Deer Island Effluent Characterization: June - November 1993

Massachusetts Water Resources Authority

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DEER ISLAND EFFLUENT CHARACTERIZATION
JUNE - NOVEMBER, 1993

by

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EXECUTIVE SUMMARY

Concentrations of selected trace metals and anthropogenic organic compounds were monitored in the effluent of the Deer Island wastewater treatment plant as part of the Massachusetts Water Resources Authority (MWRA) Harbor and Outfall Monitoring Program (HOM). Bimonthly 24-h composite samples were collected between June and November 1993 and analyzed for Ag, Cd, Cr, Cu, Hg, Ni, Pb, and Zn, an extended list of 40 polynuclear aromatic hydrocarbons (PAH), C_{10} to C_{14} linear alkyl benzenes (LAB), 20 polychlorinated biphenyl (PCB) congeners, and 16 persistent chlorinated pesticides. Analytical work was carried out using ultra-trace techniques capable of providing detection limits in the low parts-per-trillion (ng/L) for organic compounds and low parts-per-billion (μg/L) for trace metals.

Total effluent flow at the Deer Island treatment plant was monitored on the days of sampling by MWRA; month-to-month variation in total flow was within 10%. The concentrations of trace metals in the effluent were relatively consistent over the six-month period, suggesting that the source of the metals to the waste stream was essentially invariant. No trends in metals concentrations were noted except that the highest concentrations for most of the metals occurred in September. Conversely, total PAH concentrations were 10-15% higher in October and November compared to the summer months. PCB congeners—primarily those of lower levels of chlorination—were detected in the effluent in the low part-per-trillion range. Little change was noted in total PCB concentration over the six-month period. Of the 16 chlorinated pesticides, dieldrin showed the most notable trend; concentrations were approximately 75 ng/L in June and July, but dropped to <2 ng/L in September through November. Hexachlorobenzene was elevated (ca. 150 ng/L) in June and July, dropped to <10 ng/L in August and September, then climbed to about 50 ng/L in October and November. The remaining pesticides (Aldrin, DDT family, chlordane, endrin, heptachlor, heptachlor epoxide, lindane, mirex, and trans-nonachlor) were found sporadically at concentrations generally <10 ng/L.

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1.0 INTRODUCTION

Waste water from the greater Boston metropolitan area is treated at two primary treatment plants located on Deer Island and Nut Island in Boston Harbor and the effluent discharged near the mouth of the Harbor into Massachusetts Bay (Figure 1).

As part of the Harbor and Outfall Monitoring Program, the MWRA is performing bi-monthly monitoring of the effluent from the Deer Island plant in an effort to characterize the nature of the effluent being discharged into the Harbor and Massachusetts Bay. This report summarizes the results of that characterization task between June and November 1993.

The objectives of this effluent characterization task were to evaluate:

- *Selected trace metal and persistent anthropogenic organic contaminant concentrations in the effluent.* The trace metal and organic contaminants of particular concern in the MWRA effluent are listed in Table 1; these compounds are of interest because established EPA Water-Quality Criteria exist for them and/or they have been detected in the MWRA effluent or otherwise found in receiving waters or sediments of Boston Harbor and Massachusetts Bay.

- *Short-term (e.g., 2-3 day) variability in effluent contaminant concentrations.* Two-day interval, twenty-four hour composite bi-monthly samplings of Deer Island effluent were made each month beginning in June 1993. The objective of this facet of the task was to monitor for short-term fluctuations in the concentrations of the target metals and organic compounds in the waste stream. Short-term fluctuations could indicate episodic inputs of contaminants that might otherwise be overlooked using a one-time sampling strategy.

- *Long-term (e.g., monthly and seasonal) changes in effluent contaminant concentrations.* Monthly sampling of the effluent was undertaken in order to discover if there was a seasonal component to the composition of the effluent. For example, certain organic compounds such as pesticides might be used more frequently during certain months of the year, possibly resulting in elevated levels of such compounds in the effluent.

- *Monthly and annual contaminant-specific loading to Massachusetts Bay.* Effluent flow data (measured by MWRA), coupled with the contaminant concentration data collected during this task, provide a means for calculating estimated loadings of contaminants into the Harbor and Bay. These data are valuable both for computing contaminant inputs and as one type of long-term gauge for measuring change in inputs to the Harbor/Bay system as waste stream treatment practices change.

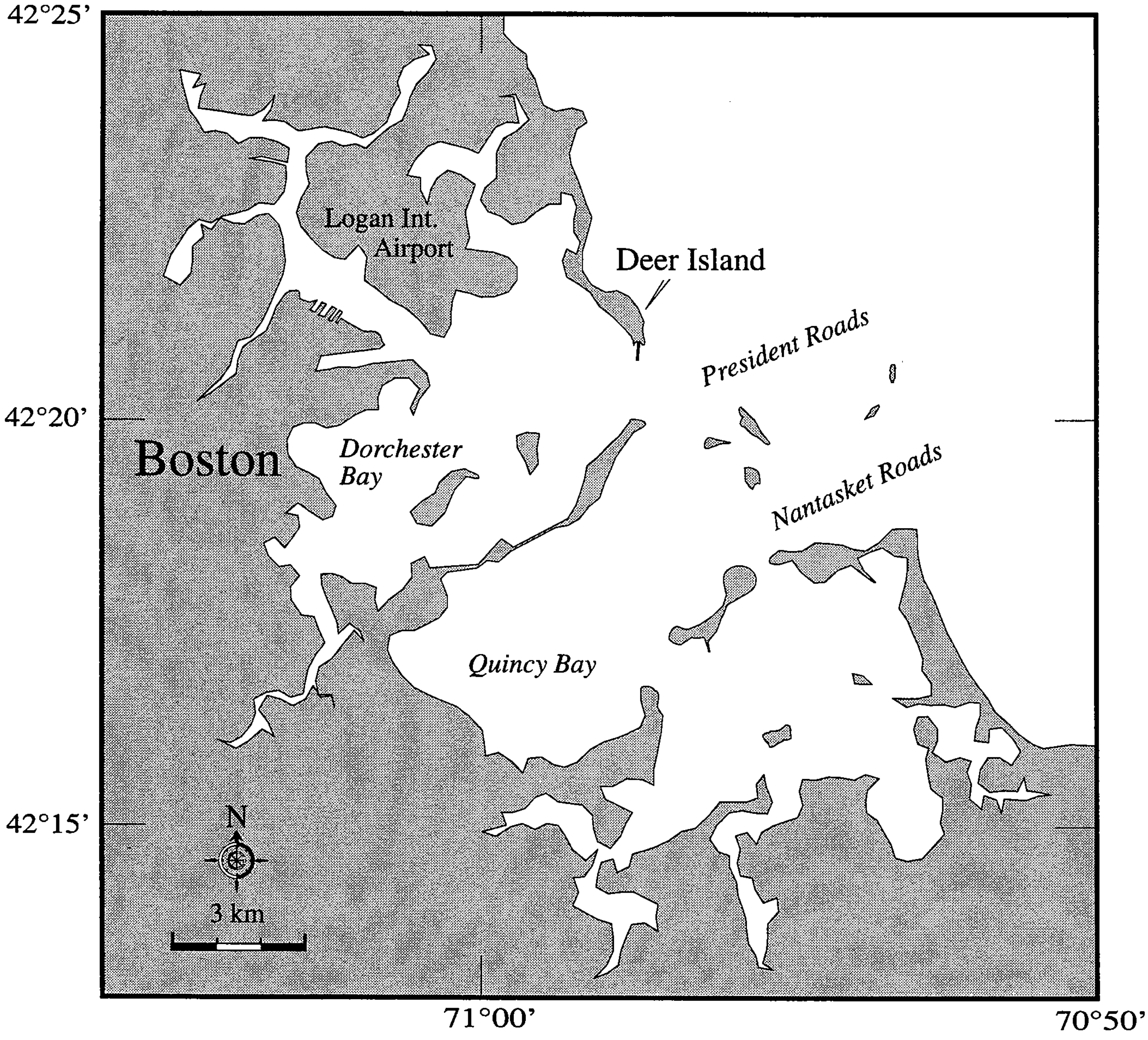

Figure 1. The location of Deer Island in Boston Harbor.

Table 1. Organic and trace metal analytes for the Deer Island effluent characterization task.

Polynuclear Aromatic Hydrocarbons
Naphthalene (N)
C_1-C_4 naphthalene
Biphenyl (BI)
Acenaphthylene (AE)
Acenaphthene (AC)
Fluorene (F)
C_1-C_3 fluorenes
Phenanthrene (P)
Anthracene (A)
C_1-C_4 phenanthrene/anthracenes
Fluoranthene (FL)
Pyrene (PY)
C_1-fluoranthene/pyrene (FP1)
Dibenzothiophene (D)
C_1-C_4 dibenzothiophenes
Benz[*a*]anthracene (B)
Chyrsene (C)
C_1-C_4 chyrsenes
Benzo[*b*]fluoranthene (BB)
Benzo[*k*]fluoranthene (BK)
Benzo[*e*]pyrene (BE)
Benzo[*a*]pyrene (BA)
Perylene (PER)
Indeno[1,2,3-*c,d*]pyrene (IP)
Dibenz[*a,h*]anthracene (DA)
Benzo[*g,h,i*]perylene (BP)

Linear Alkyl Benzenes
Phenyl decanes (C_{10})
Phenyl undecanes (C_{11})
Phenyl dodecanes (C_{12})
Phenyl tridecanes (C_{13})
Phenyl tetradecanes (C_{14})

Pesticides
Hexachlorobenzene
Lindane
Heptachlor
Aldrin
Heptachlorepoxide
cis-Chlordane
trans-Nonachlor
Dieldrin
Endrin
Mirex
2,4'-DDD
4,4'-DDD
2,4'-DDE
4,4'-DDE
2,4'-DDT
4,4'-DDT

Polychlorinated Biphenyls
2,4,-Cl2(8)
2,2',5-Cl3(18)
2,4,4'-Cl3(28)
2,2',3,5'-Cl4(44)
2,2',5,5'-Cl4(52)
2,3',4,4'-Cl4(66)
3,3',4,4'-Cl4(77)
2,2',4,5,5'-Cl5(101)
2,3,3',4,4'-Cl5(105)
2,3',4,4',5-Cl5(118)
3,3',4,4',5-Cl5(126)
2,2',3,3',4,4'-Cl6(128)
2,2',3,4,4',5'-Cl6(138)
2,2',4,4',5,5'-Cl6(153)
2,2',3,3',4,4',5-Cl7(170)
2,2',3,4,4',5,5'-Cl7(180)
2,2',3,4,5,5',6-Cl7(187)
2,2',3,3',4,4',5,6-Cl8(195)
2,2',3,3',4,4',5,5',6-Cl9(206)
Decachlorobiphenyl-Cl10(209)

Trace Metals
Silver (Ag)
Cadmium (Cd)
Chromium (Cr)
Copper (Cu)
Mercury (Hg)
Nickel (Ni)
Lead (Pb)
Zinc (Zn)

- *Possible chemical "fingerprints" that might be unique to the effluent or suggest possible sources of the contaminants in the effluent.* The presence and distribution of metals and organic compounds in the effluent, if unique, might be useful for tracking the fate of the discharge plume and/or some of the contaminants in the aquatic environment. Similarly, a characteristic pattern in the distribution of certain contaminants might suggest a source or type of source to the effluent. For example, the distribution of polynuclear aromatic hydrocarbons (PAH) reveals the predominant type of petroleum hydrocarbons in the waste stream which, in turn, could be linked to a source or source type.

- *Comparability of the results of effluent analysis between ultra-trace metal and organic contaminant techniques and standard methods used to support National Pollutant Discharge Elimination System (NPDES) methods.* Because the concentrations of many of the metal and organic contaminants in the Deer Island effluent were expected to be very low (e.g., low micrograms-per-liter for metals; low nanogram-per-liter for organics [Shea, 1993a]), Battelle utilized very sensitive ultra-trace methods for measurement of the target compounds in the effluent. Coincident with the sampling for this study, MWRA collected samples of effluent for routine NPDES monitoring in which standard EPA methods were used for contaminant analysis. This provided an excellent opportunity to compare results of the two methods. Because the ultra-trace methods were more likely to detect contaminants, there are notable implications for contaminant loading estimates using data from the two analysis programs.

2.0 METHODS

2.1 SAMPLING

Effluent samples were collected each month from the Deer Island treatment plant by MWRA personnel beginning in June 1993. Twenty-four hour composite samples were collected using Isco automated samplers. Each month, two composite samples were taken two days apart. The composite effluents were subsampled as follows:

- 2 L for trace organic analysis (PAH, pesticides, PCB)
- 500 mL for trace metal analysis (Ag, Cd, Cr, Cu, Ni, Pb, Zn)
- 500 mL for Hg analysis in Teflon bottle

Additional samples were also collected for use as matrix spike quality control material. The composite samples were stored on ice and shipped by courier to the Battelle Ocean Sciences laboratory. All bottles for metals and mercury analysis were rigorously cleaned in dilute, high purity acids to ensure extraneous contaminants was not contributed to the samples. Sample bottles for organic samples were recycled solvent bottles that had only contacted pesticide grade solvents.

2.2 METHODS OF CHEMICAL ANALYSIS

Because the concentrations of most of the target analytes in the MWRA effluent were known to be in the low nanogram-per-liter range for organics and low microgram-per-liter range for metals, effluent samples collected for this task were analyzed using methods that have been specially modified for measurement of ultra-trace levels of contaminants in fresh and marine water matrices. These methods were chosen because conventional EPA methods used for analysis of water and wastewater have detection limits that are too high for detection of the generally low levels of contaminants expected in the Deer Island effluent (Shea, 1993a). A brief summary of the detection limits for the methods used in this task are presented in Table 2; for comparison, detection limits for conventional EPA methods used to support NPDES monitoring are also given.

The extraction techniques for organic contaminant analysis follows EPA Method 3510; sample cleanup and instrumental analysis techniques—modifications or derivations of several standard EPA methods—are those from the National Oceanic and Atmospheric Administration (NOAA) National Status and Trends (NS&T) Program. The methods have been developed and refined over the last eight years by Battelle, NOAA, and National Institute of Standards and Testing (NIST) scientists to support the low-level contaminant measurement requirements of the NS&T program. Descriptions of these methods in standard operating procedure (SOP) form have been prepared by Battelle scientists and published in a NOAA Technical Memorandum (Peven and Uhler, 1993) that is the cornerstone of the NS&T analytical program.

Methods for the determination of trace metals in effluent are standard EPA techniques modified for ultra-clean analysis. Total recoverable metals were determined following modified EPA 600-01-79-020m Section 4.1.4; Ag, Cd, Cu, Ni, Pb, and Zn were determined by graphite furnace atomic absorption spectrometry (GFAAS), while Hg was measured using cold vapor atomic absorption spectroscopy (CVAAS).

The specific details of the methods used in the MWRA effluent characterization task are presented in the Task 18 Combined Work/Quality Assurance Project Plan (Shea, 1993b). Summaries of the methods follow.

Table 2. Method Detection Limit (MDL) goals.

Parameter	MDL Goal	NPDES MDL[1]
Metals	(μg/L)	(μg/L)
Ag (silver)	0.50	10.0
Cd (cadmium)	0.50	4.0
Cu (copper)	0.50	10.0
Cr (chromium)	1.0	10.0
Hg (mercury)	0.005	0.2
Ni (nickel)	1.00	10.0
Pb (lead)	0.50	1.0
Zn (zinc)	2.00	6.0
Organic Analytes	(ng/L)	(ng/L)
Polychlorinated biphenyls (PCB) (as congeners)	1	500
Linear alkyl benzenes (LAB)	50	NA
Polynuclear aromatic hydrocarbons (PAH)	10	10,000
Pesticides	1	50-100

[1] NPDES MDLs are typical MDLs reported by MWRA in their NPDES monitoring reports; the listed MDLs meet the EPA Contract Laboratory Program (CLP) requirements.

2.2.1 Trace Organics

Effluent samples were serially extracted for PAH, LAB, chlorinated pesticides, and PCB following EPA Method 3510. Each 2-L effluent sample was transferred to a 3-L separatory funnel. The sample bottle was rinsed with dichloromethane (DCM) and the rinseate added to the separatory funnel to ensure that any organic compounds adhering to the wall of the bottle were scavenged. The appropriate PAH and LAB surrogate internal standards were added to the sample and the sample was serially extracted three times with 120-mL portions of DCM. The first phase of extract cleanup was accomplished following modified EPA Method 3610. The extract was passed through a 20-g alumina column and eluted with 50 mL of DCM. The filtrate was reduced in volume to about 1 mL using Kuderna-Danish and nitrogen concentration techniques; the concentrated extract was further cleaned using size-exclusion (gel permeation) high-performance liquid chromatography (HPLC) (modified EPA Method 3640). The gel permeation HPLC cleanup removes common biogenic contaminants that can interfere with low-level instrumental analysis. The post-HPLC extract was concentrated to approximately 0.5 mL under nitrogen, recovery internal standards were added, and the final extract was split for analysis—one half for PAH and LAB analysis; the other half was solvent-exchanged with isooctane and used for PCB and pesticide analysis.

Sample extracts were analyzed for PAH and LAB compounds by selected ion monitoring (SIM) gas chromatography mass spectrometry (GC/MS) following a modification of EPA Method 8270. PAH compounds were determined by monitoring for the most intense parent ion plus one confirmation ion for each target compound; LAB compounds were determined as five separate LAB groups (those with alkyl chains containing 10, 11, 12, 13, and 14 carbon atoms) by monitoring the characteristic LAB m/z 91 molecular ion during the GC/MS analysis and summing the structural homologues within each group (Eganhouse *et al.*, 1983). Pesticides and PCB congeners were analyzed by capillary gas chromatography with electron capture detection (GC/ECD) using EPA Method 8080, modified to include additional analytes. All analytes were quantified using the internal standard method.

2.2.2 Trace Metals

The sample preparation procedures for determining total recoverable metals are defined by EPA (Section 4.1.4 of 600-01-79-020, March, 1983). For all metals except Hg, 100 mL of the sample was spiked with 5 mL of hydrochloric acid and the sample reduced in volume to about 10-20 mL by evaporation. The solution was then filtered through a Nuclepore 0.4-μm membrane. To increase sensitivity, the filtrate was not diluted back to 100 mL. To reduce sample contamination, all sample preparation was performed in a Class-100 clean room, and all sample containers and sample preparation equipment were rigorously cleaned according to the procedures of Patterson and Settle (1976). All effluent samples are directly analyzed by GFAAS for Ag, Cd, Cr, Cu, Ni, Pb, and Zn.

A modification of EPA Method 245.1 was used for Hg analysis. The samples were prepared by digesting approximately 50 mL of sample with $KMnO_4$ and $K_2S_2O_8$ and reduced to elemental mercury with $SnCl_2$. Mercury measurements were made using CVAAS.

3.0 RESULTS AND DISCUSSION

Monthly concentrations of trace metals, PAH and LAB, and pesticides and PCB in Deer Island effluent from the period June to November 1993 are presented in Tables 3, 4, and 5, respectively. In each table, results from two 24-hour composites for each month are presented. Sample collection dates and MWRA sample identification codes are also given. All trace metal and organic analyses were carried out under the quality control regiments described in the Task 18 Combined Work/Quality Assurance Project Plan (Shea, 1993b). Instrumental calibration and batch quality control objectives as described in the WQAPjP were met with the exception of recovery of LAB from matrix spike samples--LAB levels in the actual effluent samples was sufficiently elevated to preclude accurate determination of recovery of fortified LAB from the matrix spike samples.

To accurately interpret any short- or long-term changes in effluent contaminant concentrations and to perform contaminant loading calculations, MWRA collected effluent flow data on the days that effluent samples were collected for chemical analysis (Hall, 1994a). This information is depicted graphically in Figure 2, where the mean (midpoint of bar) and the range in flow between the two sampling days for each month are shown. The average flow for the six-month period—based on the 12 data points presented here—was 198 million gallons per day (MGD). The monthly flow derived from these samples were generally within the 10 percent of the average monthly flow derived from daily measurements during the month (M. Hall, personnel communication). Flow ranged from a low of 184 MGD (August) to a high of 209 MGD (September). During each month, little variation (<2%) in flow was measured between sampling events. In general, little variation in the monthly

Table 3. Concentrations (μg/L) of trace metals in Deer Island effluent (June - November 1993).

Month:	June		July		August		September		October		November	
Event Code:	E9301	E9301	E9302	E9302	E9303	E9303	E9304	E9304	E9305	E9305	E9306	E9306
Collection Date:	6/16/93	6/18/93	7/14/93	7/16/93	8/11/93	8/13/94	9/15/93	9/17/93	10/13/93	10/15/93	11/10/93	11/12/93
MWRA ID:	39307241	39307242	39308543	39308544	39310239	39310242	39312031	39312032	39313118	39313117	39314666	39314667
Ag	5.08	5.87	2.40	3.25	7.11	6.03	3.39	5.09	4.09	1.75	3.16	2.82
Cd	0.42	0.41	0.58	0.81	0.42	0.44	0.57	0.47	0.46	0.57	1.15	0.29
Cr	3.39	2.86	3.42	4.48	3.21	3.36	3.70	7.61	2.96	2.02	2.37	1.65
Cu	75.3	75.6	80.9	73.2	68.8	67.9	85.9	81.4	68.9	66.0	62.9	56.2
Hg	0.165	0.204	0.094	0.143	0.120	0.289	0.234	0.232	0.087	0.079	0.101	0.127
Ni	5.89	5.97	6.69	3.81	7.31	5.86	5.66	5.29	6.39	6.40	5.38	7.62
Pb	13.0	11.1	11.2	7.81	9.53	10.2	16.7	23.3	8.73	7.49	13.3	8.64
Zn	124	95.0	75.9	81.3	66.6	72.5	91.5	94.2	85.9	67.9	109	76.2

Table 4. Concentrations (μg/L) of polycyclic aromatic hydrocarbons (PAH) and linear alkyl benzenes (LAB) in Deer Island effluent (June - November 1993).

Month:	June		July		August		September		October		November	
Event Code:	E9301	E9301	E9302	E9302	E9303	E9303	E9304	E9304	E9305	E9305	E9306	E9306
Collection Date:	6/16/93	6/18/93	7/14/93	7/16/93	8/11/93	8/13/94	9/15/93	9/17/93	10/13/93	10/15/93	11/10/93	11/12/93
MWRA ID:	39307241	39307242	39308543	39308544	39310239	39310242	39312031	39312032	39313117	39313118	39314666	39314667
Naphthalene	1408	1434	1015	1081	2453	1281	2236	1394	927	1348	954	1064
C1-naphthalenes	1755	1761	1136	1167	1935	1737	3987	2331	1520	2730	1881	2139
C2-naphthalenes	2575	2543	1488	1470	3100	3028	6377	3952	2825	5040	3546	3927
C3-naphthalenes	2351	2345	1339	1282	3128	3241	5472	3941	7080	10899	9091	9715
C4-naphthalenes	1073	1124	631	556	1921	1976	2897	2381	1805	2764	2177	2489
Biphenyl	232	219	134	120	224	206	425	277	142	270	177	192
Acenaphthylene	16	18	6	11	13	12	20	11	547	462	556	549
Acenaphthene	147	154	112	126	153	175	189	162	113	187	184	163
Dibenzofuran	92	91	80	68	101	121	12	112	66	111	90	92
Fluorene	190	192	137	124	205	237	275	231	96	156	214	200
C1-fluorenes	733	457	281	358	417	517	602	419	312	567	487	521
C2-fluorenes	398	417	241	226	582	617	754	660	392	584	535	640
C3-fluorenes	413	463	241	232	652	675	807	674	823	1015	1059	1001
Phenanthrene	405	432	329	306	406	495	497	472	139	461	476	448
Anthracene	48	50	21	32	47	59	57	51	42	74	70	60
C1-phenanthrenes/anthracenes	475	517	306	287	527	565	657	588	435	677	674	755
C2-phenanthrenes/anthracenes	547	589	317	304	590	580	737	643	586	828	797	949
C3-phenanthrenes/anthracenes	325	342	154	159	361	373	418	362	ND	ND	ND	ND
C4-phenanthrenes/anthracenes	164	200	107	107	214	206	209	210	258	346	336	397
Dibenzothiophene	70	73	45	45	74	82	89	98	48	82	70	70
C1-dibenzothiophenes	214	182	118	115	211	209	271	227	182	254	233	251
C2-dibenzothiophenes	303	301	166	156	317	339	395	352	205	322	292	340
C3-dibenzothiophenes	292	256	158	142	289	272	354	316	250	318	326	377
Fluoranthene	176	206	167	146	160	189	181	168	123	271	237	171
Pyrene	174	200	144	136	146	172	173	156	113	239	223	167
C1-fluoranthenes/pyrenes	126	136	95	87	124	123	130	118	123	199	253	201
Benz[a]anthracene	61	76	66	54	46	45	54	41	33	82	79	52
Chrysene	75	75	65	50	51	58	58	48	40	97	91	58
C1-chrysenes	66	68	46	51	57	53	61	42	24	48	58	51
C2-chrysenes	46	58	33	33	41	51	56	51	41	71	87	79
C3-chrysenes	ND	ND	ND	ND	31	27	31	23	ND	ND	ND	ND
C4-chrysenes	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Benzo[b]fluoranthene	62	85	72	55	50	50	57	42	35	109	87	53
Benzo[k]fluoranthene	23	27	21	21	18	20	23	17	11	34	28	17
Benzo[e]pyrene	35	39	34	30	28	28	28	18	18	50	45	30
Benzo[a]pyrene	33	39	21	25	23	ND	30	20	16	58	51	28
Perylene	12	12	8	8	6	ND	10	5	6	17	15	8
Indeno[1,2,3-c,d]pyrene	75	75	58	62	127	128	145	81	39	95	84	50
Dibenz[a,h]anthracene	ND	ND	ND	ND	7	6	7	5	6	12	10	6
Benzo[g,h,i]perylene	35	52	43	33	27	24	27	17	16	50	38	24
Total PAH	15224	15307	9434	9266	18863	17976	28804	20716	19437	30924	25607	27334
Phenyl decanes	3351	3387	2819	2701	2144	2153	2115	1737	2184	2623	2994	2974
Phenyl undecanes	8290	10708	7726	6744	7242	8557	6935	6244	7864	9408	12859	8512
Phenyl dodecanes	10243	11887	9055	8717	9054	10100	8272	7519	10657	11831	14594	11381
Phenyl tridecanes	5741	5328	4223	4153	4748	5249	4494	4168	8245	8979	9923	9622
Phenyl tetradecanes	2890	2933	1759	1657	2020	2110	1872	1608	2998	3337	3696	3279
Total LAB	30515	34242	25582	23973	25208	28168	23688	21276	31948	36178	44066	35768

Table 5. Concentrations (μg/L) of chlorinated pesticides and polychlorinated biphenyl congeners (PCB) in Deer Island effluent (June - November 1993).

Month:	June		July		August		September		October		November	
Event Code:	E9301	E9301	E9302	E9302	E9303	E9303	E9304	E9304	E9305	E9305	E9306	E9306
Collection Date:	6/16/93	6/18/93	7/14/93	7/16/93	8/11/93	8/13/94	9/15/93	9/17/93	10/13/93	10/15/93	11/10/93	11/12/93
MWRA ID:	39307241	39307242	39308543	39308544	39310239	39310242	39312031	39312032	39313117	39313118	39314666	39314667
Aldrin	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
cis-chlorodane	3.61	6.15	8.13	4.30	1.07	0.82	1.12	0.83	2.31	2.55	2.00	4.82
2,4-DDD	ND	ND	2.42	1.22	ND	ND	ND	ND	1.03	1.63	1.22	1.00
2,4-DDE	17.26	15.76	20.60	9.98	3.81	28.22	5.08	4.80	ND	ND	ND	ND
2,4-DDT	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
4,4-DDD	23.90	25.79	17.74	16.79	ND	ND	ND	ND	ND	ND	ND	ND
4,4-DDE	3.98	3.99	3.47	2.80	3.36	3.36	13.17	12.67	2.43	2.43	2.84	2.33
4,4-DDT	6.31	9.38	9.81	6.73	4.59	0.80	11.97	4.36	5.46	8.91	6.85	6.83
Dieldrin	76.09	69.63	78.08	82.60	1.84	2.20	2.03	1.15	ND	ND	ND	ND
Endrin	ND	ND	ND	ND	7.38	57.85	3.26	2.37	ND	ND	ND	4.07
Heptachlor	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Heptachlor Epoxide	ND	ND	ND	ND	0.96	0.95	1.16	1.33	ND	ND	ND	ND
Hexachlorobenzene	101.45	93.80	165.14	106.53	ND	5.62	ND	ND	48.17	69.69	39.12	52.37
Lindane	14.03	15.80	15.02	12.83	16.04	16.29	16.87	11.91	13.25	20.19	12.97	12.44
Mirex	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	2.50	11.73
Trans-nonachlor	3.82	7.11	4.48	5.11	10.12	16.90	1.90	0.76	1.63	1.57	1.41	0.88
Cl2(08)	ND	ND	8.64	ND	ND	ND	ND	ND	ND	ND	ND	ND
Cl3(18)	7.94	7.61	13.80	8.44	1.97	ND	ND	ND	1.43	0.88	1.04	0.55
Cl3(28)	25.46	28.29	20.37	21.48	3.69	3.90	3.89	ND	3.16	4.99	2.50	3.16
Cl4(44)	ND	5.77	5.25	3.43	1.99	8.26	3.77	ND	1.69	3.58	1.68	2.65
Cl4(52)	13.40	13.03	13.58	4.54	2.57	1.74	3.65	2.05	2.69	8.03	3.94	5.28
Cl4(66)	1.24	1.52	1.21	1.30	ND	ND	ND	ND	0.53	0.94	0.63	0.33
Cl4(77)	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Cl5(101)	2.31	2.03	2.78	2.60	ND	ND	2.76	1.30	1.99	2.50	1.96	1.13
Cl5(105)	1.88	2.53	ND	ND	ND	ND	ND	ND	1.79	1.59	1.73	1.68
Cl5(118)	ND	ND	4.64	2.23	ND	ND	2.97	2.14	2.77	2.94	2.81	2.15
Cl5(126)	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Cl6(128)	ND	ND	ND	ND	ND	ND	ND	2.14	0.53	0.79	0.53	0.30
Cl6(138)[a]	2.88	3.51	3.52	3.23	36.27	14.90	55.72	39.93	11.57	11.75	13.99	43.34
Cl6(153)	6.89	10.10	4.45	8.59	ND	ND	1.96	2.17	3.67	4.61	4.78	3.14
Cl7(170)	1.83	2.61	5.27	3.85	313.98	271.91	349.29	248.51	1.54	1.54	2.53	ND
Cl7(180)	35.74	34.52	ND	ND	32.62	34.12	36.36	24.15	32.40	29.60	28.85	54.81
Cl7(187)	ND	1.75	1.45	1.72	2.67	2.93	2.64	1.89	1.27	1.24	1.42	ND
Cl8(195)	ND	ND	ND	ND	ND	ND	11.41	7.97	0.77	0.62	0.78	ND
Cl9(206)	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Cl10(209)	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

[a] Not included in total due to suspected matrix interference.

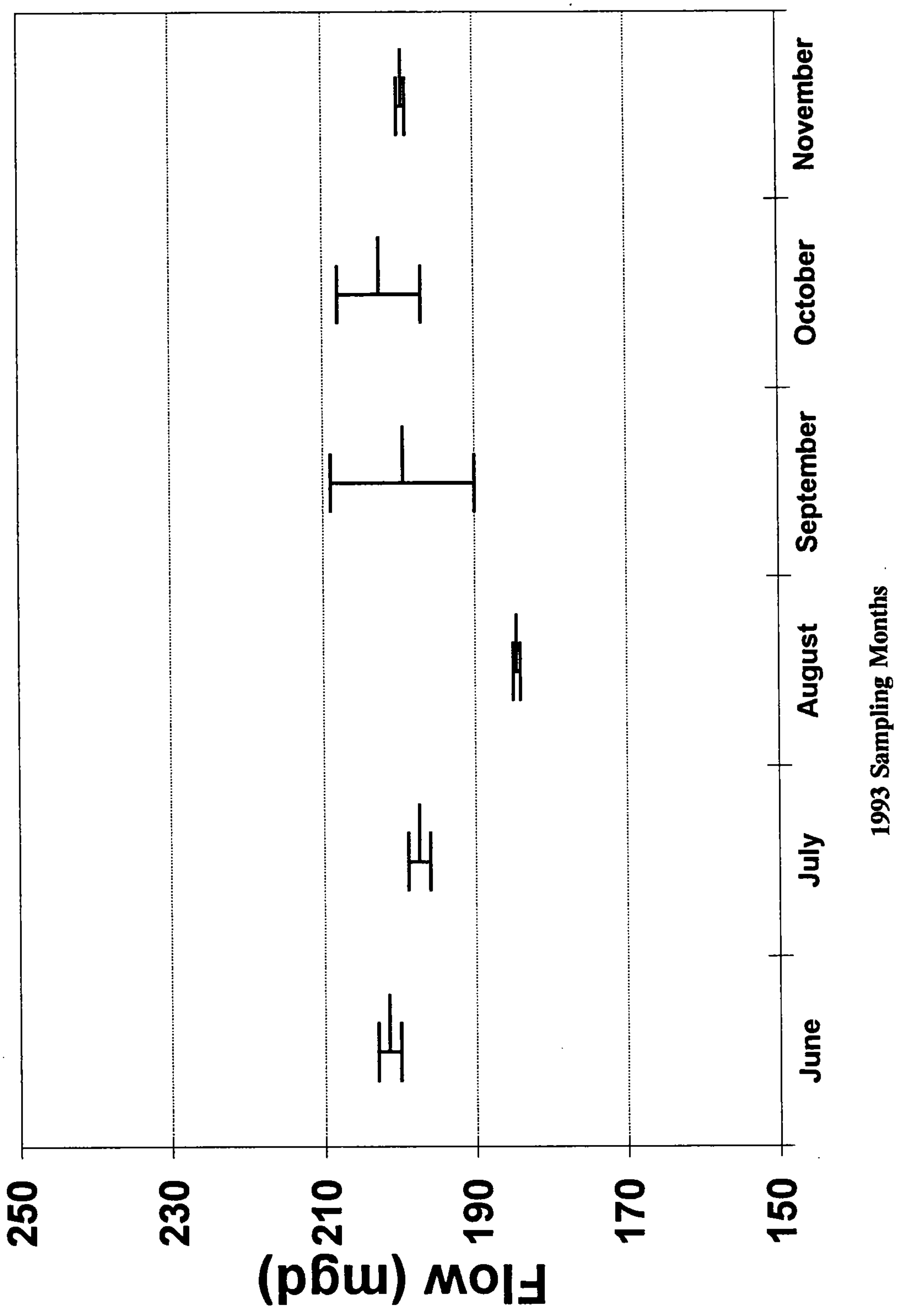

Figure 2. Flow (millions of gallons per day) of effluent from the Deer Island treatment plant on the days of monthly sampling for this task. Mean flow (midpoint of bar) and the range in flow between the two sampling days for each month are shown.

flows relative to the mean (<10%) during the study period was observed; August flow showed the largest deviation from the mean, it being some 7% below the six-month average.

3.1 TRACE METALS

Concentrations of eight trace metals (Ag, Cd, Cu, Cr, Hg, Ni, Pb, and Zn) were measured in the Deer Island effluent during the course of this study. The metals chosen are of particular interest because they reflect anthropogenic inputs and represent different potential industrial and municipal sources to the waste stream. Additionally, the U.S. EPA has established marine water-quality criteria (acute and, in most cases, chronic) for these metals because of concern for potential ecological impacts due to chronic exposure to these metals. Additional discussion about the water-quality criteria is presented in Section 3.5.

The concentration of each of the total recoverable trace metals measured in the effluent stream was relatively consistent over the six-month sampling period (Table 3). Figures 3a, 3b, and 3c show the concentration of the eight target metals over the six-month sampling period. Marine acute and chronic EPA water-quality criteria are shown on the graphs if they exist for the metal. For each sampling month, the mean concentrations for the two-day sampling events are depicted by the mid-point of the bar while the bar represents the range (high to low) between the two measurements. Metals and their mean concentrations in the effluent during this reporting period were: Ag (4.2 μg/L); Cu (72 μg/L); Cd (0.55 μg/L); Cr (3.4 μg/L); Hg (0.16 μg/L); Pb (12 μg/L); Ni (6.0 μg/L); and Zn (87 μg/L). No particularly dramatic temporal trends were noted for any of the metals measured in the effluent; in certain cases, it appears that the highest concentrations for the metals in the effluent occurred in August (Ag and Ni) or September (Cu, Cr, Hg, and Pb). These concentrations are similar to levels measured in 23 effluents from the great New York City area (EPA, 1991) using comparable sampling procedures and "clean" processing and analysis procedures. Measured total recoverable values in early 1991 ranged as follows across a variety of sewage treatment levels, Ag, (0.2 to 16 μg/L); Cu (10 to 100 μg/L); Cd (0.1 to 2.6 μg/L); Hg (<0.004 to 0.15 μg/L); Pb (1 to 14 μg/L); Ni (2 to 70 μg/L); and Zn (15 to 175 μg/L).

Typically, the waters of in Massachusetts Bay have low total metals concentrations. For example, total metal concentrations measured in 1987 during the MWRA outfall siting program (Battelle, 1987) and also at two stations sampled in the Bay in the summer of 1992 (EPA, 1992a) were in the

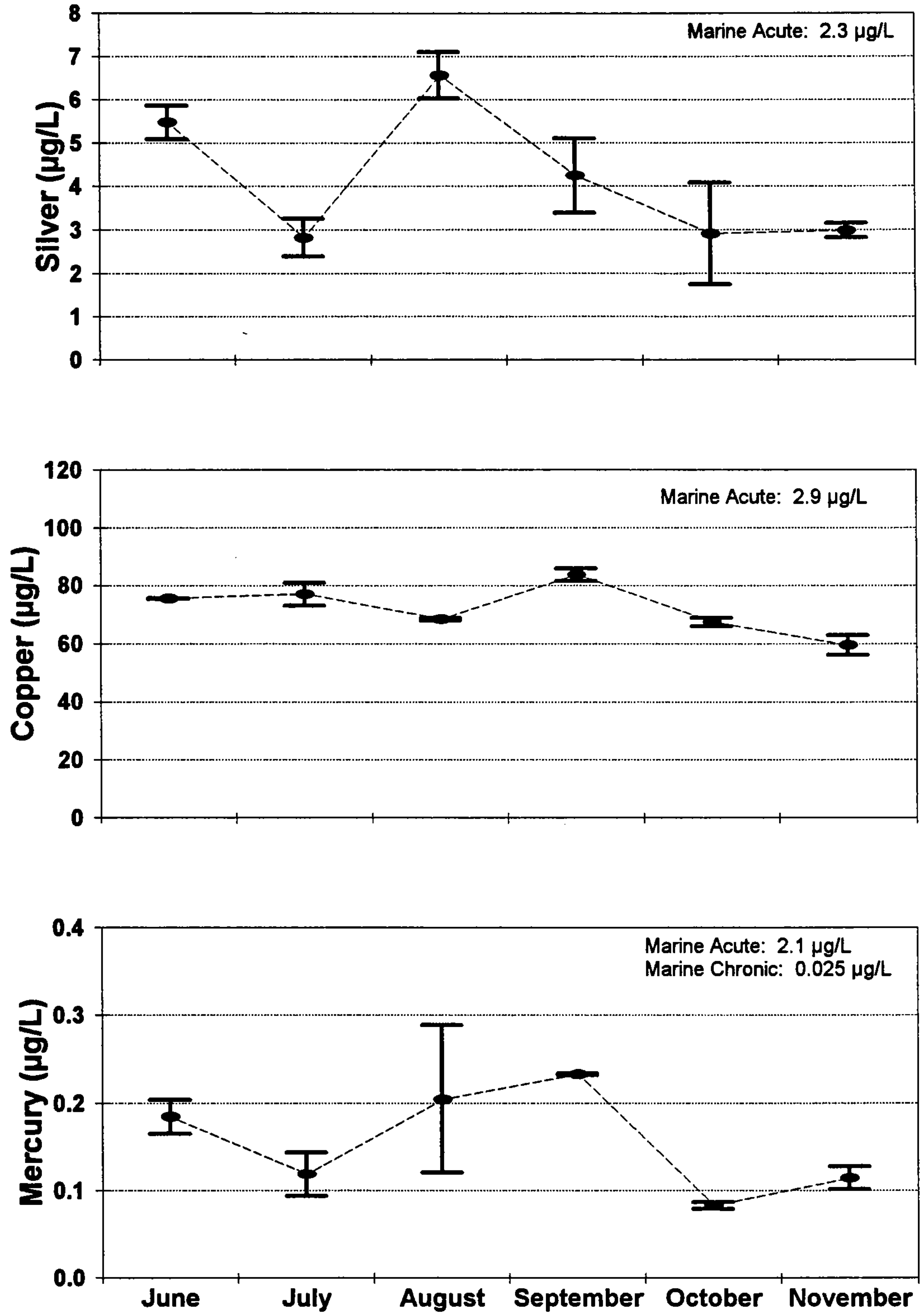

Figure 3a. Concentrations of silver, copper, and mercury in the Deer Island effluent. Mean (midpoint of bar) and the range between the two sampling days for each month are shown.

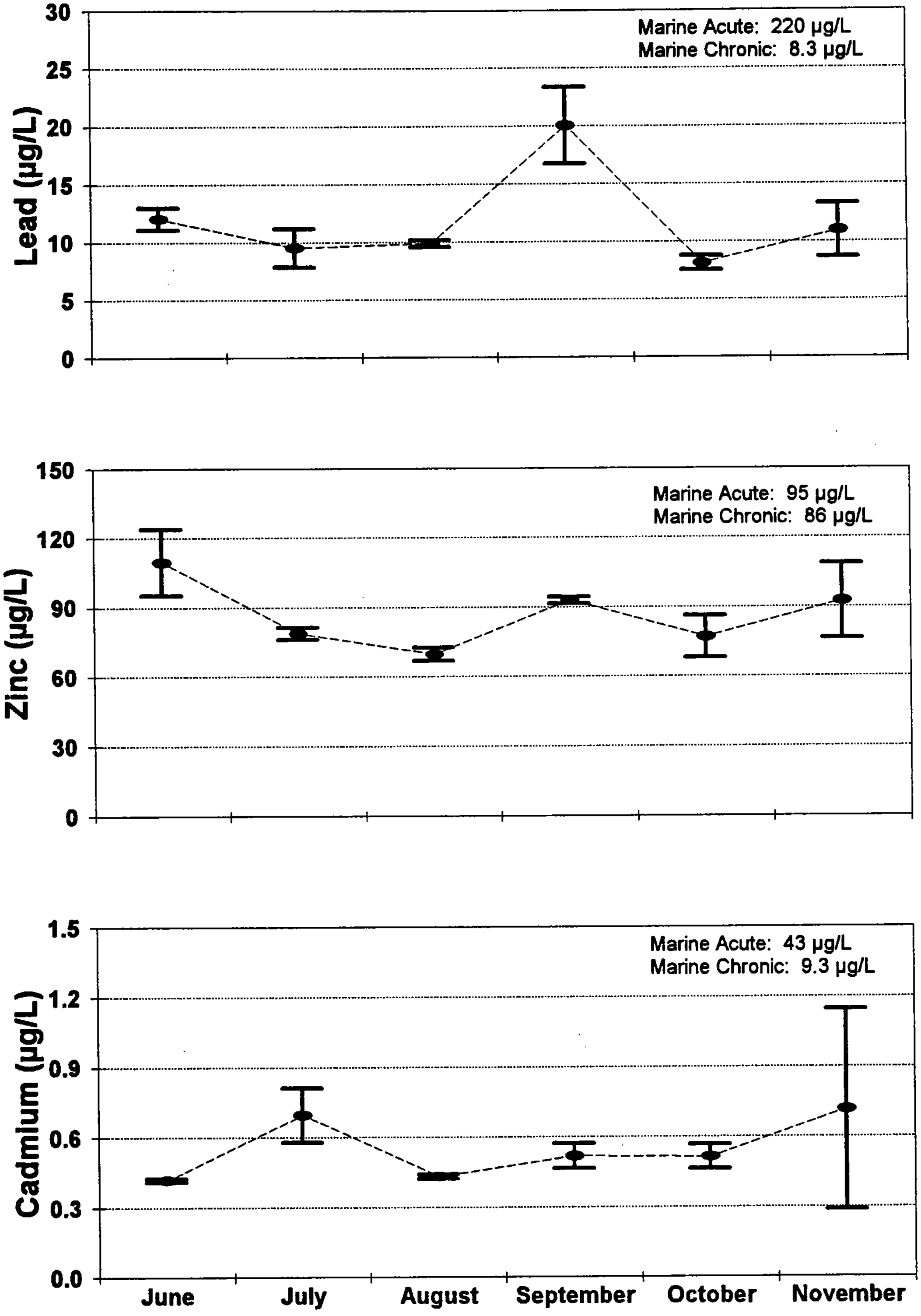

Figure 3b. Concentrations of lead, zinc, and cadmium in the Deer Island effluent.

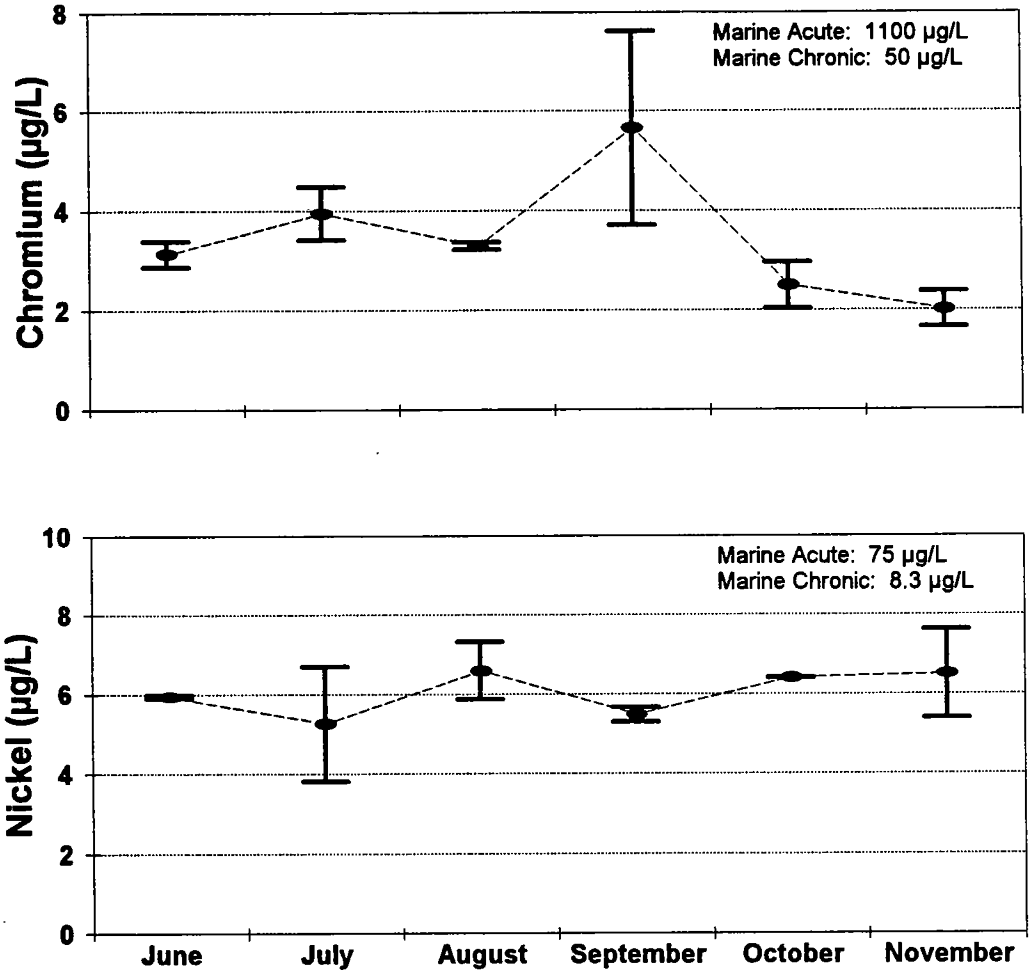

Figure 3c. Concentrations of chromium and nickel in the Deer Island effluent.

following ranges: Cu (0.1 to 0.3 μg/L); Cd (0.02 to 0.3 μg/L); Cr (0.2 to 1 μg/L); Hg (0.0007 to 0.002 μg/L); Pb (0.2 to 0.2 μg/L); Ni (0.3 to 1.5 μg/L); and Zn (0.1 to 0.6 μg/L). These values are generally a factor of 10 less than in the effluent.

Detection Limit Issues

It is noteworthy to point out that the ultra-trace methods used in this study allowed measurement of metals that normally would be undetected by standard EPA methods of analysis. The table below summarizes the reporting limits for the NPDES monitoring data and for those used in this study.

	Ag (μg/L)	**Cd** (μg/L)	**Cr** (μg/L)	**Cu** (μg/L)	**Pb** (μg/L)	**Hg** (μg/L)	**Zn** (μg/L)
NPDES Monitoring Laboratory Reporting Limit	7	5	10	55	30	0.5	5
HOM Reporting Limit (this study)	0.55	0.06	0.2	0.87	1.2	0.025	0.28

Of the eight metals measured during this Task and analyzed concurrently for NPDES compliance, only Cu, Zn, and occasionally Pb were above NPDES reporting limits. NPDES monitoring data for the effluent were reported as below the detection limit for all other metals.

3.2 TRACE ORGANICS

The trace organic compounds measured in this task can be broken down into four broad categories:

- aromatic hydrocarbons
- linear alkyl benzenes
- chlorinated pesticides
- polychlorinated biphenyls

The possible sources and fate of each class of compounds vary. The aromatic hydrocarbons of potential environmental concern are the PAH compounds, the sources of which are often both pyrogenic (resulting from combustion) and petrogenic (non combusted petroleum based) in nature. For this task, linear alkyl benzenes — by-products of commercial detergent formulations — are included in this class of compounds. The LAB are not generally considered deleterious contaminants;

rather, they represent a suite of compounds that may serve as useful tracers of municipal effluent in receiving environments.

The chlorinated pesticides examined in this study are environmentally persistent compounds that, although banned now in the United States, can still be found in most waste streams and receiving waters in the United States because of chronic release or illegal use. Similarly, PCBs—a group of compounds with almost 75 years of a myriad of historic industrial uses—are still found in effluent streams despite being banned for almost 20 years. PCB formulations are made up of 209 possible chlorinated homologues called congeners. For this task, 20 of the most prevalent and environmentally persistent congeners were selected for analysis. These are the same 20 congeners that have been monitored in United States coastal environments by the NOAA Status and Trends Program for the last 9 years (Lauenstein and Cantillo, 1993).

As with metals, EPA marine water-quality criteria for some of these compounds have been established because of concern for potential ecological impacts due to chronic elevated levels of the compounds. A discussion regarding water-quality criteria for organic compounds is presented in Section 3.5.

The concentration of each of the aromatic hydrocarbons, chlorinated pesticides, and selected PCB congeners measured in the effluent stream over the six-month sampling period is summarized in Tables 4 and 5.

3.2.1 Aromatic Hydrocarbons and LAB

Total PAH (ΣPAH) concentrations (the sum of all target PAH compounds in Table 1) in Deer Island effluent as well as the average distribution of PAH compounds for each sampling month are presented in Figure 4.[1] Concentrations of ΣPAH were noticeably lower in the summer months, with the lowest

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[1] Key to compound names: Naphthalene (N), C_1-naphthalene (N1), C_2-naphthalene (N2),C_3-naphthalene (N3), C_4-naphthalene (N4), Biphenyl (BI), Acenaphthylene (AE), Acenaphthene (AC), Fluorene (F), C_1-fluorenes (F1), C_2-fluorenes (F2), C_3-fluorenes (F3), Phenanthrene (P), Anthracene (A), C_1-phenanthrene/anthracenes (P1), C_2-phenanthrene/anthracenes (P2), C_3-phenanthrene/anthracenes (P3), C_4-phenanthrene/anthracenes (P4), Fluoranthene (FL), Pyrene (PY), C_1-fluoranthene/pyrene (FP1), Dibenzothiophene (D), C_1-dibenzothiophenes (D1), C_2-dibenzothiophenes (D2), C_3-dibenzothiophenes (D3), C_4-dibenzothiophenes (D4), Benz[*a*]anthracene (B), Chyrsene (C), C_1-chyrsenes (C1), C_2-chyrsenes (C2), C_3-chyrsenes (C3), C_4-chyrsenes (C4), Benzo[*b*]fluoranthene (BB), Benzo[*k*]fluoranthene (BK), Benzo[*e*]pyrene (BE), Benzo[*a*]pyrene (BA), Perylene (PER), Indeno[1,2,3-*c,d*]pyrene (IP), Dibenz[*a,h*]anthracene (DA), Benzo[*g,h,i*]perylene (BP).

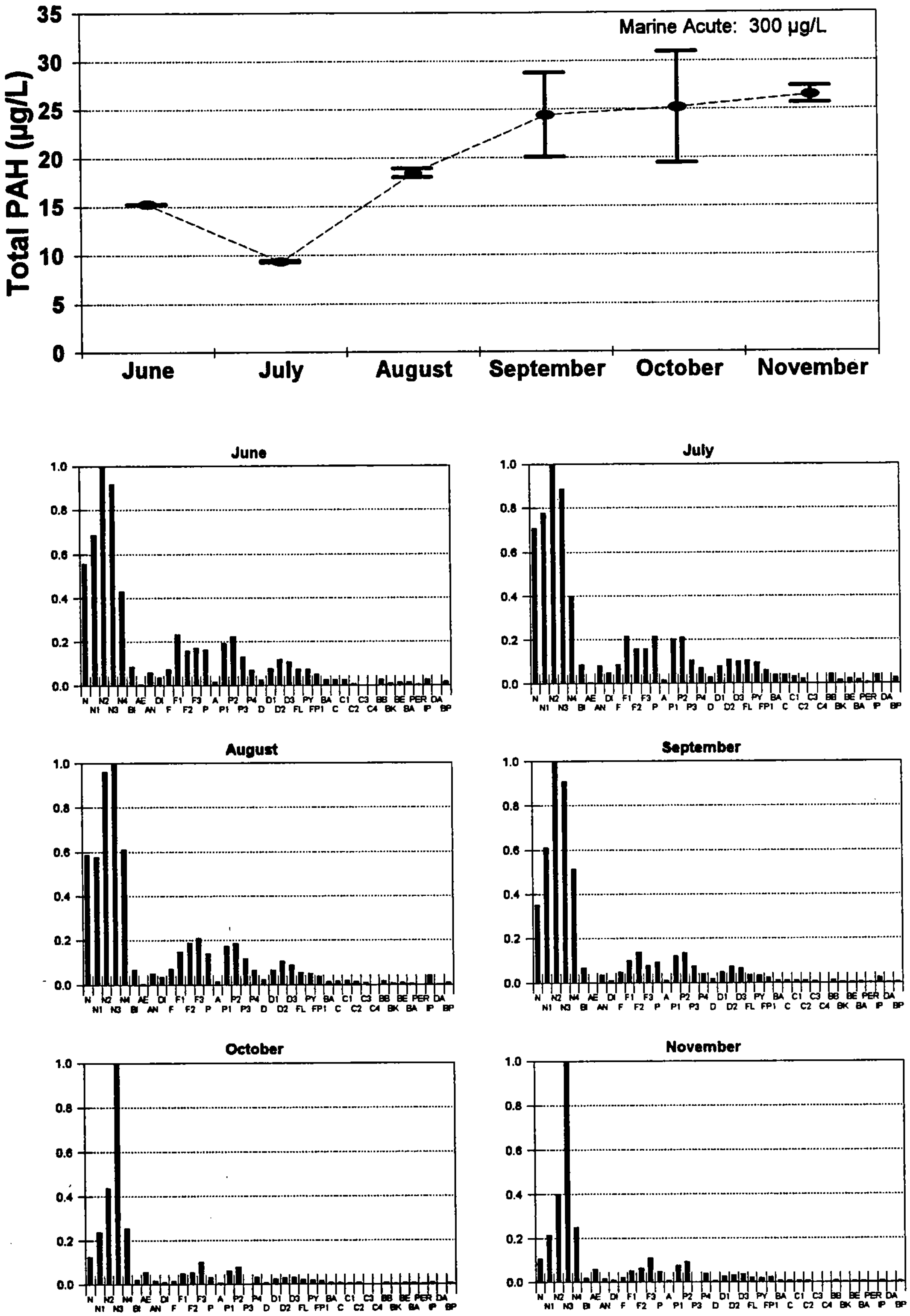

Figure 4. **Total PAH (ΣPAH) in Deer Island effluent. Concentration of ΣPAH versus time (upper graph). Relative PAH distribution (normalized to the compound of highest concentration) for each sampling month (lower graphs). Mean concentration (midpoint of bar) and the range in concentration between the two sampling days for each month are shown.**

concentration measured in July (9.3 μg/L). The ΣPAH concentrations measured in this task were highest in September through November at an average of approximately 25 ng/L during this period. These values are similar to values measured in Massachusetts Bay in 1987 and 1992 (Battelle, 1987; EPA, 1992a). The distribution of PAH compounds in the effluent remained essentially constant over the six-month study period (Figure 4), although the lower concentrations in the mid summer period relative to the higher concentrations in the fall period may relate to the unseasonably dry summer experienced in 1993 followed by a relatively wet fall period. The PAH assemblage is dominated by low molecular weight PAH, most notably naphthalene and its C_1 to C_4 alkylated homologues, which make up about 60% of the total PAH assemblage. The major pyrogenic PAH compounds fluoranthene and pyrene, as well as other 5- and 6- ring PAH often associated with pyrogenic sources, are present in the effluent but at much lower concentrations relative to the lower molecular weight 2- and 3-ring PAH compounds usually associated with petrogenic hydrocarbons. These data strongly suggest that the source(s) of PAH are likely petrogenic in nature and more likely a refined petroleum product or products. Further discussion on the likely source of PAH to the Deer Island effluent is presented below in Section 3.4. Total linear alkyl benzene concentrations in the effluent over time (Figure 5) followed a pattern similar to total PAH although the LAB concentrations were significantly higher than any of the target organic contaminants. Total LAB averaged approximately 20-30 μg/L during June through September, with an increase to approximately 40 μg/L noted by November. Although the concentration of total LAB varied somewhat during the six-month study period, the distribution of C_{10} to C_{14} LAB homologues (lower graphs in Figure 5) remained virtually unchanged, suggesting that the source of LAB to the effluent was constant in composition.

3.2.2 Chlorinated Pesticides

Figure 6 shows examples of the relationship between effluent concentration and time for the 16 chlorinated pesticides examined in this task. Highlights of the results include the following:

- dieldrin showed the most notable trend in concentration over time (Figure 6); concentrations were approximately 75 ng/L in June and July, but dropped to <2 ng/L in September through November;
- hexachlorobenzene was elevated in June and July (ca. 150 ng/L), dropped to <10 ng/L in August and September, then climbed to about 50 ng/L in October and November;
- lindane concentrations were found at almost a uniform concentration of 15 ng/L over the six-month sampling period (note values in Massachusetts Bay are approximately an order of magnitude lower, EPA, 1992a);

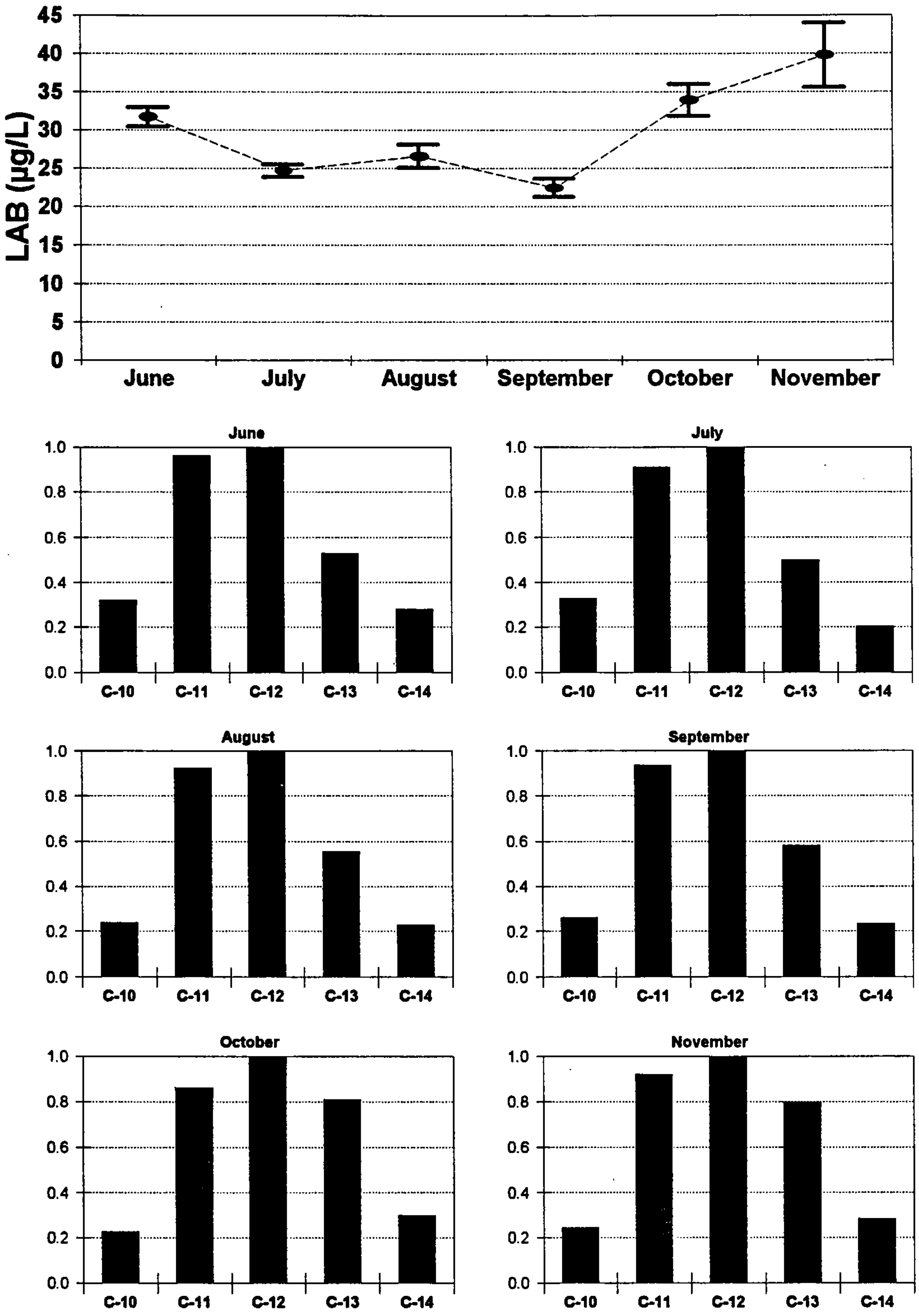

Figure 5. Total LAB (ΣLAB) in Deer Island effluent. Concentration of ΣLAB versus time (upper graph). Mean concentration (midpoint of bar) and the range in concentration between the two sampling days for each month are shown. LAB homologue distribution relative to C_{12}-LAB for each sampling month (lower graphs).

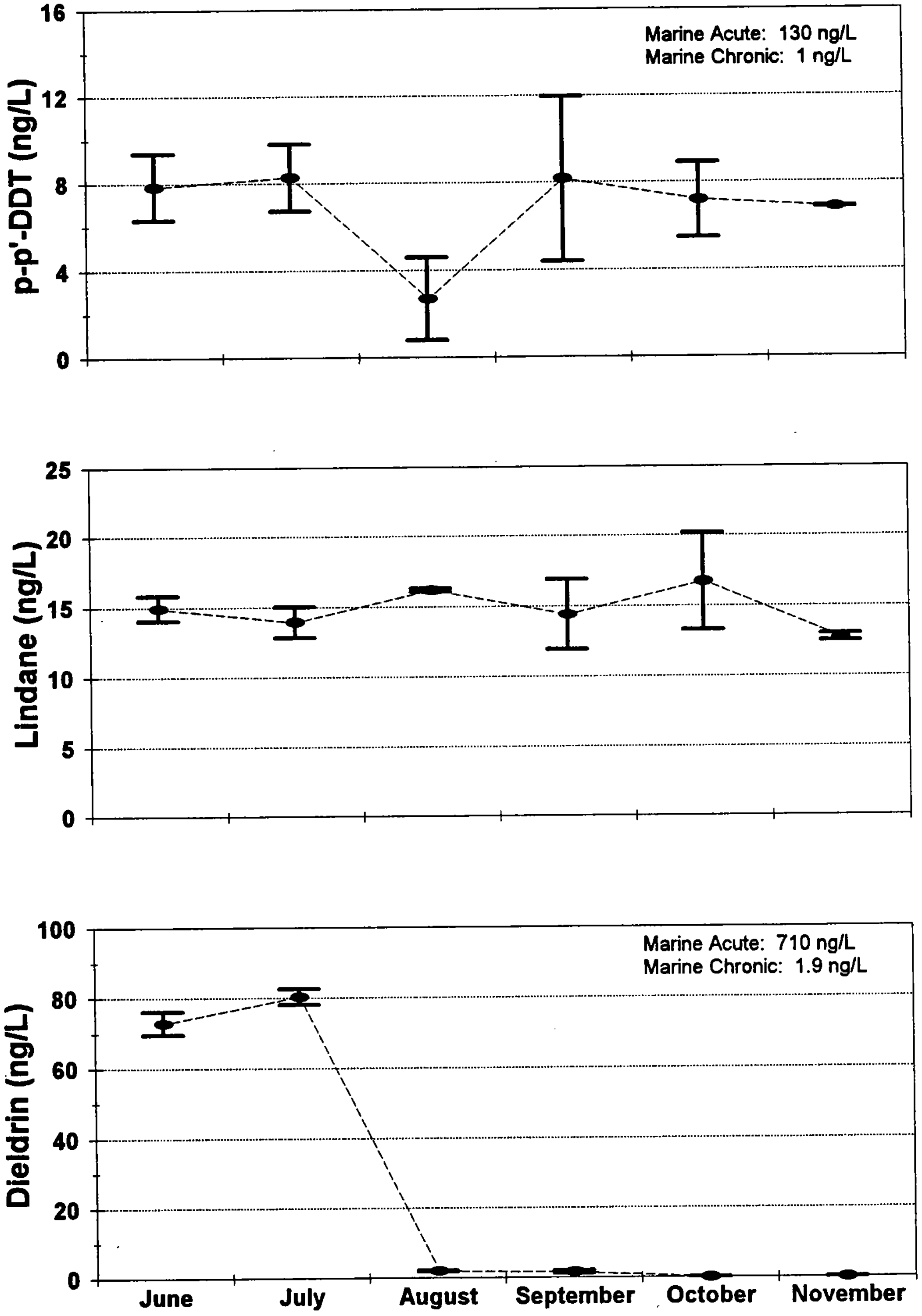

Figure 6. Selected chlorinated pesticides in the Deer Island effluent: p,p'-DDT, lindane, and dieldrin. Mean concentration (midpoint of bar) and the range in concentration between the two sampling days for each month are shown.

- the DDT pesticide family of compounds was composed of both the parent DDT (2,4'-DDT and 4,4'-DDT) and significant amounts of DDT breakdown products (2,4'-DDE, 4,4'-DDE, 2,4'-DDD and 4,4'-DDD). In the fresh commercial pesticidal product, the sum of the DDT breakdown compounds make up less than 10% of total DDTs in the neat pesticide formulation (Stetter, 1983). Because of its breakdown kinetics, Rapaport *et al.* (1985) estimate that in a 20-y weathered DDT formulation, about 50% of the total should be 2,4'- DDT plus 4,4'-DDT. While the percentage of parent DDT (2,4'- DDT plus 4,4'-DDT) in the Deer Island effluent varied from 10 to 60% of the total DDT compounds, the ratio of parent to breakdown compounds suggests the DDT measured in this study is highly weathered (e.g., there are no fresh inputs of the pesticide to the waste stream);

- the remaining pesticides (Aldrin, chlordane, endrin, heptachlor, heptachlor epoxide, mirex, and trans-nonachlor) were either not detected above 2 ng/L or found sporadically at concentrations generally < 10 ng/L.

3.2.3 Polychlorinated Biphenyl Congeners

Throughout the study period, total PCB concentrations were very low in the effluent; typically individual PCB concentrations were in the 2-25 ng/L range; total PCB concentrations ranged from 50 to 100 ng/L. These values are within the range (9 to 96 ng/L) of total PCB concentrations measured in six sewage effluents collected in New York City area in the early winter of 1992 (EPA, 1993a).

Total PCB congener effluent concentrations were highest in June, and lower between July and November (Figure 7).

In comparison, the total PCB values detected in the waters of Massachusetts Bay are generally < 10 ng/L (EPA, 1992a). The distribution of PCB congeners in the effluent are favored, for the most part, by those congeners of lower levels of chlorination (i.e., by the Cl_3 and Cl_4 congeners). This distribution is typical for aqueous matrices because the congeners of lower levels of chlorination are more soluble than their higher molecular weight homologues (e.g., Brown *et al.*, 1990). One note of analytical interest: the high molecular weight congener Cl_7(170) was detected in very high concentrations in the August and September samples. Because it was surprising to find this congener in the absence of other high molecular weight PCB at similar concentrations, the presence of this compound is suspect and was very likely due to a matrix interference. Because of this concern, the concentrations of Cl_7(170) were not used to calculate total PCB for during August and September. Additional chromatographic investigations will be undertaken in 1994 to resolve this matter.

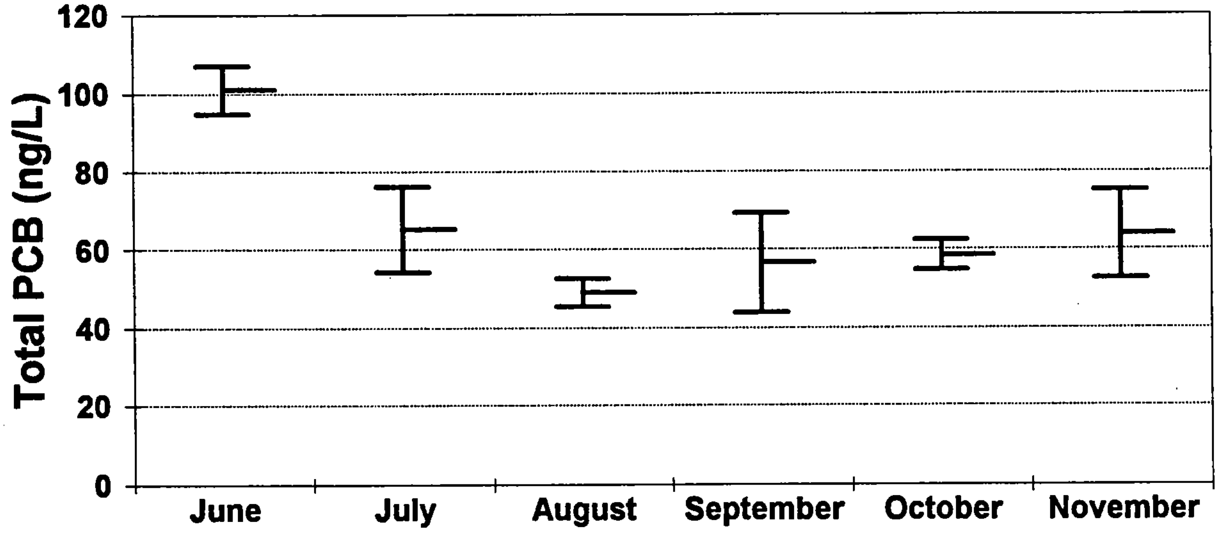

Figure 7a. Total PCB in Deer Island effluent. Concentration of ΣPCB versus time. Mean concentration (midpoint of bar) and the range in concentration between the two sampling days for each month are shown.

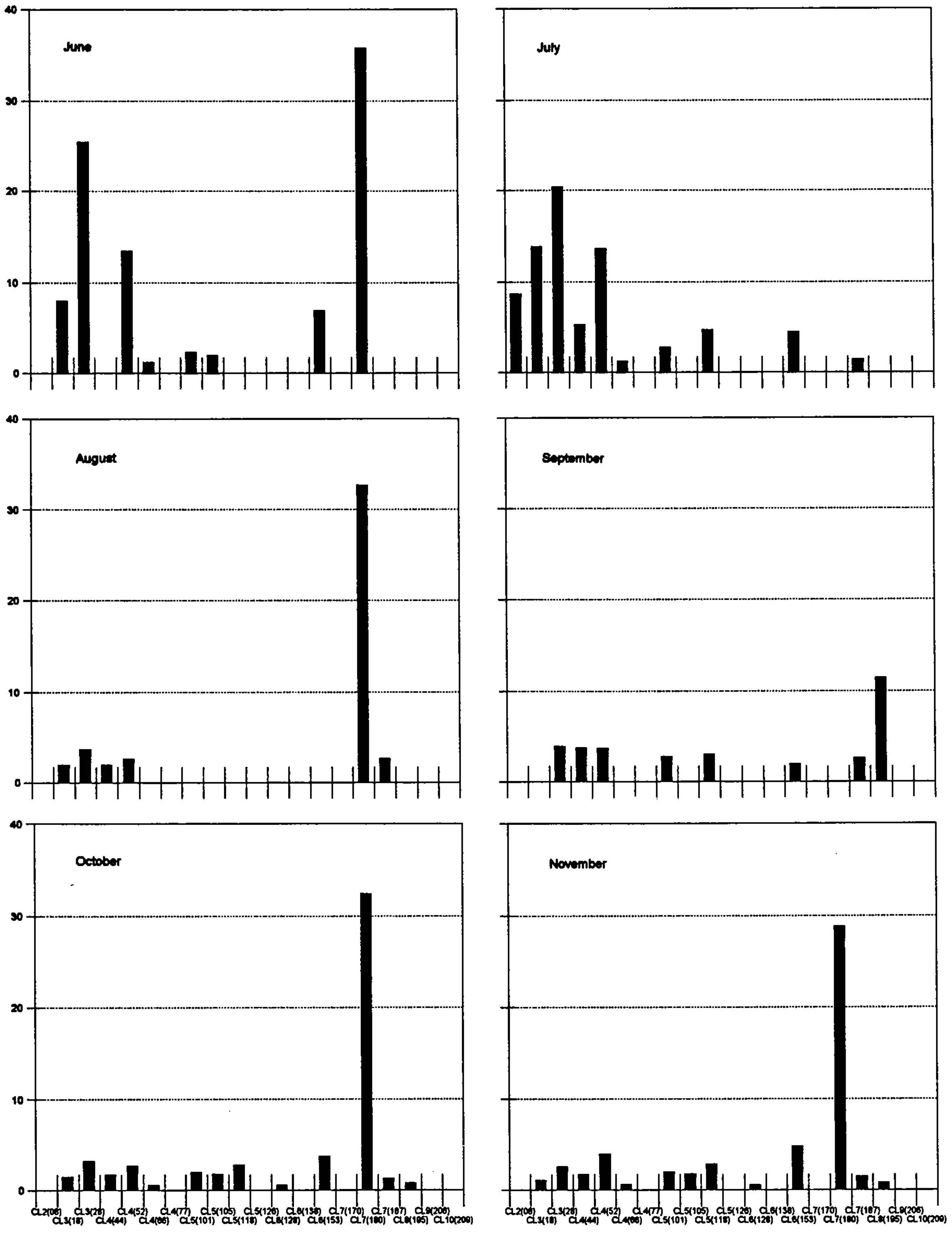

Figure 7b. Relative distribution of PCB congeners for each sampling month.

3.2.4 Detection Limit Issues

The utility of ultra-trace methods of analysis for measurement of contaminants in Deer Island effluent is clearly demonstrated in this study. Nominal detection limits for the methods utilized in this study are presented below and contrasted with those used for the NPDES monitoring program. The concentration of almost all organic contaminants in the Deer Island effluent was below the reporting limits of NPDES analytical methods. NPDES analyses of the Deer Island effluent collected at the same time as those analyzed in this study found no detectable quantities of the target organic compounds except for the occasional chlorinated pesticide (e.g., α-BHC, β-BHC, δ-BHC, γ-BHC, aldrin, DDD, DDT, endosulfan sulfate) — no patterns or trends in the concentrations of the organic compounds can be seen (Hall, 1994b). While the results fulfill NPDES monitoring requirements, the data do not provide an accurate representation of the true composition of the effluent and, as will be shown below, can result in erroneously high calculations of contaminant loadings to the Harbor/Bay system.

Compound Class	Battelle Nominal Detection Limit (ng/L)	NPDES Monitoring Program Nominal Detection Limit (ng/L)
Individual PAH Compounds[a]	10 - 50	10,000 - 50,000
Linear Alkyl Benzenes	20	not measured
Chlorinated Pesticides	2	50
Individual PCB Congeners	2	not measured
Total PCB	10	1000

[a] 40 parent and alkylated PAH measured in this study. 16 priority pollutant PAH measured in NPDES monitoring program.

3.3 CONTAMINANT LOADING

The annual loading of contaminants to Boston Harbor can be estimated using the six-month data from this study. The following assumptions were made to obtain the estimates:

- The average of the two effluent flow measurements taken at the time of effluent sampling is representative of that entire month

- The average concentration of contaminants measured in the effluent for a given month is representative of the entire month

- The loading calculated for the first six months (June - November) is equivalent to the loading for the remaining six months (December - May).

The annual loading for each contaminant of interest was calculated from the equation

$$L_i\ (\mathrm{kg}) = [\Sigma\ (C_{i,m} \times F_m)] \times 2$$

where

- L_i is the annual loading of contaminant in kilograms

- $C_{i,m}$ is the average concentration of contaminant i in the effluent measured in month m in kg/gal; m ranges from June to November

- F_m is the effluent flow at Deer Island in millions of gallons per day, measured on the days that the effluent samples were collected for analysis in month m

- x 2 is the multiplication factor needed to adjust the loading factor to an annual (12 month) loading estimate

The calculation, although simplistic, allows a first-order estimate of the inputs of anthropogenic contaminants to the Harbor and Bay, and provides a basis for comparison of contaminant loadings that have been estimated by other investigators. For comparison, the loading factors calculated using 1993 NPDES monitoring data for the same effluent are presented below. Where possible, loading factors for Deer Island compiled by Alber and Chan (1994) are provided, as are total estimated 1992 loadings *from combined Deer and Nut Island effluent* (Shea, 1993a).

3.3.1 Trace Metals

The annual loading factors for the eight trace metals measured in this program are presented in Table 6. All eight target metals were found in the effluent well above the method detection limits for the analysis techniques used in this task. As such, the data in Table 3 and the loading factors calculated in Table 6 (from the standpoint of the metal concentration variable in the equation used to calculate the loading factors) are accurate.

In cases where metals (Cu, Zn, Pb, Cr) were detected in the effluent by the NPDES monitoring laboratory, there is good agreement in the monthly effluent Cu and Zn concentrations and in the calculated annual loading factors for these metals based on Battelle HOM and the NPDES; loadings

Table 6. Estimates of trace metal loadings to Boston Harbor and Massachusetts Bay.

Metal	This Study (kg-yr^{-1})	1993 NPDES (kg-yr^{-1})	Alber and Chan (1993) (kg-yr^{-1})	1992 Combined Nut/Deer Island Shea (1993) (kg-yr^{-1})
Ag	1,129	1,050[a]	—	2,028
Cd	150	682[a]	—	435
Cr	931	2,279	—	2,445
Cu	19,626	18,825	20,138	30,776
Hg	42	136[a]	164	138
Ni	1,642	2,728[a]	—	4,800
Pb	3,198	5,347	4,395	5,667
Zn	23,645	25,063	26,264	37,626

[a] Most or all data points for this metal were reported as below the NPDES method detection limit. In such cases, ½ the MDL was used in the loading calculation.

calculated for Cu were within 4% and within 6% for Zn between the two data sets. Poor agreement is obtained for Pb (Battelle HOM data 1.7 times lower than NPDES) and Cr (Battelle HOM data 2.4 times lower than NPDES). The NPDES data overestimate Pb and Cr loadings by these factors, most likely because of analytical detection and contamination issues that artificially increase the NPDES values. Both Cr and Pb analyses are known to suffer from chronic laboratory contamination unless clean-room techniques are used to control the environment where the samples are prepared for analysis.

The metals Ag, Cd, Hg, and Ni were not detected in the effluent using NPDES methods; as such, loading factors based on the NPDES data were computed using one-half the reported detection limit in the loading calculation. Using this approach, loadings calculated using NPDES data are overestimated by a factor of 1.7 for Ni, 4.5 for Cd, 3.2 for Hg, and 4.5 for Cd. Interestingly, Ag loadings calculated from both data sets were coincidentally similar even though Ag was reported as not detected in the NPDES data set.The annual loading factors of Cu and Zn, as compiled by Alber and Chan (1994), suggest very reasonable agreement with those calculated with data obtained by this study, however it appears likely that Hg loadings computed by Alber and Chan are overestimated by about a factor of four as compared to the loading calculated in this task. The differences observed between historical loading estimates and those computed in this task will be better understood after data from an entire year is accrued.

In comparison to the combined Deer and Nut Island loading for 1992 (Shea, 1993a), trace metal loadings calculated in this study suggest that the proportional loading from Deer Island is likely metal-specific, e.g., Deer Island effluent only accounts for about 30% of the total Hg discharged but may be responsible for as much as 60% of Cu and Zn discharges.

One additional note regarding analytical considerations for metals loading calculations can be made: Copper and Zn analyses from the NPDES program appear to be sufficiently accurate and precise to provide accurate estimates of the loadings of these metals to the Harbor and Bay. From the standpoint of loading estimation, ultra-trace, “clean” analytical method are necessary in order to obtain the detection limits and accuracy needed for reliable measurement of Ag, Cd, Cr, Pb, Ni, and Hg. Perhaps more importantly, measuring the true reduction of inputs of metals to the Bay and Harbor over time will only be accomplished using analytical methods that provide detection limits that are comparable to or below ambient metals levels in the receiving waters.

3.3.2 Trace Organics

Loading factors for selected anthropogenic organic compounds and classes of compounds (i.e., total PAH and total PCB) are presented in Table 7.

As with the metals, comparison of the loading factors calculated using 1993 NPDES monitoring data for the same effluent and 1992 combined Deer Island and Nut Island loadings estimated are also presented. Where possible, loading factors for Deer Island compiled by Alber and Chan (1994) are provided for comparison. Rationale for the selection of compounds or classes of organic compounds for loading calculation include the following:

- total PAH, because of interest in the fate and effect of this entire class of compounds in the aquatic environment;
- certain individual PAH compounds: total naphthalenes, because collectively these compounds make up over 60% of the total PAH burden of the effluent; pyrene, because this compound is one of the dominant pyrogenic PAH and is cited by other authors estimating loadings to the Bay and Harbor; benzo[a]pyrene, because of the interest in tracking the fate of this potentially carcinogenic compound;
- representative chlorinated pesticides: p-p'-DDT, dieldrin, and lindane, because these compounds were found routinely at low levels in the effluent;
- total PCB, as the summation of the 20 congeners measured in this study, because many of the lower molecular weight, water soluble congeners were found in the effluent.

3.3.3 Polynuclear Aromatic Hydrocarbons

Annual loading of total PAH — defined as the sum of the 40 PAH compounds listed in Table 1 — from Deer Island was found to be approximately 5,400 kg-yr^{-1}, with approximately 60% of that total due to naphthalene and its C_1 - C_4 alkyl homologues. The comparison of these figures with loadings calculated using NPDES data is striking. For the NPDES data, total PAH are defined as the sum of the target PAH compounds in the NPDES method which include the 16 priority pollutant PAH plus 2-methyl naphthalene. Because no PAH compounds were reported above the NPDES method detection limit of 50 μg/L, one-half the MDL of each compound was used in the loading calculation for total PAH. Using this approach, the NPDES data set yields a total PAH loading of almost 116,000 kg-yr^{-1}—more than 20-times higher than that computed using the data from this study. This

Table 7. Estimates of trace organic compound loadings to Boston Harbor and Massachusetts Bay.

Compound/Class of Compound	This Study (kg-yr^{-1})	1993 NPDES (kg-yr^{-1})	Alber and Chan (1993) (kg-yr^{-1})	1992 Combined Deer/Nut Island (Shea 1993) (kg-yr^{-1})
ΣPAH[a]	5,414	115,936[b]	—	4,700
ΣNaphthalenes[c]	3,692	—	—	—
2-methylnaphthalene	—	6,820[b]	1,473	—
Pyrene	46	6,820[b]	49	—
Benzo[a]pyrene	8	6,820[b]	4	—
p-p'-DDT	2	14[b]	—	—
Dieldrin	7	14[b]	—	—
Lindane	4	14[b]	—	—
ΣPCB[d]	18	136[b]	—	36

[a] ΣPAH calculated as sum of 40 parent + alkylated homologues in this study; calucated as sum of 16 priority pollutant PAH + 2-methylnaphthalene using NPDES data.

[b] Most or all data points for this compound were reported as below the NPDES method detection limit. In such cases, ½ the MDL was used in the loading calculation.

[c] ΣNaphthalenes: sum of naphthalene + C_1-C_4-alkyllated npahthalenes.

[d] Total PCB: sum of 21 congeners in this study; total Aroclors using NPDES data.

is perhaps the most striking example in this study of contaminant loading overestimation because of limitations in method detection limits.

Annual total PAH loadings computed in this study are somewhat higher than those estimated for the 1992 combined Deer and Nut Island loading made by Shea (1993a). This discrepancy may be due to the limitations in the data set available to Shea (two sampling events at two treatment plants) whereas the loading computed in present study is based on six months of data or, in fact, these data may indeed reflect an increase in the total PAH currently released in the Deer Island effluent as compared to that presented by Shea (1993a). A more accurate accounting of this difference will be assessed at the end of 18 months of effluent monitoring.

Similar comparisons can be made for loading factors for individual PAH compounds computed using data from this study and those computed using NPDES data or cited by other authors. For example, Alber and Chan (1994) used 2-methylnaphthalene as a surrogate for PAH loading for Deer Island effluent (a reasonable choice because [1] naphthalene and its alkyl homologues make up such a large percentage of the total PAH in the effluent, and [2] 2-methylnaphthalene is one of the few compounds historically detected during NPDES monitoring). Alber and Chan cite a loading of approximately 1500 kg-yr^{-1} for 2-methylnaphthalene which compares favorably with total C_1 naphthalenes (comprised primarily of 2-methylnaphthalene) of 547 kg-yr^{-1} computed in this task. These values are in stark contrast to the overestimated loading of approximately 6,800 kg-yr^{-1} that is computed using NPDES monitoring data (again, because 2-methylnaphthalene was not detected in the effluent by NPDES monitoring during June - November, 1993, one-half the NPDES MDL was used to compute the loading factor).

3.3.4 Pesticides and PCB

Annual loadings for p-p'-DDT, dieldrin, and lindane estimated in this task were 2, 7, and 4 kg-yr^{-1}, respectively. Comparisons to loading factors calculated with corresponding NPDES data were estimated using one-half the MDL because none of these chlorinated pesticides were detected in the effluents using NPDES techniques. Using this approach, the loading factors from NPDES monitoring data for p-p'-DDT, dieldrin, and lindane were 14 kg-yr^{-1} for each of the compounds. Use of the NPDES monitoring data for assessing loading overestimates the loading of these pesticides by a factor of 7 for p,p'-DDT, 2 for dieldrin and 3.5 for lindane.

In this task, annual PCB loading from Deer Island was calculated to be about 18 kg-yr^{-1}. This compares reasonably with the 1992 combined Deer and Nut Island loading estimate of 36 kg-yr^{-1} made by Shea (1993a). The PCB loading factors calculated from corresponding NPDES data were again estimated using one-half the MDL because no PCB were detected in the effluents using NPDES analysis techniques. The PCB loading factor from NPDES monitoring data was calculated to be 136 kg-yr^{-1}, an eight-fold overestimate.

3.3.5 Summary Remarks on Loading Estimates

The most accurate loading estimates for trace metal and organic contaminants in the Deer Island effluent can only be made with data obtained from methods that can reliably measure ambient concentrations of the analytes of concern. NPDES analytical methods are an excellent tool for judging compliance with NPDES discharge requirements, but the data generated using these methods are, with the exception of Cu and Zn, clearly inadequate for making loading estimates for the metals and organic compounds of interest to MWRA either because the analytes are simply not detected in the effluent using NPDES methodologies (as is the case for all the organics and some of the metals) or because the techniques suffer from possible laboratory contamination or analytical bias that cause an overestimate of the true concentration of the component in the effluent (e.g., Pb and Cr). When provided with "non-detect" results (as is the case for most of the NPDES data), modelers will often use one-half the method detection limit of the analytical techniques for estimating effluent contaminant concentrations and loading factors. As demonstrated in this section of the report, such an approach generally leads to modest (e.g., dieldrin—factor of 2), and often dramatic (e.g., total PAH—factor of 20) overestimates of true loadings of contaminants to the Harbor/Bay. Similar loading overestimates would be made for other point and non-point sources if NPDES analytical methods were used to determine contaminant concentrations in waters from those sources.

3.4 UNIQUE CHEMICAL INDICATORS

Some of the chemical parameters measured in the Deer Island effluent could potentially provide information about the source or nature of the source of certain contaminants to the waste stream or, because of a potentially unique relationship to the effluent, be used as chemical tracers of effluent in the Harbor/Bay systems. Three such parameters are discussed below.

Polynuclear Aromatic Hydrocarbons

Polynuclear aromatic hydrocarbons in effluent arise from two primary source types: pyrogenic and petrogenic. Given the complex composition and varied nature of the sources, it is likely that both types of PAH contribute to the PAH assemblage of the effluent. Products of efficient combustion have assemblages of PAH which are dominated by nonalkylated 4-, 5- and 6-ring PAH, the most common of these being fluoranthene and pyrene. Common products of incomplete combustion (e.g., soot) have PAH assemblages composed of both classic nonalkylated combustion PAH plus mid- to higher molecular weight PAH from uncombusted fuels. PAH arising from petrogenic sources can vary widely in composition and depend strongly on the type of petroleum or refined petroleum present. Refined petroleum tends to contain significant amounts of 2-, 3-, and 4-ring PAH and almost always contain significant amounts of alkylated analogs of the parent PAH. Because the effluent samples collected in this task were analyzed for ultra-trace levels of 2- through 6-ring PAH and their alkylated homologues, detailed information is available to potentially identify the type of source or sources responsible for inputs of PAH to the waste stream (Douglas and Uhler, 1993). The following observations concerning the nature of the PAH in the effluent can be made:

- *The PAH in the effluent arise primarily from petrogenic sources.* First-level evaluation of the PAH distributions in the effluent samples (Figure 4) reveal that the PAH are dominated by low molecular weight PAH (especially naphthalene) and their alkyl homologues. This is completely consistent with petrogenic PAH distributions.

- *The source of PAH in the effluent is likely from a refined petroleum product such as lube oil or mid-range diesel-like fuels.* The PAH assemblage, dominated by 2- and 3-ring PAH is strongly reminiscent of a refined fuel product and does not contain a strong signal often associated with petrogenic material such as coal tars and creosotes which have much greater percentages of 4, 5- and 6-ring PAH. To illustrate this point, Figure 8 shows typical PAH[2] distributions for several types of refined petroleum products, a coal tar, and a diesel soot. Clearly, the PAH assemblages in the effluent more closely resemble lube oil and diesel-like fuels. Principle component analysis, performed on the PAH data from the six monthly effluent samples and several different types of refined products clearly shows that the effluent is very similar in composition to these types of products (Figure 9). Note that the principle component analysis confirms that the effluent PAH composition does not closely resemble very light refined products such as gasoline or jet

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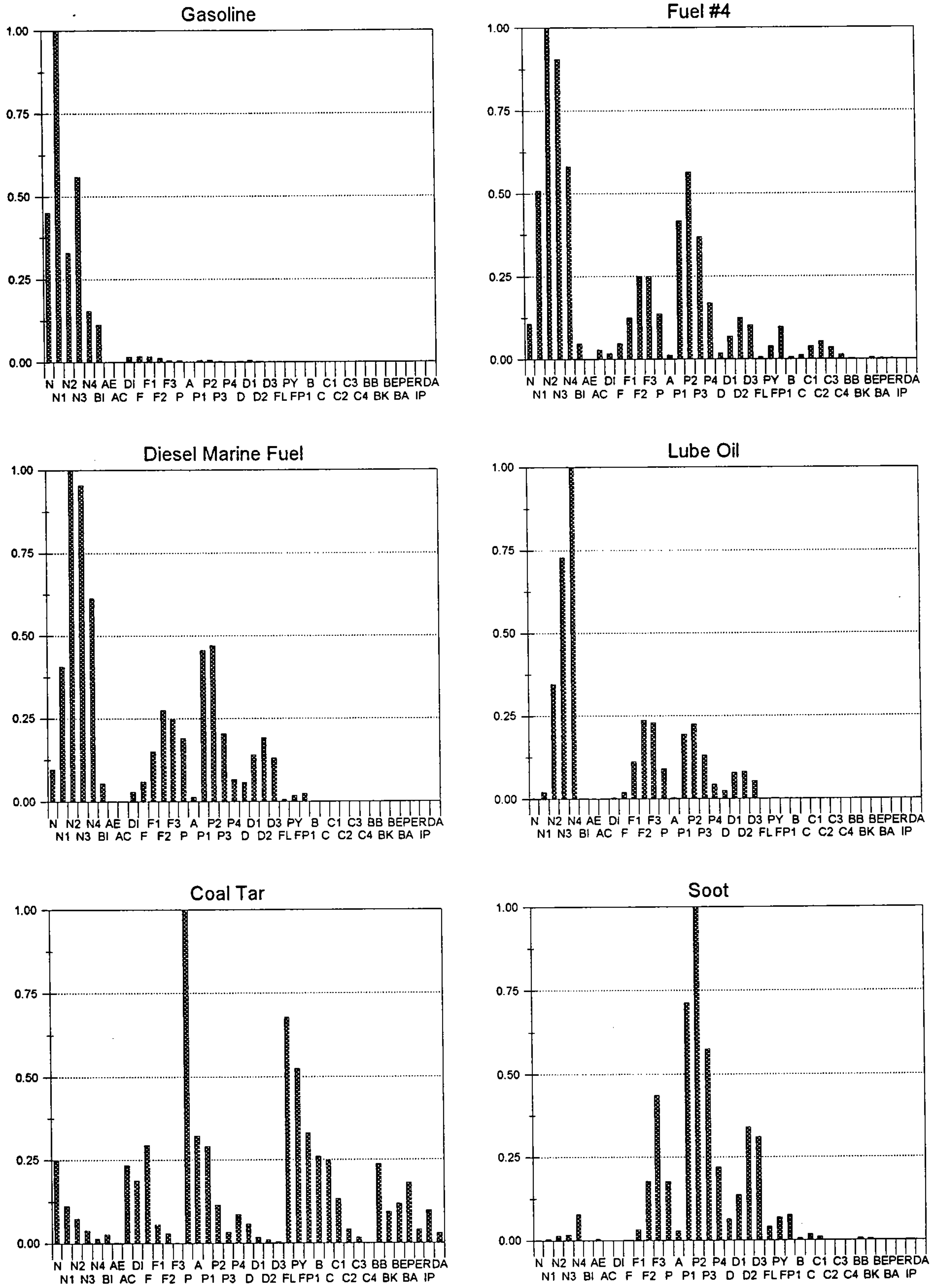
[2] Key to compound names: Naphthalene (N), C_1-naphthalene (N1), C_2-naphthalene (N2),C_3-naphthalene (N3), C_4-naphthalene (N4), Biphenyl (BI), Acenaphthylene (AE), Acenaphthene (AC), Fluorene (F), C_1-fluorenes (F1), C_2-fluorenes (F2), C_3-fluorenes (F3), Phenanthrene (P), Anthracene (A), C_1-phenanthrene/anthracenes (P1), C_2-phenanthrene/anthracenes (P2), C_3-phenanthrene/anthracenes (P3), C_4-phenanthrene/anthracenes (P4), Fluoranthene (FL), Pyrene (PY), C_1-fluoranthene/pyrene (FP1), Dibenzothiophene (D), C_1-dibenzothiophenes (D1), C_2-dibenzothiophenes (D2), C_3-dibenzothiophenes (D3), C_4-dibenzothiophenes (D4), Benz[*a*]anthracene (B), Chyrsene (C), C_1-chyrsenes (C1), C_2-chyrsenes (C2), C_3-chyrsenes (C3), C_4-chyrsenes (C4), Benzo[*b*]fluoranthene (BB), Benzo[*k*]fluoranthene (BK), Benzo[*e*]pyrene (BE), Benzo[*a*]pyrene (BA), Perylene (PER), Indeno[1,2,3-*c,d*]pyrene (IP), Dibenz[*a,h*]anthracene (DA), Benzo[*g,h,i*]perylene (BP).



Gasoline

Fuel #4

Diesel Marine Fuel

Lube Oil

Coal Tar

Soot

Figure 8. Examples of relative PAH distributions in various petroleum products and diesel soot.

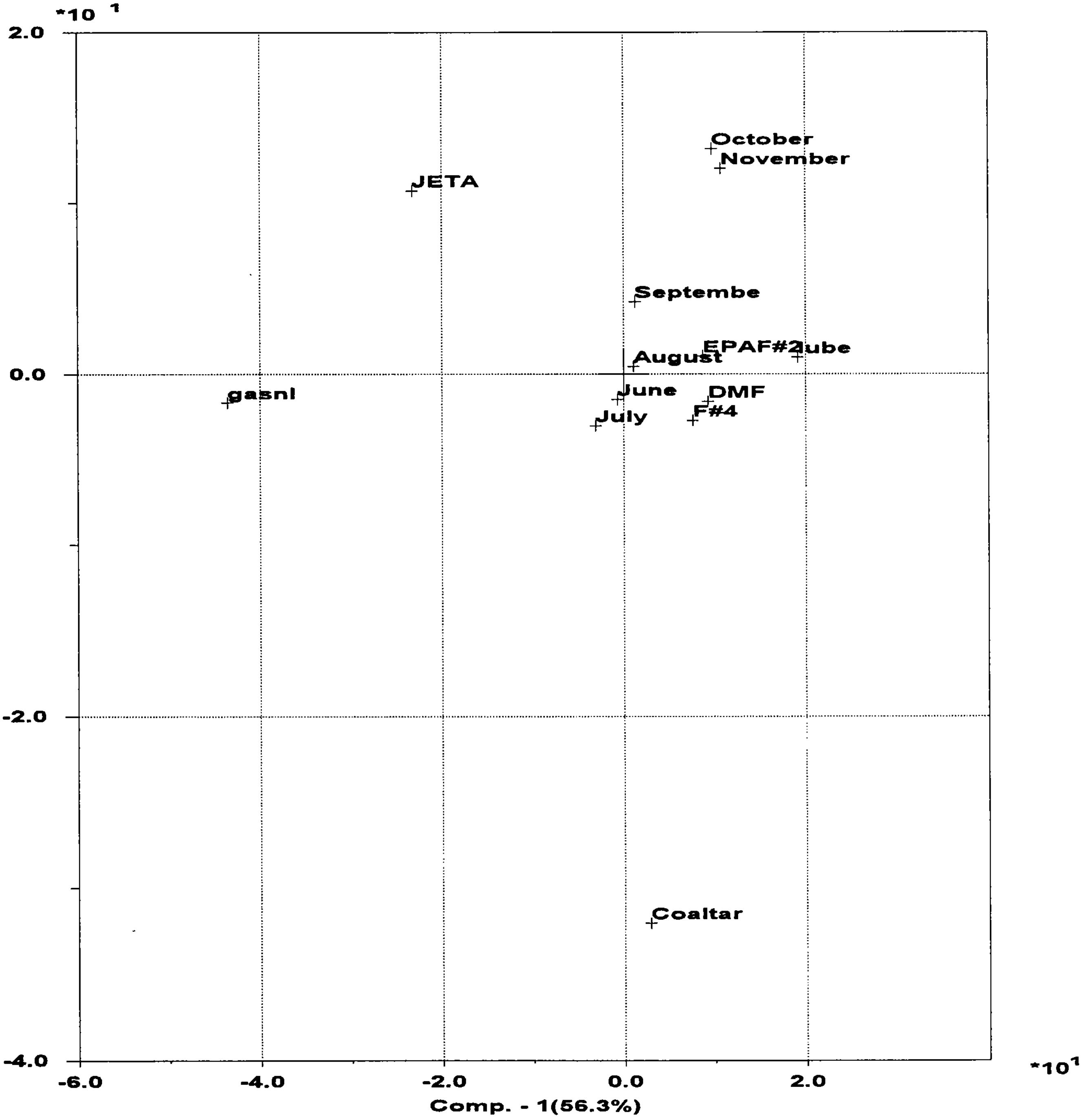


Figure 9. Principal component analysis of the PAH assemblage concentrations in the monthly Deer Island effluent samples (designated by month) and jet fuel (JetA), gasoline (gasnl), diesel marine fuel (DMF), fuel oil #2 (EPAF#2), fuel oil #4 (F#4), lubricating oil (lube), and coal tar (Coaltar).

fuel or products such as coal tar whose PAH assemblages are dominated by high molecular weight PAH.

- *The composition of the PAH in the effluent is relatively consistent but shows some minor variation over time.* Overall, the PAH assemblages determined in this study were very similar over this six-month period. Close inspection of the PAH distribution data (and confirmed in the principle component analysis in Figure 9) shows that there are some differences in PAH distribution, with the strongest differences observed in the C_1- C_4 naphthalene distributions between the June - September period and in November and August. Even with this slight shift in PAH composition, the refined product in the effluent still strongly resembles diesel or lube-like oils.

The PAH data from this study reveal the likely petroleum types that dominate the Deer Island effluent. The fact that even subtle changes in the PAH assemblages can be detected by principle component analysis suggests that changes in inputs to the waste stream can be readily detected.

One limiting concern about this source characterization approach is the fact that the PAH in the Deer Island effluent may represent only the water soluble portion of the source petroleum. In the next effluent characterization report, chromatographic and principle component analyses will be made using reference standards of water soluble and weathered petroleum products in an effort to better characterize the potential sources of PAH to the MWRA effluent. Even with this caveat, the relatively unweathered appearance of the PAH assemblage and the logical distribution of higher molecular weight PAH strongly support the characterization of the petroleum type postulated to be the source of PAH in the effluent.

Linear Alkyl Benzenes (LAB)

Linear alkyl benzenes—nonpolar byproducts of the production of alkyl sulfonate detergents—are compounds that have a very strong, almost unique association with municipal and industrial effluents (Eganhouse *et al.*, 1988). Because the LAB are aromatic, nonpolar compounds of modest molecular weight (ca. 200 - 300 amu), they are expected to reasonably model the behavior of compounds of similar chemistry (e.g., PAH, phthalates, etc.). The total LAB measured in this study represents the sum of the C_{10}, C_{11}, C_{12}, C_{13} and C_{14} homologues. The distribution of the homologues in the effluent reflects the source of the alkyl sulfonate detergent with which the LAB are associated. It is possible for the distribution of the LAB homologous series to change if the industrial source or some aspect of the production of the LAB changes. Clearly, the data in this report suggest that the distribution of LAB in the Deer Island effluent, depicted in the lower part of Figure 5, remained constant over the time period of this study, with the predominant homologues in the LAB assemblage represented by $C_{12} > C_{11} > C_{13} > C_{10}, C_{14}$. This very stable homologue pattern implies that LAB in the Deer Island effluent would be a reliable tracer for many nonpolar organic compounds of similar molecular weight found in Deer Island effluent. As an added benefit in its potential role as a tracer compound, the concentrations of LAB are quite high relative to most other anthropogenic organic compounds in the effluent — e.g., total LAB concentrations are in the 30 μg/L range as compared to individual PAH concentrations which are, at most, on the order of 1 μg/L; similarly, chlorinated pesticide and PCB congeners are only on the order of 0.05 μg/L. This means that LAB can be measured in dilute effluent or receiving environments long after most other individual organic compounds of concern are no longer detectable. Such an approach has been used successfully by EPA Region II to track the fate of sludge disposed at the 106-Mile Site over the course of many tens of miles from the discharge point (EPA, 1992b; Hunt *et al.*, 1994).

Silver

In recent years, investigators have suggested that Ag is an excellent, often unique indicator of municipal and industrial effluent and sludge waste (Sanudo-Wllhelmy and Flegal, 1992; Bothner *et al.*, 1992, 1994; Hunt *et al.* 1993; Hunt *et al.* 1994). The data from this study also suggest that Ag might be an excellent inorganic tracer for the effluent, because, as expected, concentrations of the metal in the Deer Island effluent (average of about 4 μg/L in 1993) are significantly elevated relative to background conditions in the Harbor and Bay. For example, recent survey work in the open Harbor suggests that total recoverable Ag concentrations are typically in the 0.01 - 0.02 μg/L range (Battelle, 1993b). Silver concentrations outside the Harbor are lower (e.g., 0.003 μg/L [Krahforst, 1994]). The utility of Ag as an effluent tracer depends on the strength of the relationship between receiving environment concentrations and potential sources. That is, if treated effluent is the major source of Ag to the Harbor/Bay, the metal becomes an excellent tracer for tracking the fate of some portion of the effluent; if however, other sources contribute significant amounts of Ag to the Harbor/Bay and confound the Ag signal in the environment, its utility as an effluent tracer becomes limited. Currently, there is a scarcity of information regarding Ag concentration in other potential sources such as combined sewer overflows (CSOs) or runoff to the Harbor. Until such data become available, the utility of Ag as an effluent tracer is questionable. However, if supplemental Ag data become available for point- and non-point sources to the Harbor, the usefulness of Ag as an effluent tracer may be proven.

3.5 COMPARISON TO WATER-QUALITY CRITERIA

The question posed regarding the presence of anthropogenic chemical contaminants in the effluent is often reduced to "What are the potential environmental implications of these contaminants to the receiving environment?" The answer to this question is extremely complex and beyond the scope of this report. However, as a first level evaluation, comparison of the effluent data to existing EPA water-quality criteria (WQC) can help address this question. Tables 8 (metals) and 9 (organics) present the existing marine acute and chronic WQC, list the mean Deer Island effluent concentration over the six-month monitoring period, and tabulate the number of times effluent concentrations were higher than either water quality criteria (assuming zero dilution) over the monitoring period. Refer to Figures 3 through 7 for an understanding of any temporal trends in the relationship between effluent contaminant concentrations and WQC.

3.5.1 Trace Metals

Mercury and Pb concentrations in undiluted effluent generally were higher than the marine WQC for most or all of the samples taken between June and November, 1993. The mean Hg effluent concentration was approximately six times higher than the chronic WQC. Lead concentrations were approximately 10 to 12 times higher than the chronic WQC, although the mean effluent Pb concentration was only 1.3 times higher than the criterion. Zinc concentrations were higher than the chronic WQC 5 of 12 times, although the mean effluent Zn was only 1.07 times higher than the criterion.

Copper exceeded the acute WQC in all 12 samples taken during this study; the mean effluent concentration of 71.9 μg/L was a factor of 25 higher than the criterion. Silver concentrations in the effluent exceeded the acute WQC 11 of 12 times, although the mean effluent concentration was less than a factor of two higher than the criterion. Finally, Zn concentrations were higher than the acute criterion in two of the 12 sampling events.

3.5.2 Trace Organics

Because there seemed to be a temporal relationship for many of the trace organic compounds in the effluent, it would not be proper to be contrast mean effluent concentrations to the WQC to compare

Table 8. EPA water-quality criteria (μg/L) and number of occurrences where samples exceeded criteria in undiluted effluent.

Parameter	Marine Acute Criteria	Marine Chronic Criteria	Mean Effluent Concentration	Number[a] of Exceedances of Marine Acute	Number[a] of Exceedances of Marine Chronic
Silver	2.3	b	4.17	11	b
Cadmium	43	9.3	0.55	0	0
Chromium	1100	50	3.42	0	0
Copper	2.9	b	71.9	12	b
Mercury	2.1	0.025	0.156	0	12
Nickel	75	8.3	6.02	0	0
Lead	220	8.5	11.8	0	10
Zinc	95	86	86.6	2	5

[a] Number of exceedances out of 6 bimonthly measurements (i.e., 12 samples total).
[b] No established criterion.

Table 9. EPA water-quality criteria (ng/L) and number of occurrences where samples exceeded criteria in undiluted effluent.

Parameter	Marine Acute Criteria	Marine Chronic Criteria	Mean Effluent Concentration	Number[a] of Exceedances of Marine Acute	Number[a] of Exceedances of Marine Chronic
Pesticides					
Aldrin	1,300	b	<0.5	0	-
p,p'-DDT	130	1	6.8	0	6
Dieldrin	710	1.9	26	0	6
Endrin	37	2.3	6.2	1	4
Heptachlor	53	3.6	<0.5	0	0
Heptachlor Epoxide	53	3.6	0.4	0	0
Lindane	160	b	14	0	-
PAH					
Acenaphthene	970,000	710,000	155	0	0
Fluoranthene	40,000	16,000	183	0	0
Naphthalene	2,350,000	b	1,382	0	-
ΣPAH	300,000	b	19,840	0	-

[a] Number of exceedances out of 6 bimonthly measurements (i.e., 12 samples total).

[b] No established criterion.

the relationship between effluent concentration with the WQC — time-related comparisons are more revealing.

Six samples of undiluted effluent that exceeded the chronic WQC for p,p'-DDT; one of each of the two samples taken in June, July, September, October and November were about five times higher than the WQC. Similarly, four of the 12 samples (2 in August and 2 in September) collected for this task were above the chronic WQC for endrin. Dieldrin concentrations were above the chronic WQC in both samples collected in June and July, and in one of the two samples collected in August and September.

Endrin was the only organic compound in the undiluted effluent that was higher than an established acute WQC. One sample, collected in August, exceeded that criterion.

None of the non-pesticidal organic compounds measured in this study exceeded either the chronic or acute WQC.

3.5.3 Summary Remarks on the WQC

Selected metal and organic contaminants in undiluted Deer Island effluent were found at concentrations that occasionally were higher than established acute and/or chronic WQC. Among the metals, Cu concentrations show the greatest difference between the effluent concentration and the WQC—a factor of about 30 higher in the effluent as opposed to the marine acute WQC. For organics, the concentrations of dieldrin in June and July samples exceeded the chronic WQC by a factor of about 25. The remaining metals and organics generally exceeded the established criteria by more modest degrees — generally less than a factor of five.

In terms of environmental impact, the concentrations of the contaminants in the undiluted effluent itself are not paramount; rather, it is the concentration of the contaminants in the receiving environment after dilution with receiving water against which the WQC should be judged. Assuming that the concentrations of metal and organic contaminants in the effluent remain essentially constant, dilution of the effluent at its anticipated 50 to 100-fold level in the zone of initial dilution at the proposed outfall diffuser will ensure that all metal and organic contaminants will be at concentrations below established acute or chronic WQC.

Furthermore, it is well documented through a large body of literature that a phase transition between the dissolved and particulate forms of metals occurs as fresh water mixes with salt water. This salting out effect is very strongly linked to high concentrations of organic matter, particularly large molecular weight organic molecules, e.g. humic and fulvic acids, that form colloidal phases as the ionic strength of the water changes. Because sewage effluent has high dissolved organic carbon content, this same effect would be expected in the discharge plume. Thus, physicochemical repartitioning of dissolved metals to particulate phases is likely to occur on contact of the effluent with the seawater resulting in even lower dissolved phase concentrations in the receiving waters. Thus, the supposition that marine aquatic life criteria will not be exceeded based on simple dilution, is further amplified when this physicochemical phenomena is considered. Thus, planned dilution and chemical physical transformation of biologically available forms of metal will decrease expected metals concentrations and likely organic chemicals well below any applicable WQC, even when the criteria are applied to the dissolved phase as recommended now by EPA (EPA, 1993b). Thus, monitoring the effluent for toxics using total recoverable methods, as recommended by EPA, should provide adequate information from which compliance can be determined and exceedances of any WQC measured in undiluted Deer Island effluent must, in and of themselves, be considered inconsequential in terms of the resulting concentrations in the receiving water because the effluent is rapidly diluted in the environment.

Lastly, the estimates included in this report comparing effluent concentrations to marine WQC are based on the present level of primary treatment and current contaminant levels in the discharge. As source point reduction continue and improvements to the primary treatment plant become operational, and certainly when secondary treatment is phased in, further reductions the concentrations of toxic compounds in the effluent can be expected with concomitant decreases in loadings to the system and even less likely exceedance of applicable WQC.

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