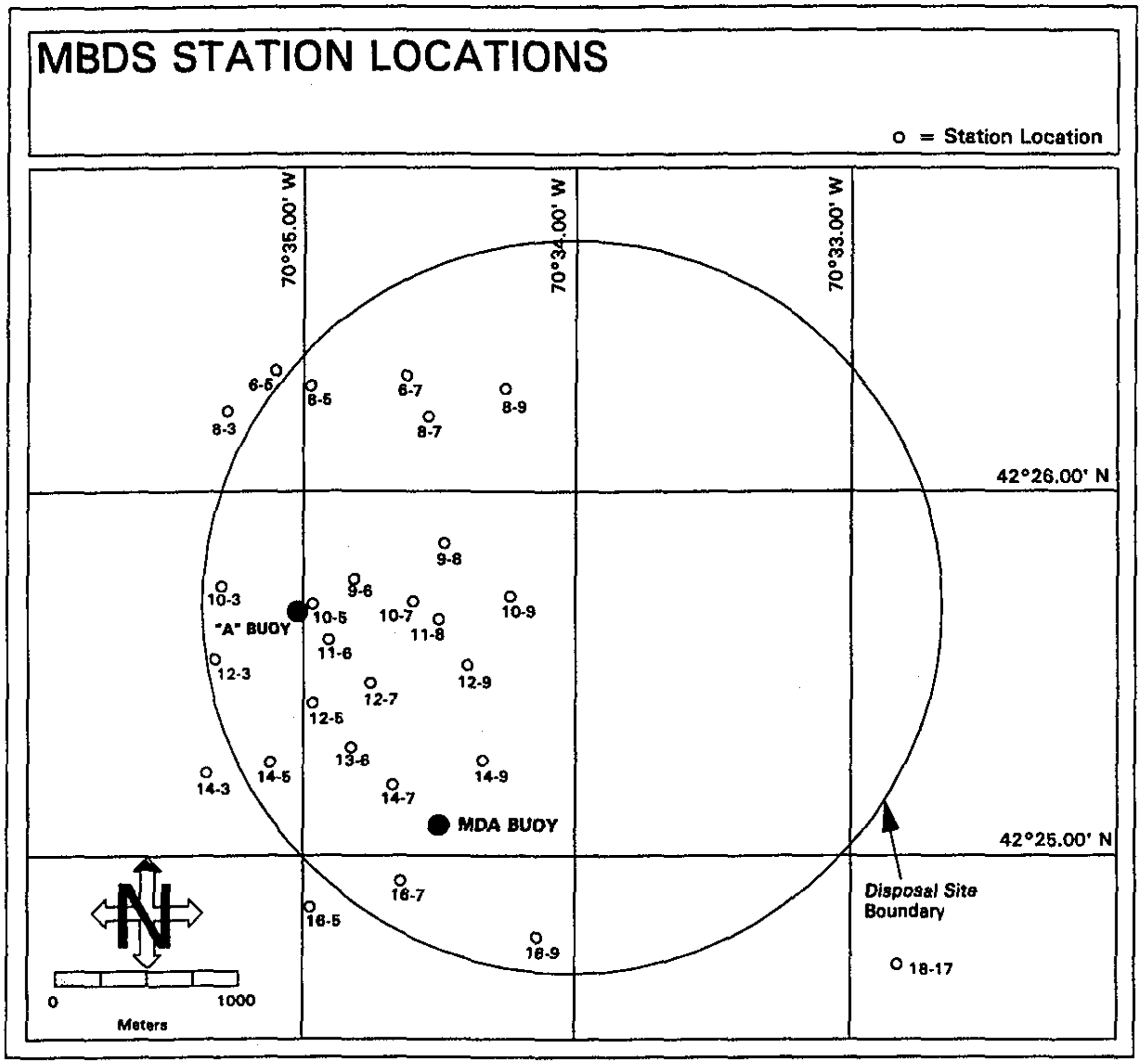

Figure 2-1. Approximate station locations averaged from three replicate grabs, MBDS, June 1989

Table 2-1

Summary of Laboratory Analytical Methods

ANALYTE	SW-846 TEST METHOD NO.		INSTRUMENTATION	LABORATORY
Metals	Sample Prep	Analytical		NED
Cadmium	3050	7130	AA	
Chromium	3050	7190	AA	
Copper	3050	7210	AA	
Lead	3050	7420	AA	
Mercury	--	7471	CVAA	
Nickel	3050	7520	AA	
Zinc	3050	7950	AA	
BNA	3550	8270	GC/MS	Chemrox
Pesticides/PCBs	3540	8080	GC/ECD	NED
Total Organic Carbon		9060		NED

Instrumentation:

AA	Direct Aspiration Atomic Absorption
CVAA	Cold Vapor Atomic Absorption
ECD	Electron Capture Detector
GC	Gas Chromatograph
MS	Mass Spectrometer

Analytes:

BNA	Basic, Neutral, and Acidic Semivolatiles
PCB	Polychlorinated Biphenyl

Laboratories:

NED	US Army Corps of Engineers, New England Division Laboratory
Chemrox	Chemrox Laboratory Services

All methods from EPA SW-846 (EPA 1986).

(CVAA). AA determinations are completed as single element analyses which allow for low detection limit thresholds (the direct aspiration method is not as sensitive as graphite furnace AA).

TOC was measured using protocols described in SW-846 Method 9060 (EPA 1986). Organic carbon in the samples was converted by the analyzer to carbon dioxide (CO_2), which was subsequently measured by an infrared detector. The amount of CO_2 is directly proportional to the concentration of carbonaceous material in the sample. Inorganic forms of carbon (carbonate and bicarbonate) are not included as part of the reported total organic carbon value. Total organic carbon is a measurement of organic matter (both labile and refractory) in sediments.

Composited MBDS samples were analyzed for semivolatile organics using SW-846 Method 8080 (pesticides and PCBs) by the NED laboratory, and Method 8270 (basic, neutral, and acidic semivolatiles or BNA) by Chemrox Laboratory Services in Shelton, Connecticut. BNA compounds include a full suite of polynuclear aromatic hydrocarbons (PAHs; Table 2-2). Method 8080 measures the concentrations of several chlorinated pesticides and PCBs from a sample extract using a gas chromatograph with an electron capture detector. Method 8270 measures the concentration of semivolatile organic compounds soluble in methylene chloride using a gas chromatograph with a mass spectrometer detector (GC/MS).

Table 2-2

Organic Compound Method Detection Limits

Organic Compound Method Detection Limits			
Pesticides (Method 8080)	DL (ppb)	Base Neutrals/Acid, continued	DL (ppb)
4,4'-DDD	2.0	4-Chloroaniline	1300
4,4'-DDE	1.0	4-Chlorophenyl-phenylether	660
4,4'-DDT	2.0	4-Methylphenol	660
Aldrin	0.5	4-Nitroaniline	3300
alpha-BHC	0.5	4-Nitrophenol	3300
beta-BHC	0.5	Acenaphthene	660
delta-BHC	0.5	Acenaphthylene	660
Dieldrin	1.0	Anthracene	660
Endosulfan I	1.0	Benzo(a)anthracene	660
Endosulfan II	1.0	Benzo(a)pyrene	660
Endosulfan Sulfate	2.0	Benzo(b)fluoranthene	660
Endrin	1.0	Benzo(g,h,i)perylene	660
Endrin Aldehyde	2.0	Benzo(k)fluoranthene	660
gamma-BHC (Lindane)	0.5	Benzoic acid	3300
Heptachlor	0.5	Benzyl alcohol	1300
Heptachlor Epoxide	0.5	Bis(2-chloroethoxy)methane	660
Methoxychlor	1.0	Bis(2-chloroethyl)ether	660
		Bis(2-chloroisopropyl)ether	660
Total PCBs (Method 8080)	20	Bis(2-ethylhexyl)phthalate	660
		Butylbenzylphthalate	660
Base Neutrals/Acid (Method 8270)		Chrysene	660
1,2,4-Trichlorobenzene	660	Di-n-butylphthalate	660
1,2-Dichlorobenzene	660	Di-n-octyl phthalate	660
1,3-Dichlorophenol	660	Dibenzo(a,h)anthracene	660
1,4-Dichlorobenzene	660	Dibenzofuran	660
2,4,5-Trichlorophenol	660	Diethylphthalate	660
2,4,6-Trichlorophenol	660	Dimethylphthalate	660
2,4-Dichlorophenol	660	Fluoranthene	660
2,4-Dimethylphenol	660	Fluorene	660
2,4-Dinitrophenol	3300	Hexachlorobenzene	660
2,4-Dinitrotoluene	660	Hexachlorocyclopentadiene	660
2,6-Dinitrotoluene	660	Hexachlorobutadiene	660
2-Chloronaphthalene	660	Hexachloroethane	660
2-Chlorophenol	660	Indeno(1,2,3-cd)pyrene	660
2-Methylnapthalene	660	Isophrone	660
2-Methylphenol	660	N-Nitroso-di-n-propylamine	660
2-Nitroaniline	3300	N-Nitrosodiphenylamine	660
2-Nitrophenol	660	Napthalene	660
3,3-Dichlorobenzidine	1300	Nitrobenzene	660
3-Nitroaniline	3300	Pentachlorophenol	3300
4,6-Dinitro-2-methylphenol	3300	Phenanthrene	660
4-Bromophenyl-phenylether	660	Phenol	660
4-Chloro-3-methylphenol	1300	Pyrene	660

3.0 RESULTS

3.1 Data Quality Analysis

Results submitted by the NED laboratory and Chemrox were found to be acceptable and supported by appropriate documentation, with some data qualified as discussed below. Sample data were evaluated using protocols developed by the EPA (EPA 1988a, 1988b), including a review of laboratory detection limits, sample holding times, and laboratory quality control (QC) samples. QC samples consisted of method blanks, matrix spikes, and duplicate samples. No QC sample results were submitted with the TOC data; consequently, all TOC data were qualified "J" as estimated. Data qualified as estimated are acceptable, but a greater degree of uncertainty is associated with these values than with unqualified data.

Method detection limits (MDLs) are the minimum concentrations of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. The MDL incorporates all of the analytical operations. All MDLs were acceptable as proscribed by each method (Table 2-2) for all sample results, except for two basic, neutral, acidic semivolatile (BNA) results for samples 8-5 and 9-8. These samples were diluted tenfold which resulted in detection limits an order of magnitude higher than the other samples. Samples are diluted either because the presence of high concentrations of a measured compound can interfere with accurate quantification of chromatographic peaks, or because the sediment matrix itself causes interference. All compounds were below detection in these samples except for one estimated value of di-n-octyl phthalate (1900 ppb). The result of this dilution is that the potential presence of PAHs at concentrations above the normal detection limit at these two stations cannot be determined. This uncertainty was taken into account in discussing the MBDS chemical results (Section 4.1).

The EPA recommends a limit to the amount of time samples can be stored before analysis; this period is called the holding time. There are no formal holding times for sediment matrix samples. Samples were extracted for organic analyses less than forty-five days after sampling, and analyzed less than thirty-eight days after extraction. No organics or metals samples were qualified based on excessive holding times (EPA 1988a, 1988b).

Method blanks are laboratory QC samples processed with the samples but containing only reagents, and are used to test for contamination which may have been contributed by the laboratory during sample preparation. An acceptable number of method blanks were analyzed with all sample sets except that there were no method blanks for Hg or total organic carbon (TOC) analyses. TOC results were already qualified, so no further qualification was necessary. Mercury results were also qualified as estimated. Method blanks were below detection for all pesticides, PCBs, and metals except Hg. BNA compounds were also undetected in the associated method blanks with the exception of bis(2-ethylhexyl)phthalate which was detected in three of the four BNA method blanks at estimated concentrations below the MDL. Phthalates are common constituents of plastic and may have been introduced in the laboratory sample preparation process. All sample detections of bis(2-ethylhexyl)phthalate were qualified with a "J" because of the laboratory method blank detections.

Detected phthalates in MBDS samples may have been introduced in the laboratory; in addition, samples may have been contaminated with phthalates from the plastic storage bags. All phthalate detections were qualified due to the uncertainty. There was no apparent difference between replicate samples taken with and without the use of the stainless steel spoon in the field.

Matrix spike samples are spiked with a known concentration of a particular inorganic or organic analyte. The percent recovery of the spiked compound indicates the efficiency and effectiveness of sample preparation and analysis procedures, and how tightly bound a compound is to the sample matrix. One sample and sample duplicate (10-7) were spiked with six pesticide compounds; percent recoveries were within acceptance ranges (EPA 1988a). No samples were spiked with PCBs. Two matrix spike duplicate pairs were analyzed for eleven BNA compounds; all recoveries were within acceptance limits.

Pesticide, PCB, and BNA samples were also spiked with surrogate compounds, which are artificial compounds not normally found in environmental samples. Surrogate recovery is also used to indicate the efficiency and effectiveness of sample preparation and analysis procedures. Pesticide and PCB samples were spiked with the surrogate TCMX, and BNA samples were spiked with six surrogate compounds. Percentage recoveries of surrogates indicated acceptable laboratory sample extraction.

Laboratory duplicate samples indicate precision (replicability) of laboratory procedures. Calculation of the relative percent difference (RPD) between the duplicate samples is the common method to compare duplicate results as a measure of laboratory precision. Matrix spike duplicate samples were analyzed for pesticide, PCB, and BNA analyses, and eight duplicate sample pairs were analyzed for all of the metals analyzed in the MBDS samples. RPDs for all duplicate analyses were acceptable within EPA required limits (EPA 1988a, 1988b), indicating acceptable laboratory precision.

Field replicate analysis is an indicator of field precision as well as degrees of difference between individual samples. The pesticide 4,4'-DDE (DDE) was the only compound detected in the two field replicates collected at Station 18-18. Measured concentrations were 2.81 ppb and 1.16 ppb with a resulting RPD of 83%. Since only one trace compound was detected, this information is not sufficient to comment on the precision of field sampling.

3.2 Trace Metal Results

The results from the three replicates were averaged for each station (Table 3-1). Almost all of the metals concentrations were within the "low" category of contaminated sediments as classified by the New England River Basin Commission (Oceanic Society 1982). Exceptions, which fell in the moderately contaminated category, include four (out of twenty-eight) Cr results, five Pb results, and one Zn result.

Cadmium concentrations were below detection (<2 ppm) in all samples except for one replicate from Station 8-7 (4 ppm). Average Cr concentrations ranged from 38 ppm (16-9) to 123 ppm (10-9). Nickel concentrations were below detection (<14 to <16 ppm) at several stations, and reached a maximum of 35 ppm at Station 8-3 (Table 3-1). Copper concentrations ranged from 19 ppm (8-9) to 78 ppm (Station 12-3). The lowest Zn concentration was also measured at Station 8-9 (66 ppm), and the highest, 221 ppm, was again found at Station 12-3. Mercury was below detection limits (<0.05 ppm) in all replicates at Station 8-7, and in two out of three replicates at Stations 8-3 and 8-5. The highest Hg concentration was measured at Station 12-3 (0.47 ppm), followed closely by Station 14-9 (0.45 ppm), which is the station located by the "MDA" buoy (Figure 2-1). Finally, Pb concentrations ranged from 29 ppm at Stations 16-7 and 16-9 to 155 ppm at Station 9-6 (Table 3-1).

3.3 TOC, Pesticides, and PCB Results

All of the samples collected in the June 1989 survey were analyzed for TOC. Average TOC values ranged from 0.44% at Station 10-7 to 2.2% at Station 18-17 (Table 3-2).

Composited samples, and two replicates of 18-17, were analyzed for pesticides and PCBs. Most of the analyzed pesticides were below detection limits in all of the samples. The most commonly detected pesticide was 4,4'-DDE (DDE), which was detected in seventeen of the thirty samples at concentrations ranging from 0.65 (Station 10-7) to 10.5 ppb (Station 18-17; Table 3-2). The only other pesticides detected, including endrin, dieldrin, and 4,4'-DDD, were all at Station 10-7 (Table 3-2).

PCBs were not detected (<20 ppb) in any sample except in the composite sample from Station 16-9, at barely above the detection limit (20 ppb; Table 3-2).

3.4 BNA Results

Composited samples were analyzed for BNA compounds including PAHs. Many of the PAH sample results were qualified ("J") as estimated when they were less than the MDL but were able to be quantified from the chromatographic peaks (above the practical

Table 3-1

Metals Results of MBDS Sediment Samples, June 1989

		MBDS STATIONS													
Metal (ppm)	Sample	12-3	12-5	12-7	12-9	13-6	14-3	14-5	14-7	14-9	16-5	16-7	16-9	18-17	FG-23
Chromium	HM-1	29	<9	68	88	65	43	61	63	82	60	49	25	66	69
	HM-2	70	40	72	81	13	80	55	36	64	70	36	65	70	66
	HM-3	319	<9	51	128	74	81	68	66	52	68	51	23	114	56
	Mean	139	19	64	99	51	68	61	55	66	66	45	38	83	64
Copper	HM-1	64	37	40	45	37	52	40	39	48	38	23	29	50	18
	HM-2	80	53	51	56	40	34	38	18	39	48	27	26	25	22
	HM-3	77	49	42	52	43	58	46	49	37	48	24	24	35	24
	Mean	74	46	44	51	40	48	41	35	41	45	25	26	37	21
Lead	HM-1	123	153	66	42	70	69	52	92	57	61	29	21	53	33
	HM-2	78	136	69	70	63	38	40	51	75	66	31	47	51	39
	HM-3	129	157	70	56	65	70	62	20	51	59	28	18	82	43
	Mean	110	149	68	56	66	59	51	54	61	62	29	29	62	38
Mercury	HM-1	0.49	0.19	0.3	0.38	0.38	0.11	0.18	0.41	0.36	0.3	0.26	0.21	0.21	0.15
	HM-2	0.52	0.33	0.26	0.41	0.29	0.3	0.31	0.41	0.39	0.23	0.18	0.18	0.11	0.17
	HM-3	0.39	0.22	0.3	0.4	0.42	0.21	0.18	0.23	0.61	0.22	0.37	0.08	0.31	0.26
	Mean	0.47	0.25	0.29	0.40	0.36	0.21	0.22	0.35	0.45	0.25	0.27	0.16	0.21	0.19
Nickel	HM-1	<16	<16	<14	24	<16	<14	<14	21	21	21	<14	<14	37	17
	HM-2	<16	<16	<14	21	21	21	<14	<14	16	22	<14	<14	20	18
	HM-3	<16	<16	<14	<14	22	17	<14	<14	15	23	16	<14	22	27
	Mean	16	16	14	20	20	17	14	16	17	22	15	14	26	21
Zinc	HM-1	190	127	100	153	101	147	109	148	99	118	76	99	112	87
	HM-2	211	85	127	119	112	136	123	62	102	114	74	54	109	98
	HM-3	262	110	127	107	95	96	104	90	123	142	67	70	183	105
	Mean	221	107	118	126	103	126	112	100	108	125	72	74	135	97

Mercury values are qualified; see text for explanation.

Values below the method detection limit are listed as less than (<) the appropriate detection limit.

Table 3-1 (cont.)

		MBDS STATIONS													
Metal (ppm)	Sample	6-5	6-7	8-3	8-5	8-7	8-9	9-6	9-8	10-3	10-5	10-7	10-9	11-6	11-8
Chromium	HM-1	69	65	83	84	69	50	71	93	70	57	120	174	17	58
	HM-2	76	67	48	69	73	31	67	146	44	52	22	98	32	81
	HM-3	102	62	52	59	70	44	75	128	66	35	65	96	35	201
	Mean	82	65	61	71	71	42	71	122	60	48	69	123	28	113
Copper	HM-1	29	26	26	26	36	13	55	91	56	54	60	53	53	103
	HM-2	38	26	40	25	28	24	49	58	45	40	63	48	88	45
	HM-3	46	24	27	47	33	19	73	69	33	43	28	77	70	50
	Mean	38	25	31	33	32	19	59	73	45	46	50	59	70	66
Lead	HM-1	65	51	24	41	69	48	213	88	54	43	24	80	175	133
	HM-2	70	46	69	89	66	50	176	85	85	117	102	95	132	53
	HM-3	71	43	25	60	63	29	77	132	76	66	79	79	60	42
	Mean	69	47	39	63	66	42	155	102	72	75	68	85	122	76
Mercury	HM-1	0.09	<0.05	<0.05	<0.05	<0.05	0.08	0.37	0.27	0.16	0.35	0.12	0.32	0.39	0.23
	HM-2	0.11	0.12	<0.05	0.05	<0.05	<0.05	0.32	0.19	0.08	0.18	0.26	0.06	0.33	0.34
	HM-3	0.14	0.06	0.05	0.22	<0.05	0.05	0.17	0.29	0.1	0.2	0.22	0.13	0.28	0.21
	Mean	0.11	0.08	0.05	0.11	0.05	0.06	0.29	0.25	0.11	0.24	0.20	0.17	0.33	0.26
Nickel	HM-1	<15	26	39	25	26	<15	<15	26	21	24	28	32	<16	19
	HM-2	<15	26	39	18	31	19	<15	<15	23	22	30	40	<16	<16
	HM-3	35	28	28	28	29	<15	<15	<15	26	24	24	31	<16	37
	Mean	22	27	35	24	29	16	15	19	23	23	27	34	16	24
Zinc	HM-1	103	103	115	178	137	82	180	261	161	112	76	152	131	131
	HM-2	130	100	135	89	104	67	189	146	92	97	158	197	175	175
	HM-3	143	101	96	116	116	50	118	184	110	165	150	147	154	270
	Mean	125	101	115	128	119	66	162	197	121	125	128	165	153	192

Mercury values are qualified; see text for explanation.

Values below the method detection limit are listed as less than (<) the appropriate detection limit.

Table 3-2

Pesticides and TOC Results of MBDS Sediment Samples, June 1989

	Pesticides (ppb)				TOC
	4,4'-D	4,4'-D	Dieldrin	Endrin	(%)
6-7					0.86
8-3					0.63
8-5					0.77
8-7					0.96
8-9					0.54
9-5					0.88
9-6					0.59
9-8					0.84
10-3		0.95			0.85
10-5		1.78			0.68
10-7	0.98	0.65	2.61	4.25	0.44
10-9		2.70			0.79
11-6		4.01			0.55
11-8		2.57			0.76
12-3		2.94			0.80
12-5					0.61
12-7		1.77			0.60
12-9		10.14			0.67
13-6		1.73			0.56
14-3					1.20
14-5		3.12			0.61
14-7					0.88
14-9		2.95			0.55
16-5		4.31			0.95
16-7					0.57
16-9		6.56			1.10
18-17		10.50			2.20
FG-23		4.43			0.97

Only values above the detection limit are shown.

quantitation limit; Table 3-3). Two types of BNA compounds were detected in MBDS samples: phthalate esters and PAHs. Almost all of the samples contained bis(2-ethylhexyl)phthalate (including three of four method blanks), and ten out of thirty samples contained di-n-octyl phthalate (Table 3-4). Samples containing bis(2-ethylhexyl)phthalate were qualified due to method blank contamination.

About one-third of the MBDS stations were below detection limits in all PAH compounds, including the reference area 18-17. FG-23 contained an estimated concentration of pyrene (130 ppb). PAH results were separated into low molecular weight (LMW) and high molecular weight (HMW) compounds (Table 3-3). Total LMW PAH concentrations ranged from 100 to 510 ppb, except for a maximum LMW PAH concentration measured at Station 12-3 (1500 ppb). Phenanthrene was the most commonly detected LMW PAH compound; naphthalene was detected only at Station 12-3. Eight HMW PAH compounds were detected, and total HMW concentrations ranged from 130 to 6520 ppb (Station 12-3) (Table 3-3).

Table 3-3

PAH Results of MBDS Sediment Samples, June 1989

	MBDS STATIONS																				
PAHs (ppb)	6-7	8-7	9-6	10-3	10-5	10-9	11-6	11-8	12-3	12-5	12-7	12-9	13-6	14-3	14-5	14-7	14-9	16-5	16-7	16-9	FG-23
Low Molecular Weight																					
Napthalene									***1100***												
Phenanthrene				510	300		250	110	400		120		110	250	190	100	120	180			
Total LMW				510			250	110	1500		120		110	250	190	100	120	180			
High Molecular Weight																					
Fluoranthene	120		250	600	510		290	140	***1100***		200		180	530	420	170	180	250			
Pyrene	190	140	510	***820***	***800***	190	480	250	***1800***	260	450	250	280	530	580	260	350	350	130		130
Benzo(a)anthracene			140	440	330		145		***870***				140	330	320						
Chrysene			140	420	340		190		***920***				150	390	280					150	
Benzo(b)fluoranthene				530			200		***960***					650	500						
Benzo(a)pyrene				310					470					350	260						
Benzo(g,h,i)perylene									210												
Indeno(1,2,3-cd)pyrene									190												
Total HMW	310	140	1040	3120	1980	190	1305	390	6520	260	650	250	750	2780	2360	430	530	600	130	150	130

PAH = Polynuclear Aromatic Hydrocarbon

Only detected compound concentrations are shown; method detection limit (MDL) for all compounds is 660 ppb.

All data are estimated (<MDL) except for values in bolded italics.

Table 3-4

Phthalate Results of MBDS Sediment Samples, June 1989

Stations	Di-n-octyl phthalate	Bis(2-ethylhexyl) phthalate
6-5		1200 J
6-7	610 J	5000 J
8-3		2200 J
8-7		2300 J
8-9		790 J
9-8	1900 J	
9-6	470 J	1200 J
10-3	540 J	1400 J
10-5	380	
10-7	1000	580 J
11-6		660 J
11-8		4800 J
12-3		1900 J
12-5	400 J	570 J
12-7		2100 J
12-9		2600 J
13-6	970 J	
14-3		1100 J
14-5		2600 J
14-7		830 J
14-9		1600 J
16-5	5300	2400 J
16-7		570 J
16-9	520 J	150 J
18-17		200 J
FG-23	1900	640 J

Qualified data ("J") are estimated.
Only detected compounds are shown.
Units are all ppb.

4.0 DISCUSSION

Since 1985, the majority of dredged material has been disposed in the southwestern quarter of MBDS near the MDA buoy (Figure 2-1; Germano et al. 1994). The distribution of metals and organics was examined in order to determine the nature and extent of contaminants in the western half of MBDS, and to identify areas that should be capped with material suitable for open ocean disposal.

Sediment samples have been collected at MBDS and at the MBDS reference areas several times since 1985. Sample results from the 1989 survey were compared both with these historical MBDS data, and with sediment chemistry data from coastal Massachusetts collected by the National Oceanic and Atmospheric Administration (NOAA) through the National Status and Trends (NS&T) Program.

4.1 Spatial Distribution of Chemical Constituents

Historical disposal activity north and west of the current disposal point may have influenced the present distribution of sediment contaminants; the distribution of each metal shows a similar pattern. The ranges of trace metal concentrations were limited. A contour plot of Cu concentrations shows a band of higher concentrations in the center of western MBDS (along Stations 12-3, 11-6, and 11-8; Figure 4-1). Station 12-3, located on the far western edge of MBDS, had the highest measured concentrations of Cr (139 ppm), Cu (78 ppm), Zn (221 ppm), and Hg (0.47 ppm).

The distribution of DDE is relatively random, with two distinct highs at Stations 12-9 and 18-17 (> 10 ppb). The spatial distribution of PAHs is even more indicative of an offsite concentration to the west (Figure 4-2). Although PAH concentrations are questionable at Stations 9-8 and 8-5 due to elevated detection limits, the contoured pattern suggests that these samples were taken in an area of relatively lower PAH concentrations (Figure 4-2).

4.2 Comparative Analysis of MBDS Sediment Chemistry Data

4.2.1 Historical MBDS Data

Reference area concentrations of trace metals were near or below the average of MBDS stations sampled in the 1989 survey. Concentrations of trace metals at both reference areas have remained relatively constant since reference area 18-17 was first sampled in 1985 (SAIC 1987; Table 4-1). Concentrations of trace metals detected at a few isolated stations at MBDS, when compared with reference area results, indicated no significant accumulation of trace metals, relative to the reference areas.

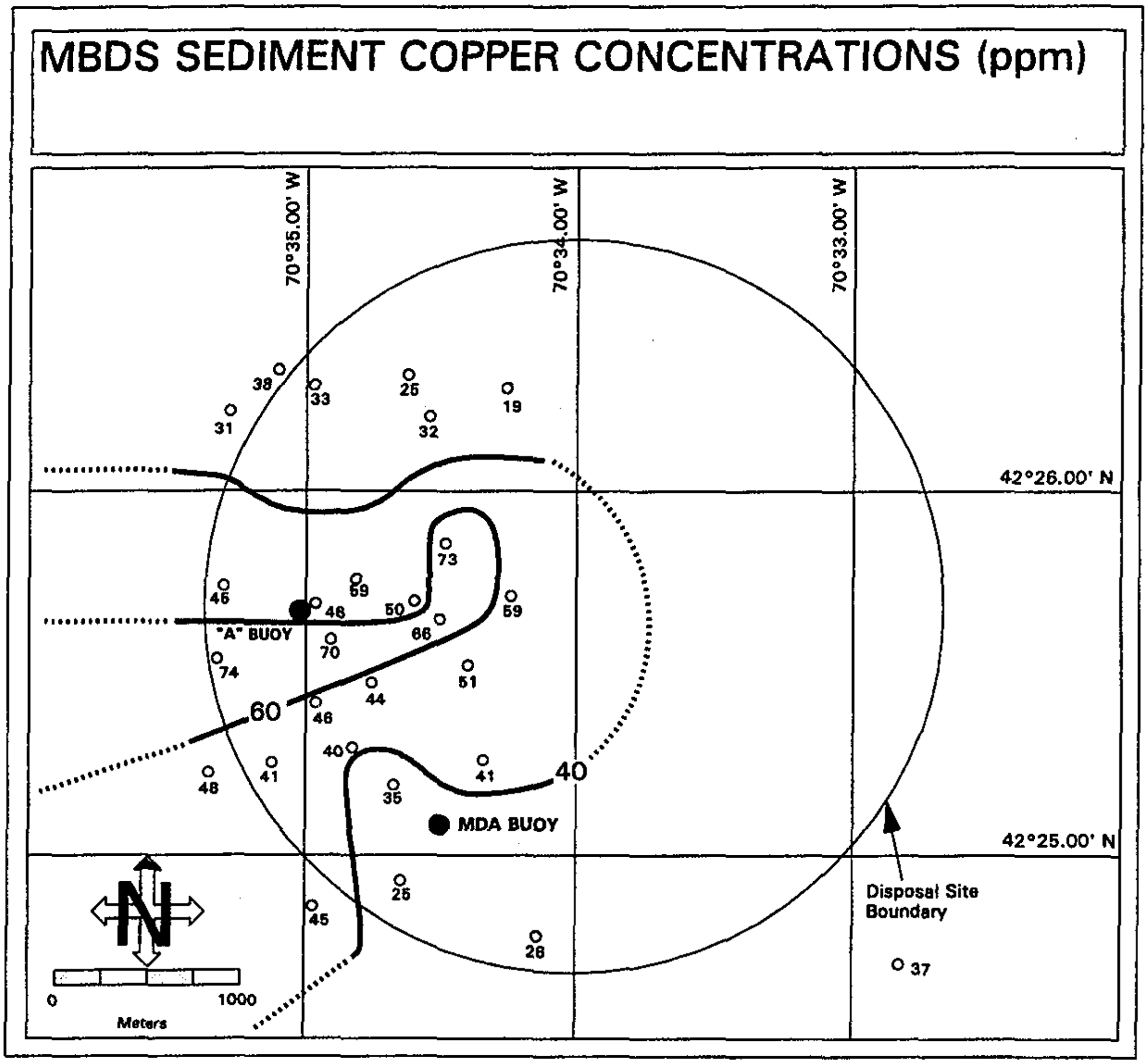

Figure 4-1. Contour map of copper concentrations (ppm)

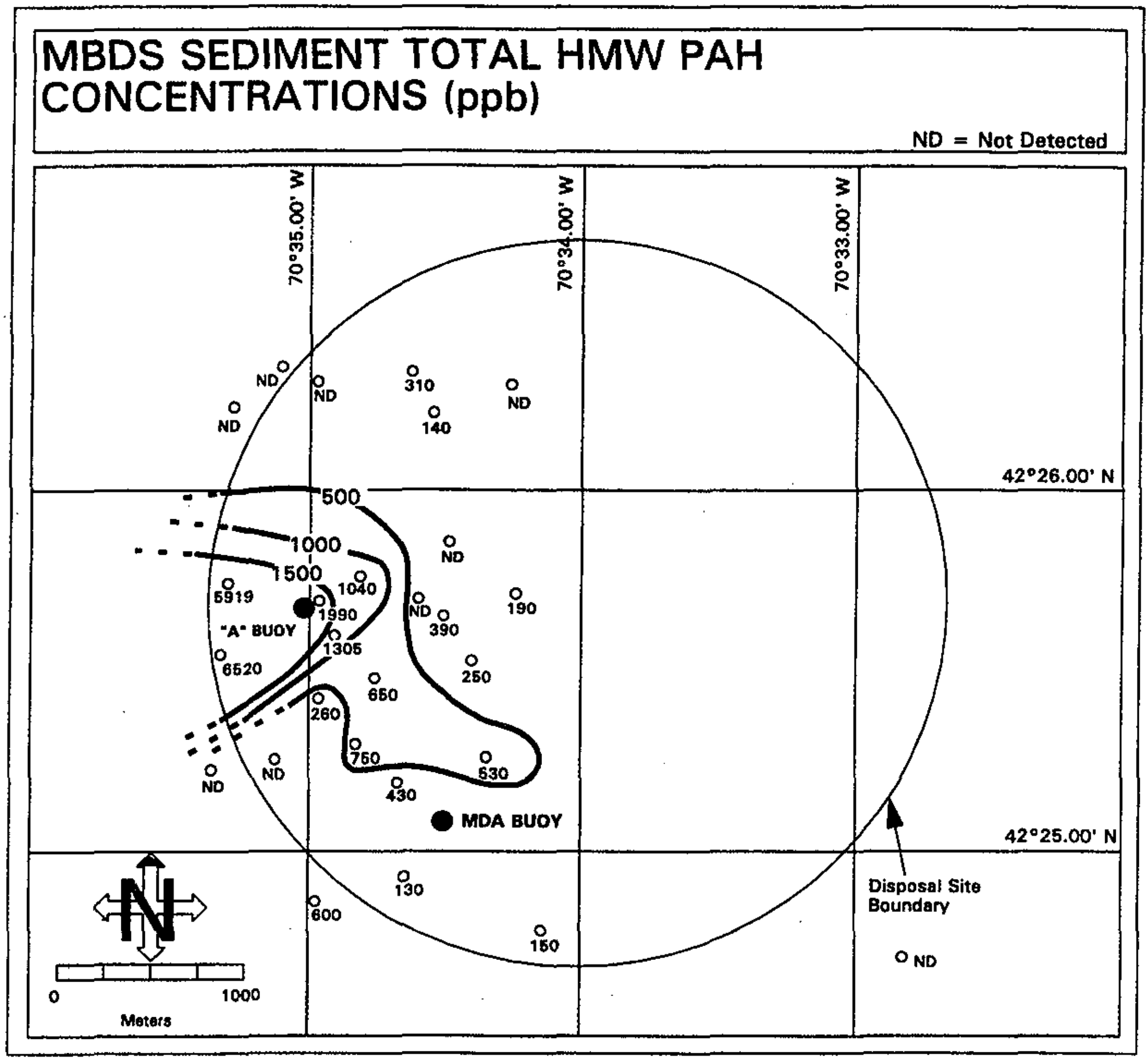

Figure 4-2. Contour map of total high molecular weight PAH concentrations (ppb)

Table 4-1

Historical MBDS Reference Station Metal Data

Reference Station	Sample Date	Cr	Zn	Pb	Ni	Cu
		(ppm)				
18-17	June 85	70	95	41	33	18
18-17	January 86	64	110	97	12	24
18-17	October 87	50	95	47	33	22
18-17	June 89	83	135	62	26	37
FG-23	October 87	40	95	40	33	19
FG-23	June 89	64	97	38	21	21
Mean MBDS*	June 89	70	127	72	21	44

*Data include all stations sampled in June 1989 except for reference stations.

Pesticides were present (DDE) at both reference areas, including the maximum measured concentration of 10.5 ppb at 18-17. The two replicate samples from 18-17 contained less than 3 ppb of the same compound, indicating that the elevated concentration of DDE measured in the composite sample from 18-17 was not distributed across the entire reference area. As will be discussed in Section 4.2.2, pesticides are fairly common in Massachusetts Bay sediments in concentrations similar to those measured at most of the MBDS stations (NOAA 1991).

PAHs and pesticides generally have been undetected in previous surveys. Pesticide detection limits were higher in the past, so the trace detections of DDE may have been missed. The HMW PAH fluoranthene was detected prior to the June 1989 survey (510 ppb at Station 14-9; SAIC 1990).

Although all but one PCB replicate sample from MBDS were below detection, PCBs have been detected in sediments at MBDS prior to the June 1989 survey. In September 1985, replicate samples were taken at Stations 18-17 and 9-8. Average concentrations of PCBs were 75 and 1240 ppb, respectively. Sampling was duplicated at Stations 18-17 and 9-8 in January of 1986 with lower results (48 and 329 ppb, respectively; all from SAIC 1987). The 1985 sampling was repeated in 1986 with similar, although slightly lower, results, which increases the validity of the historical data. The 1989 PCBs data were accompanied by reasonable surrogate and matrix spike recoveries, which also indicates that these data are valid. Therefore, the decrease in PCB concentrations in MBDS sediment is apparently real.

Commercial production of PCBs ceased in 1977 (Kennish 1992). These compounds persist in estuarine and marine sediments and have a half-life in environmental samples from 8 to 15 years (Kennish 1992). They may be nearly undetectable in the water column, but tend to accumulate in biota (Pequegnat et al. 1990). The observed decreases in PCB concentrations may be related to a lower environmental input than in the past. Reduced inputs through better management have now allowed reductions to occur over the past 5-10 years or more. Subsequent burial or dilution with newer deposited (natural) sediments containing lower levels of PCBs seems the most likely explanation.

4.2.2 Regional Data Comparison

Samples from coastal and estuarine sediment data from 300 sites in the United States have been collected and analyzed during NOAA's NS&T since 1984. Several sites along the coast of Massachusetts and in Boston Harbor were sampled from 1984 to 1989 (NOAA 1991). Stations closest to MBDS, including Cape Ann, Duxbury Bay, Salem Harbor, and Quincy Bay, were compared to the MBDS results. None of the NS&T stations were located as far offshore as MBDS. However, since much of the material sampled at MBDS was presumably material dredged from Massachusetts harbors, the comparison is appropriate to place the chemistry data in a relative context.

In comparing the MBDS results with NS&T data, several qualifiers must be made. The analytical methods vary somewhat between the two; NS&T methods were developed for very low detection limits. For example, although many PAHs were lower than the MDL in MBDS samples, detection limits were higher than those of the NS&T data, so the two datasets are not directly comparable. Individual concentrations of detected PAHs (rather than total HMW or LMW PAHs) were compared with NS&T data, because of the uncertainty of summing values which are below detection. PCBs are analyzed by NS&T methods as individual isomers, and are not comparable with the total PCB measurement obtained by the NED laboratory.

Metals. MBDS metals data were compiled, and several ranges of values were compared both with regional Massachusetts and national NS&T data. The maximum and minimum metals values, and the statistical range of values (mean ± one standard deviation) were reported for MBDS data, and compared with four regional sites and the values reported by NS&T for national mean and "high" values (greater than one standard deviation above the national mean; NOAA 1991). The four regional areas used for comparison are: Cape Ann-Gap Head (CAGH), Salem Harbor (SAL), Quincy Bay (QUI), and Duxbury Bay-Clarks Island (DBCI; Figure 1-1). Data over several years were averaged from each of these sites.

SAL and QUI are reported to have "high" concentrations of many metals (Cr, Cu, Hg, Pb); CAGH has "high" concentrations of Pb only; and DBCI is a sandy site without any reported "high" concentrations of any metal or organic contaminant (NOAA 1991). In general, CAGH and DBCI have lower concentrations of all metals than SAL and QUI (Table 4-2).

The maximum measured concentration of Ni, Pb, and Zn in MBDS samples was higher than both QUI and SAL. However, the statistical ranges of all metals concentrations from MBDS samples were intermediate between the two highest metals sites (SAL and QUI), and the two lowest metals sites (CAGH and DBCI). One exception was the maximum Pb value, which was greater than that measured at QUI (Table 4-2).

Relative to national values, the mean values of MBDS metals concentrations were less than the national mean for all metals except Cu, Hg, and Pb (Table 4-2). All of the Cu and Hg concentrations measured at MBDS were less than the value classified as "high" by NS&T, but the statistical maximum value of Pb measured at MBDS was higher than this "high" value. In general, Ni values are lower in the entire Massachusetts Bay region, including the MBDS, relative to national concentrations.

Table 4-2

MBDS Trace Metal Data Relative to Regional Massachusetts Bay

	Metals (ppm)					
Location	Cr	Cu	Hg	Ni	Pb	Zn
Cape Ann - Gap Head	24	9	0.07	11	28	40
Duxbury Bay	19	5	0	7	11	20
Quincy Bay	224	134	1.38	30	96	192
Salem Harbor	1586	71	0.91	30	141	185
MBDS Maximum	139	74	0.47	35	155	221
MBDS Minimum	19	19	0.05	14	29	66
MBDS Mean	70	43	0.22	21	71	126
Statistical Range*	42-97	29-58	0.1-0.3	15-27	40-101	91-161
NS&T National Mean	110	35	0.17	34	43	140
NS&T National "High"	230	84	0.49	69	89	270

*Range is calculated as the mean +/- one standard deviation.
NS&T = National Status and Trends (NOAA 1991).

Pesticides and PAHs. All organic data for both MBDS and the NS&T sites were normalized to TOC. Natural variations in sedimentary parameters can influence the concentration of trace metal and organic constituents measured in the laboratory. For example, an increase in the fine-grained fraction and in TOC are both positively correlated with metal and organic concentrations (e.g., NOAA 1991). Consequently, MBDS organics data were normalized and compared with the same regional Massachusetts sites (CAGH, SAL, QUI, and DBCI; Figure 1-1). Data over several years were averaged from each of these sites and divided by the TOC concentration (Table 4-3).

After normalizing pesticide concentrations to TOC, the DDE concentration of Station 18-17 falls within the ranges of other values measured at MBDS. In general, DDE concentrations are similar to those measured at the NS&T sites. This factor, and the lack of any spatial distribution of DDE concentrations, indicates that the detections of DDE at MBDS are representative of background concentrations in Massachusetts Bay.

SAL and QUI are reported to have "high" concentrations (greater than one standard deviation from the national mean) of total LMW and HMW PAHs, and total DDT pesticides (NOAA 1991). CAGH also is reported to have "high" concentrations of total HMW PAHs, and actually has higher concentrations in individual HMW PAHs than the other regional Massachusetts sites examined here (Table 4-3).

About one-third of the MBDS stations were below detection for all PAHs measured, and only two LMW PAH compounds and eight HMW compounds were detected in any sample. Both reference areas were below detection in all PAHs except for an estimated value of pyrene at FG-23.

Many of the detected and estimated concentrations of individual PAHs in MBDS sediment were in the same range or higher than those measured at all of the NS&T sites used in the comparison (Table 4-3). A degree of uncertainty exists in comparing the MBDS estimated PAH concentrations, which are below the MDL and estimated from the chromatograms. This uncertainty is compounded by the different methods used by NS&T.

All of the PAHs detected (not estimated) at Station 12-3 were above the MDL and higher than all of the NS&T sites, which indicates clearly that the sediment near this station is anomalously high in HMW PAHs relative to both the NS&T stations and the national average. The distribution of HMW PAHs at MBDS indicates that the highest values are concentrated in the far western edge of MBDS, and are influenced by historical disposal of dredged and perhaps other waste materials (Figure 4-2). HMW PAHs were detected at many MBDS stations, including those near the current disposal buoy, in concentrations similar to coastal measurements made in the NS&T program (Table 4-3). HMW PAHs have long residence times in the aquatic environment, even relative to LMW PAHs, and are generally derived from fossil fuel combustion (Kennish 1992). It is currently thought that pyrogenic PAHs (HMW) are more tightly bound to particles than petroleum source (LMW) PAHs (McGroddy et al. 1992).

Table 4-3

TOC Normalized Pesticide and PAH Concentrations Relative to Regional Massachusetts Bay

LOCATION	TOC (%)	DDE	LMW PAHs		HMW PAHs							
			Naph	Phen	Fluor	Pyrene	Ben(a)a	Chrysene	Ben(b)f	Ben(a)p	Ben(g,h,i)	Indeno
Cape Ann - Gap Head	0.63	1.3	12	292	553	510	276	266	nd	250	nd	nd
Duxbury Bay - Clarks Isla	0.10	5.3	44	150	240	207	93	95	83	92	77	82
Quincy Bay	3.52	2.9	39	131	235	219	106	133	50	117	89	92
Salem Harbor	4.49	1.5	34	120	211	269	114	120	40	97	37	19
MBDS 6-5	0.88	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
MBDS 6-7	0.86	nd	nd	nd	140	221	nd	nd	nd	nd	nd	nd
MBDS 8-3	0.63	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
MBDS 8-5	0.77	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
MBDS 8-7	0.96	nd	nd	nd	nd	146	nd	nd	nd	nd	nd	nd
MBDS 8-9	0.54	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
MBDS 9-5	0.88	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
MBDS 9-6	0.59	nd	nd	nd	424	864	237	237	nd	nd	nd	nd
MBDS 9-8	0.84	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
MBDS 10-3	0.85	1.1	nd	600	706	965	518	494	624	3658	nd	nd
MBDS 10-5	0.68	2.6	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
MBDS 10-7	0.44	1.5	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
MBDS 10-9	0.79	3.4	nd	nd	nd	241	nd	nd	nd	nd	nd	nd
MBDS 11-6	0.55	7.3	nd	455	527	873	264	345	364	nd	nd	nd
MBDS 11-8	0.76	3.4	nd	145	184	329	nd	nd	nd	nd	nd	nd
MBDS 12-3	0.80	3.7	1375	500	1375	2250	1088	1150	1200	588	263	238
MBDS 12-5	0.61	nd	nd	nd	nd	426	nd	nd	nd	nd	nd	nd
MBDS 12-7	0.60	3.0	nd	200	333	750	nd	nd	nd	nd	nd	nd
MBDS 12-9	0.67	15.1	nd	nd	nd	373	nd	nd	nd	nd	nd	nd
MBDS 13-6	0.56	3.1	nd	196	321	500	250	268	nd	nd	nd	nd
MBDS 14-3	1.20	nd	nd	208	442	442	275	325	542	292	nd	nd
MBDS 14-5	0.61	5.1	nd	311	689	951	525	459	820	426	nd	nd
MBDS 14-7	0.88	nd	nd	114	193	295	nd	nd	nd	nd	nd	nd
MBDS 14-9	0.55	5.4	nd	218	327	636	nd	nd	nd	nd	nd	nd
MBDS 16-5	0.95	4.5	nd	189	263	368	nd	nd	nd	nd	nd	nd
MBDS 16-7	0.57	1.8	nd	nd	nd	228	nd	nd	nd	nd	nd	nd
MBDS 16-9	1.10	6.0	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
MBDS 18-17	2.20	4.8	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
MBDS FG-23	0.97	4.6	nd	nd	nd	134	nd	nd	nd	nd	nd	nd

nd = Not detected.

5.0 CONCLUSIONS AND RECOMMENDATIONS

Sediment chemistry results from the MBDS survey of June 1989 indicate that the distribution of both organic and inorganic constituents reflects a difference in disposal practices from the past to the present with lower contaminant concentrations observed in the area of active disposal. Conversely, the highest concentrations of contaminants, especially PAHs, are located along the western edge of MBDS where disposal in earlier decades was concentrated.

Relatively low trace metal concentrations and the spatial consistency of trace metal data indicate no specific anthropogenic point sources of trace metals; maximum measured concentrations of all metals are at stations north of the present disposal buoy. In general, the data suggest no accumulation of elevated concentrations of trace metals at MBDS. Metal concentrations are within MBDS reference area values. Overall, Pb concentrations are the highest relative to both regional and national comparisons.

Detected HMW PAHs clearly show the highest concentrations near Station 12-3, located near the approximate center of the historical disposal site (1 nmi west of present center). Approximately two-thirds of the stations at MBDS contained HMW PAHs at concentrations within the range of values measured along coastal Massachusetts by the National Status and Trends Program, and a trace of pyrene was detected (estimated) at reference area FG-23. These factors indicate that the presence of PAHs at MBDS is influenced by both background concentrations of PAHs in the Massachusetts Bay region and historic disposal.

The detection of 4,4'-DDE in many samples is consistent with the fairly common presence of pesticides in Massachusetts Bay sediments. PCBs, previously reported at the same stations measured in the 1989 survey at concentrations of up to 1 ppm, were virtually undetected; subsequent burial seems the most likely explanation.

- The presence of relatively high concentrations of HMW PAHs along the western edge of MBDS indicates that this area should be considered to receive new capping material suitable for unconfined disposal.

- Future chemical sampling at MBDS should focus on the distribution of PAHs at MBDS, including the eastern half of the site, in order to document background concentrations of PAHs in the Massachusetts Bay region. Concentrations of PAHs at MBDS are similar to coastal background, but are likely not as low as background levels found in the Stellwagen Basin.

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