

New Bedford Harbor Pilot Study

Pre-operational Monitoring - Progress Report:

Chemical Analysis Results From the Pre-operational
Water Samplings Conducted in New Bedford Harbor on
March 1988

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INTRODUCTION

Seawater samples for chemical analysis were collected from New Bedford Harbor on March 31, 1988. Composite samples from ebb and flood tides were obtained from four stations in the harbor. The samples were analyzed for polychlorinated biphenyls (PCBs), copper (Cu), cadmium (Cd) and lead (Pb). In addition to this sampling, two additional samples were obtained at Station 3 on each tide to determine sampling variability.

At station 2, six sampling locations were defined within the station. They were a surface, mid-depth and bottom site on the east and west sides of the Coggeshall Street Bridge. A sample was collected and the flow rate recorded at each location. These flow rates were used in the two types of compositing schemes. No flow data was available during the flood tide due to computer problems, so this scheme was used only for the ebb tide. For the regular composite, the volume of each of these samples which contributed to was calculated using the following formula:

$$\text{Vol}(x) = \text{Flow}(x) \times 4000 \text{ ml} / \text{Flow}(\text{tot})$$

where $\text{vol}(x)$ is the volume in milliliters taken from the location x sample, $\text{Flow}(x)$ is the measured flow at location x , $\text{Flow}(\text{tot})$ is the sum of the six flows and 4000 ml had previously been determined to be an adequate sample size. This was done at hourly intervals five times for each tide. From each of the five 4 liter samples, aliquots were taken and composited for each of the required analyses. The size of these individual aliquots was the same for each hourly sample. This sampling scheme takes into account only spacial variation in flow and

not variation in the magnitude of these flows from hour to hour over the five hours of sampling.

The purpose of the flow proportioned samples was to make the final composite reflect these changes in flow from hour to hour. To obtain a flow weighted composite sample, the following calculation was made every hour:

$$\text{Vol}(x) = \text{Flow}(x) \times 0.6 \text{ ml/cm/sec}$$

where Vol(x) and Flow(x) are the same as indicated above. To determine the 0.6, an average total flow for the six depths over 5 hours of 1500 cm/sec was used, i.e. $0.6 \text{ ml/cm/sec} \times 1500 \text{ cm/sec} = 900 \text{ ml}$, the required chemistry composite volume. This factor was determined for each of the other samples collected based on the required final volumes.

METHODS AND MATERIALS

The methods and materials used for these analyses were similar to those described in the report for the July and September cruises in New Bedford Harbor (Palmquist et al., 1987a; 1987b).

RESULTS AND DISCUSSION

PCBs

The PCB results for samples collected on March 31, 1988 are shown in Table 1. Compositated whole water samples from the ebb and flood tides were analyzed from each of Stations 1, 2, 3 and 4. The samples were analyzed for PCBs as Aroclors 1242 and 1254 and these concentrations were summed as a measure of Total PCBs. The differences in the concentrations between the ebb and flood tides were

not as pronounced as in the previous sampling events with the exception of the NBH-4 samples. The four previous samplings at station NBH-4 showed very little difference between tides and also very little difference between the four dates. The mean value for total PCBs at station NBH-4 had been 0.105 ppb with SD of 0.006. In the present report, the measured value for the ebb tide sample was 0.216 ppb which is higher than the previous measured concentrations.

The concentrations of thirteen individual PCB congeners were also measured in all of the samples that were analyzed. A listing of the congeners quantified is provided in Table 2. The concentrations of each of the congeners in the samples collected on March 31 are shown in Table 3. The detection limits for these congeners vary with the compound and range from approximately 0.7 to 1 ng/liter.

During this sampling event, an experiment was conducted to measure the sample variability at station NBH-3. The results of this experiment are shown in Tables 1 and 3. Total PCB concentrations at station NBH-3 had a mean of 0.359 ppb and standard deviation of 0.020 at ebb tide (RSD 6%). At flood tide the mean and standard deviation were 0.326 ppb and 0.055 (RSD 17%), respectively .

An additional flow weighted sample was collected during ebb tide at station NBH-2. The total PCB concentration in this sample was 0.531 ppb which is very similar to the value of 0.553 ppb measured for the normal composite during the ebb tide. However, as can be seen from Table 1, the ratio of Aroclor 1242 to Aroclor 1254 is considerably shifted toward the lower molecular weight Aroclor 1242 in the flow weighted composite compared with the normal distribution seen at that station.

METALS

The trace metal results for the whole water samples collected on March 31, 1988 are shown in Table 4. The results for lead are very similar to those reported in July and September of 1987 for both concentration range and station variability, although the highest concentration found during the March sampling event, 7.19 ppb, is the highest value found for lead on all dates. Concentrations at the stations further north in the harbor were consistently higher than concentrations found at Station 4 with the highest levels being found at Stations 1 and 3. The flood tide samples were higher than the ebb composites at all four stations.

The results for cadmium and copper were much lower than those previously encountered and were less variable between stations. The highest value for cadmium was 0.192 ppb versus 0.37 ppb previously and, unlike lead, the highest concentrations were found on the ebb tide at all four stations. The highest value for copper during this sampling was 3.73 ppb compared to 12.8 ppb found in September. The mean values for whole water copper for all previous sampling periods were: Station 1 = 7.9 ± 2.6 , Station 2 = 7.5 ± 1.4 , Station 3 = 9.2 ± 1.8 and Station 4 = 2.7 ± 0.89 . Except for Station 4 these values are considerably higher than the 2.45 - 3.73 ppb found at this time. There was no apparent difference between ebb and flood samples for copper. All of the copper results were close to the U.S. EPA Marine Water Quality Criteria of 2.9 ug/l.

The data collected for the two types of composites at Station 2 during the ebb tide are included in Table 4. The results for the three metals are comparable although slightly higher in the flow

proportioned composite samples. Results for the replicate samples collected from Station 3 are summarized in the same table along with a mean and standard deviation. There was good agreement for all three metals for both tides.

CONCLUSIONS

PCBs measured as both Aroclor 1242 and Aroclor 1254 were detected in seawater samples from New Bedford Harbor. Individual PCB congeners containing 4 to 7 chlorine atoms were detected in most samples. The higher molecular weight congeners (those containing 8, 9 and 10 chlorine atoms) were generally below the detection limits in these samples. The measured concentrations of total PCBs were highest (approximately 1.0 ug/l) at Station 1 (north of the Coggeshall Street Bridge) and decreased with distance downbay to about 0.2 ug/l at the Hurricane Barrier (Station 4). These results, with the exception of station NBH-4, compare well with previous sampling events. Station NBH-4 had levels of total PCB higher than had been previously measured at that station. The total PCB concentration in the flow weighted sample from ebb tide at station NBH-2 compared well with the normally composited sample from that tide and station but this sample shows a lower molecular weight distribution of PCB congeners. This one sample is not enough to base any conclusions upon but it will bear watching in future sampling events. As in previous cruises, all samples contained PCB levels above the U.S. EPA Marine Water Quality Criteria of 0.030 ug/l for PCBs.

The results for the whole water metals samples showed some differences from the two previous sampling periods. The most notable difference was in the copper concentrations which were considerably lower than the results previously measured for Stations 1-3 while Station 4 results were not distinguishable from the previous results. Cadmium values were also lower and less variable. Lead concentrations were as high or higher than previous results. Lead values were higher on the flood tide, cadmium values were higher on the ebb tide and

copper showed no trend with tide. The results of the replicate samples at Station 3 and the two types of composites at Station 2 were in close agreement with each other.

REFERENCES

- Palmquist, R., K. Schweitzer, S. Fluck, R. Bowen and R.J. Pruell.
1987a. New Bedford Harbor Pilot Study Pre-operational
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Bedford Harbor during July of 1987.
- Palmquist, R., K. Schweitzer, S. Fluck, R. Bowen and R.J. Pruell.
1987b. New Bedford Harbor Pilot Study Pre-operational
Monitoring - Progress Report: Chemical Analysis Results From
the Two Pre-operational Water Samplings Conducted in New
Bedford Harbor during September of 1987.

Table 1. PCB concentrations as Aroclors and total PCB in seawater samples collected from New Bedford Harbor during the fifth pre-operational cruise on 3/31/88. Concentrations are in micrograms/liter (ppb).

STATION	TIDE	SAMPLE	AROCLOR		TOTAL	MEAN
			1242	1254	PCB	
NBH-1	EBB	WWC	0.864	0.120	0.984	1.04
NBH-1	FLD	WWC	0.924	0.175	1.100	
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NBH-2	EBB	WWC	0.393	0.160	0.553	0.490
NBH-2	FLD	WWC	0.325	0.102	0.427	
NBH-2	EBB*	WWC	0.450	0.081	0.531	
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NBH-3	EBB	WWC	0.298	0.071	0.369	
NBH-3	EBB	WWC	0.302	0.071	0.373	
NBH-3	EBB	WWC	0.246	0.090	0.336	
		MEAN	0.282	0.077	0.359	
		STD DEV	0.031	0.011	0.020	
NBH-3	FLD	WWC	0.213	0.062	0.275	
NBH-3	FLD	WWC	0.260	0.059	0.319	
NBH-3	FLD	WWC	0.310	0.075	0.385	0.342
		MEAN	0.261	0.065	0.326	
		STD DEV	0.049	0.009	0.055	
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NBH-4	EBB	WWC	0.164	0.052	0.216	0.173
NBH-4	FLD	WWC	0.087	0.043	0.130	

* FLOW WEIGHTED COMPOSITE SAMPLE

EBB - ebb tide
 FLD - flood tide
 WWC - whole water composite

Table 2. Listing of the PCB congeners that were quantified. The naming convention used is that described by Ballschmiter and Zell (1980).

CB052	-	2,2',5,5'-PCB
CB047	-	2,2',4,4'-PCB
CB101	-	2,2',4,5,5'-PCB
CB151	-	2,2',3,5,5',6-PCB
CB118	-	2,3',4,4',5-PCB
CB153	-	2,2',4,4',5,5'-PCB
CB138	-	2,2',3,4,4',5'-PCB
CB128	-	2,2',3,3',4,4'-PCB
CB180	-	2,2',3,4,4',5,5'-PCB
CB195	-	2,2',3,3',4,4',5,6-PCB
CB194	-	2,2',3,3',4,4',5,5'-PCB
CB206	-	2,2',3,3',4,4',5,5',6-PCB
CB209	-	CL10-PCB

Table 3. PCB congener concentrations in seawater samples collected from New Bedford Harbor during the fifth pre-operational cruise on 3/31/88. Concentrations are in nanograms/liter (pptr).

STAT	TIDE	SAM	CB052	CB047	CB101	CB151	CB118	CB153	CB138	CB128	CB180	CB195	CB194	CB206	CB209
NBH-1	EBB	WVC	39.2	18.5	21.7	2.67	20.3	11.9	6.70	1.88	1.41	ND	ND	ND	ND
NBH-1	FLD	WVC	44.8	22.7	29.7	3.67	28.8	17.3	9.56	2.52	1.95	ND	ND	ND	ND
NBH-2	EBB	WVC	26.7	24.8	22.2	6.72	28.1	17.3	9.35	2.02	2.03	ND	ND	ND	ND
NBH-2	FLD	WVC	21.8	20.9	16.4	3.79	17.3	10.3	5.94	1.37	1.22	ND	ND	ND	ND
NBH-2	EBB*	WVC	25.8	12.0	15.9	ND	14.6	8.17	4.69	ND	ND	ND	ND	ND	ND
NBH-3	EBB	WVC	19.6	18.3	13.1	3.32	13.1	7.48	4.34	ND	0.80	ND	ND	ND	ND
NBH-3	EBB	WVC	19.3	18.2	12.4	3.14	11.9	6.79	4.10	ND	0.88	ND	ND	ND	ND
NBH-3	EBB	WVC	18.1	15.9	11.6	3.14	11.9	7.25	4.49	ND	1.68	ND	ND	ND	ND
		MEAN	19.0	17.5	12.4	3.20	12.3	7.17	4.31	-	1.12	-	-	-	-
		STD DEV	0.79	1.36	0.75	0.10	0.69	0.35	0.20	-	0.48	-	-	-	-
NBH-3	FLD	WVC	14.0	13.2	9.70	2.81	10.0	5.99	3.76	ND	0.69	ND	ND	ND	ND
NBH-3	FLD	WVC	15.8	7.55	10.3	1.24	9.3	5.84	3.03	ND	1.05	ND	ND	ND	ND
NBH-3	FLD	WVC	18.3	8.21	11.7	1.51	10.8	6.35	4.14	ND	0.81	ND	ND	ND	ND
		MEAN	16.0	9.65	10.6	1.85	10.0	6.06	3.64	-	0.85	-	-	-	-
		STD DEV	2.16	3.09	1.03	0.84	0.74	0.26	0.56	-	0.18	-	-	-	-
NBH-4	EBB	WVC	11.4	10.3	7.69	5.75	8.30	4.90	2.92	ND	0.85	ND	ND	ND	ND
NBH-4	FLD	WVC	7.0	6.44	5.38	2.63	5.60	3.36	2.22	ND	0.79	ND	ND	ND	ND

* FLOW WEIGHTED COMPOSITE SAMPLE

EBB - ebb tide

FLD - flood tide

WVC - whole water composite

ND - not detected. Detection limits were approximately 1 ng/l.

Table 4. Trace metal results for seawater samples collected from New Bedford Harbor. Concentrations are in micograms/kg (ppb).

STATION	TIDE	SAMPLE	Cd	Pb	Cu
NBH-1	EBB	WWC	0.190	4.50	2.89
NBH-1	FLD	WWC	0.186	7.19	3.73
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NBH-2	EBB	WWC	0.139	1.55	2.76
NBH-2	FLD	WWC	0.098	3.20	3.08
NBH-2	EBB*	WWC	0.169	1.92	3.34
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NBH-3	EBB	WWC	0.145	3.53	2.75
NBH-3	EBB	WWC	0.136	3.53	2.91
NBH-3	EBB	WWC	0.146	3.67	2.92
		MEAN	0.142	3.58	2.86
		STD DEV	0.006	0.08	0.10
NBH-3	FLD	WWC	0.116	4.96	2.66
NBH-3	FLD	WWC	0.094	5.12	2.76
NBH-3	FLD	WWC	0.099	3.85	2.45
		MEAN	0.103	4.64	2.62
		STD DEV	0.011	0.69	0.16
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NBH-4	EBB	WWC	0.192	1.28	2.90
NBH-4	FLD	WWC	0.118	1.50	2.87

* - FLOW WEIGHTED COMPOSITE SAMPLE

EBB - ebb tide.

FLD - flood tide.

WWC - whole water sample.