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**INVESTIGATION OF 4-METHYLPHENOL
IN BOTTOM SEDIMENTS
FROM LOG RAFTING AREAS
OF COMMENCEMENT BAY, WASHINGTON**

by

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ABSTRACT

Subtidal sediments were sampled at three log rafting areas of Commencement Bay to see if a correlation exists between the presence of wood waste debris in sediments and elevated concentrations of 4-methylphenol. The only area where 4-methylphenol or other phenolic compounds were detected was in St. Paul Waterway. Mean estimated surface sediment concentrations in ppb dry weight were as follows: 4-methylphenol, 380; phenol, 200; and 2-methylphenol, 26. One additional compound, benzoic acid, was detected in all samples. Estimated concentrations ranged from 44 to 790 ppb dry weight. No correlation was observed between wood waste debris in sediments and elevated levels of 4-methylphenol. Sediments under the log rafting areas sampled were organically enriched and reducing.

INTRODUCTION

Surface sediments at 114 of 143 sites sampled during the Commencement Bay Nearshore/Tideflats Remedial Investigation were found, in general, to contain relatively low levels (>10 ug/kg) of the EPA Hazardous Substances List compound 4-methylphenol (p-cresol). The highest concentration (96,000 ug/kg dw; i.e., ppb dry weight) detected in this study was at a site adjacent to the Simpson pulp and paper mill outfall at the mouth of St. Paul Waterway (Tetra Tech, 1985). Sediments in this area characteristically contain a large amount of wood waste debris. Historically this site has also received a heavy loading of organic material, primarily via the pulp mill discharge.

These data suggest that a potential connection exists between the presence of wood wastes in sediments and elevated concentrations of 4-methylphenol, especially under anaerobic conditions. The major sites of wood waste accumulation in Commencement Bay are log rafting areas. In addition, with the exception of outer St. Paul Waterway, no sampling for 4-methylphenol has been conducted in these areas. To test this theory, the Water Quality Investigations Section (WQIS) was requested to conduct an investigation with the following objectives:

1. Determine if sediments in log rafting areas of Commencement Bay have elevated levels of 4-methylphenol.
2. If elevated levels of 4-methylphenol are found, assess the extent to which they correlate with anaerobic (reducing) conditions.

METHODS

Sample Collection

One log rafting area each in Hylebos, Blair, and St. Paul Waterways was selected for study (see Figure 1). In each area, three sites (shown in detail in Figure 2) were chosen for sediment sampling. Physical descriptions of these sampling points are provided in Table 1.

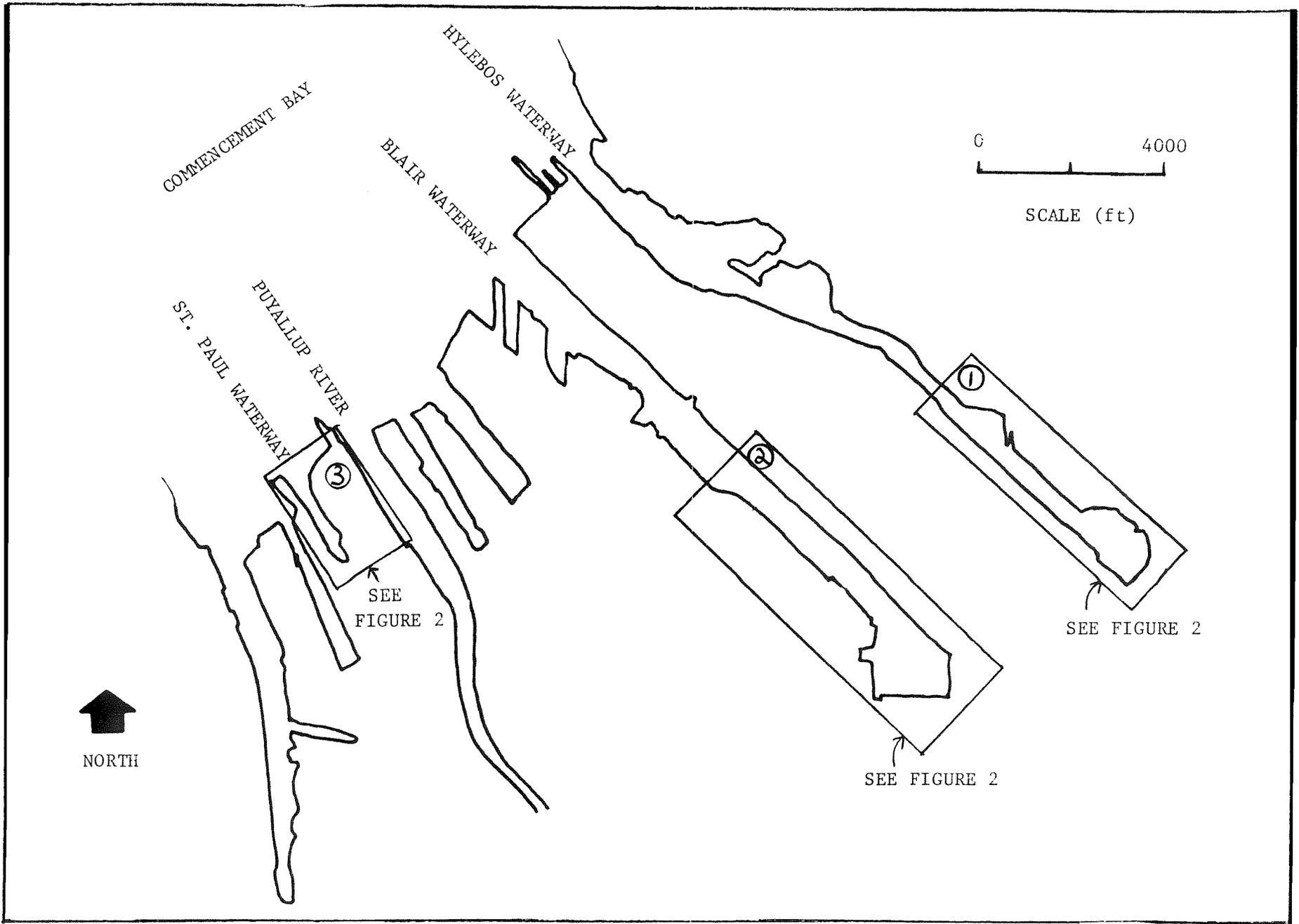


Figure 1: 4-Methylphenol Study Areas, Commencement Bay, Wa.

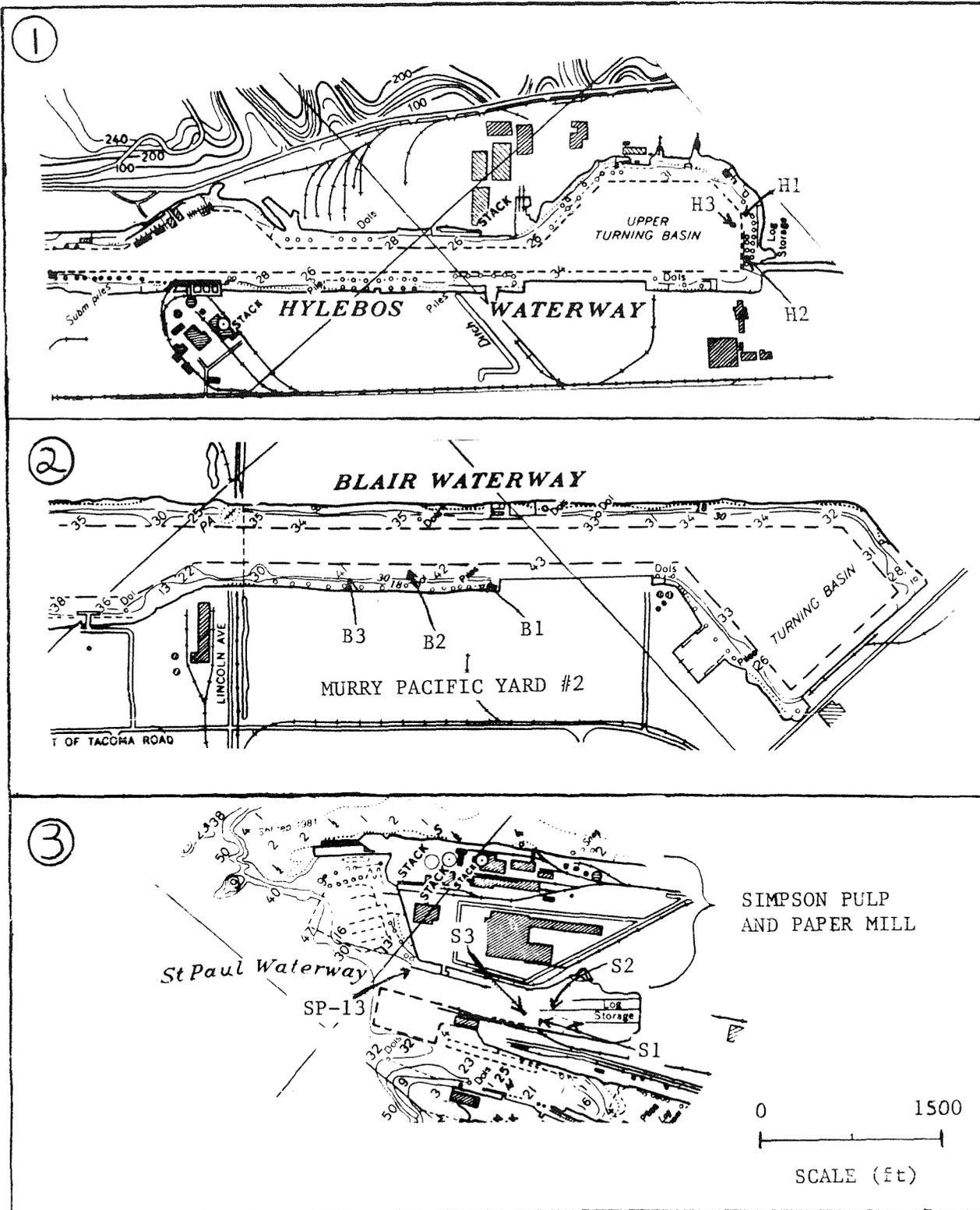


Figure 2: Locations of sediment samples collected by Ecology February 11, 1987 for 4-Methylphenol analysis in Hylebos, Blair and St. Paul Waterways.

Table 1. Locations of Hylebos, Blair, and St. Paul Waterways Sediment Samples Collected by Ecology February 11, 1987.

Station Number	Description	Depth @ MLLW (ft)	Latitude 47 ^o	Longitude 122 ^o
H1	Upper Hylebos Turning Basin 100 Yards North of Hylebos Creek Mouth and Approximately 75 feet Offshore.	38	15'44"	21'30"
H2	Upper Hylebos Turning Basin North of Hylebos Creek Mouth Approximately 75 feet Offshore.	35	15'41"	21'33"
H3	Upper Hylebos Turning Basin Between H1 and H2 Approximately 200 feet Offshore.	41	15'44"	21'32"
B1	Off Murry Pacific Yard #2 Northwest of loading Dock.	23	15'39"	23'08"
B2	Between B1 and B3 Approximately 75 feet off Murry Pacific Yard #2.	47	15'45"	23'14"
B3	Approximately 300 Yards Southeast of Lincoln Avenue Drain Off Murry Pacific Yard #2.	29	15'48"	23'20"
S1	Head of St. Paul Waterway West of Log Storage Area.	17	15'47"	25'43"
S2	Head of St. Paul Waterway Middle of Log Storage Area.	15	15'42"	25'40"
S3	Between S1 and S2 Approximately 100 feet North of Log Storage Area.	17	15'49"	25'43"

All samples were subtidal sediments collected as near to log rafts as possible using a 0.1m² Van Veen grab. The presence and extent of anaerobic conditions in the sample was evaluated by making ORP (oxidation-reduction potential) depth profiles in conjunction with visual observations. Triplicate ORP measurements were made on each sample using an Orion Research Ionalyzer Model No. 399A equipped with an Orion Model No. 96-78 platinum redox electrode. The top 2cm layer from each grab was then removed using a stainless steel spoon, placed in a stainless steel beaker, and homogenized by stirring. To determine if 4-methylphenol concentrations varied with depth, the 2- to 5-cm layer from one grab in each waterway was also retained for analysis. All sampling equipment was cleaned with sequential rinses of Liquinox detergent, distilled/deionized water, pesticide-grade methylene chloride, and pesticide-grade acetone, then stored wrapped in aluminum foil until used in the field.

Samples for organic acid extractables, percent moisture, and total organic carbon (TOC) determinations were placed in priority pollutant-cleaned glass jars with Teflon-lined screw closures supplied by I-Chem, Hayward, California. Samples for grain size analysis were placed in Whirlpack bags. All samples were stored in the dark on ice and transported the following day to the Ecology/EPA Environmental Laboratory at Manchester, Washington.

Laboratory Analysis

Organic acid extractables analysis was performed by Analytical Resources, Inc. (ARI) Seattle, Washington, using EPA Method 1625(B) Isotope Dilution Gas Chromatography/Mass Spectroscopy (Federal Register, 1984). ARI also did the percent moisture determinations, using Method 209F in APHA (1985) Standard Methods for the Examination of Water and Wastes. TOC analysis was done by Laucks Testing Laboratories, Inc., Seattle, Washington, using a modification of Method 9060 in EPA (1984) Test Methods for Evaluating Solid Waste. Grain size distribution was determined by Parametrix, Inc., Bellevue, Washington, following the method outlined in Holme and McIntyre (1971) Methods for the Study of the Marine Benthos. This method was modified to include particles larger than 2mm in a "gravel" category, and particles 62um to 2mm in a single undifferentiated "sand" category.

Quality Assurance

This investigation followed the procedures and guidelines specified in Tetra Tech (1986) Quality Assurance Project Plan for Field Investigations to Support Commencement Bay Nearshore/Tideflats Feasibility Study.

Quality assurance (QA) review of the organics data was performed by Harry Beller of Tetra Tech, Inc., Bellevue, Washington. Overall, this data set was considered acceptable under EPA Contract Laboratory Program (CLP) and Puget Sound Estuary Program (PSEP) protocols.

Accuracy of the data was assessed through analysis of matrix spikes and labeled surrogate compound recoveries. No modifications to the data were deemed necessary based on matrix spike results. In addition, all surrogate compound recoveries were acceptable being above the PSEP warning limit of <10 percent. For labeled 4-methylphenol, surrogate recoveries averaged 91 percent and ranged from 41 to 130 percent. All data reported in this study, with the exception of benzoic acid, have been recovery corrected. No surrogate compound is available for benzoic acid.

Precision was evaluated through analysis of duplicate samples. Table 2 summarizes the results of duplicate organics analysis of a St. Paul Waterway sample, the only duplicate sample in which phenolic compounds were reported above detection limits.

Table 2. Results of duplicate analysis of sediment from station SP-13 in St. Paul Waterway (concentrations in ug/kg dry weight).

Compound	Present Study		Relative Percent Difference
	04-8025	04-8026 (dup)	
Phenol	380	600	45
2-Methylphenol	29J	34J	16
4-Methylphenol	3100	3000	3.2
Benzoic Acid	320J	530J	49

J = estimated concentration

Again, overall precision was considered acceptable in this data set and did not violate CLP or PSEP advisory limits.

To evaluate comparability of data generated during the Commencement Bay Nearshore/Tideflats Remedial Investigation and the present study, an archived St. Paul Waterway sample from this earlier work was re-analyzed. These results, shown in Table 3, indicate relatively good agreement between the two analyses, especially considering that this sample had been stored for approximately 2 to 3 years.

RESULTS AND DISCUSSION

The results of sediment sample analyses are presented in Table 4. Visually, all sediments sampled appeared to have uniform dark color with depth, which is in agreement with the results of ORP measurements. Negative values (-40 to -180 mV) were obtained on all ORP measurements which suggests reducing (anaerobic) conditions were present in the sediments collected.

Table 3. Comparison of Isotope Dilution GC/MS analysis of surface sediment from station SP-13 in St. Paul Waterway (concentrations reported in ug/kg dry weight).

Compound	Present Study		Tetra Tech, 1984
	04-8025	04-8026 (dup)	SOIC
Phenol	380	600	160Z
2-Methylphenol	29J	34J	100
4-Methylphenol	3100	3000	1900
2,4-Dimethylphenol	85u	98u	71
2-Chlorophenol	86u	99u	5u
2,4-Dichlorophenol	110u	130u	10u
2,4,6-Trichlorophenol	41u	47u	10u
Pentachlorophenol	130u	150u	100u
2-Nitrophenol	48u	55u	10u
4-Nitrophenol	140u	160u	100u
4-Chloro-3-Methylphenol	10u	12u	10u
4,6 Dintro-2-Methylphenol	45u	51u	100u
Benzoic Acid	320J	530J	630

u = not detected at detection limit shown

J = estimated concentration

Z = value corrected for blank, resulting value still exceeds detection limit.

Table 4. Results of analyses of subtidal sediments collected by Ecology February 11, 1987, in Hylebos, Blair and St. Paul Waterways. (Concentrations reported in ug/kg dry weight unless otherwise noted.)

Station Description	Hylebos Waterway					Blair Waterway					St. Paul Waterway					
	H1	H2		H3		B1	B2		B3	S1	S2		S3	SP-13**		
Sample Number	Surface+ 07-8027	Surface 07-8029	(Dupl) 07-8031	Depth++ 07-8028	(Dupl) 07-8032	Surface 07-8030	Surface 07-8033	Surface 07-8034	Depth 07-8040	Surface 07-8035	Surface 07-8036	Surface 07-8037	Depth 07-8039	Surface 07-8038	Surface 07-8025	(Dupl) 07-8026
Depth (ft @ MLLW)	38	35	--	--	--	41	23	47	--	29	17	15	--	17	31	--
eh (mv)	-80	-100	--	--	--	-150	-40	-40	--	-160	-140	-180	--	-110	--	--
Moisture (%)	62.3	61.2	64.3	61.1	59.8	65.2	32.5	41.8	46.8	45.7	60.1	58.9	57.8	63.8	52.5	56.5
TDC (%)	7.8	6.9	6.1	7.3	6.8	6.9	4.2	2.8	3.8	4.2	7.1	7.9	7.4	7.9	5.7	--
Grain Size (%)																
Gravel (>2mm)	0.30	0.01	0.00	0.15	0.18	0.38	1.79	0.76	1.22	0.82	1.22	0.12	0.39	0.38	1.12*	--
Sand (2mm-62um)	8.89	11.19	12.26	13.02	10.78	14.56	66.31	52.17	34.86	44.94	42.00	22.74	24.12	18.03	29.54*	--
Silt (62um-4um)	66.28	69.12	72.21	69.14	73.07	63.68	24.46	35.97	50.14	40.93	42.22	62.26	61.12	60.69	57.22*	--
Clay (<4um)	20.33	14.36	13.40	12.73	13.34	17.21	6.16	7.92	12.79	9.80	9.08	10.57	9.80	15.86	12.12*	--
Phenol	120u	110u	140u	120u	100u	140u	73u	76u	79u	80u	120u	<u>180J</u>	210	110u	<u>380</u>	<u>600</u>
2-Methylphenol	76u	70u	84u	73u	64u	83u	45u	47u	49u	49u	72u	<u>26J</u>	<u>36J</u>	25J	<u>29J</u>	<u>34J</u>
4-Methylphenol	140u	130u	150u	140u	120u	150u	82u	86u	89u	90u	130u	<u>400J</u>	<u>520J</u>	<u>350J</u>	<u>3100</u>	<u>3000</u>
2,4-Dimethylphenol	110u	110u	130u	110u	95u	120u	67u	70u	73u	74u	110u	100u	89u	100u	85u	98u
2-Chlorophenol	120u	110u	130u	110u	97u	130u	68u	71u	74u	75u	110u	100u	90u	110u	86u	99u
2,4-Dichlorophenol	110u	100u	120u	110u	93u	120u	65u	68u	71u	71u	110u	99u	86u	100u	83u	95u
2,4,5-Trichlorophenol	150u	140u	160u	140u	120u	160u	86u	90u	94u	95u	140u	130u	110u	130u	110u	130u
2,4,6-Trichlorophenol	55u	51u	61u	53u	46u	60u	32u	34u	35u	36u	52u	49u	43u	50u	41u	47u
Pentachlorophenol	170u	160u	190u	160u	140u	180u	99u	100u	110u	110u	160u	150u	130u	150u	130u	150u
2-Nitrophenol	64u	59u	71u	62u	54u	70u	38u	40u	41u	42u	61u	57u	50u	59u	48u	55u
4-Nitrophenol	180u	170u	200u	180u	160u	200u	110u	110u	120u	120u	180u	170u	110u	170u	140u	160u
2,4-Dinitrophenol	75u	69u	83u	73u	63u	82u	45u	47u	48u	49u	72u	68u	59u	69u	57u	65u
4-Chloro-3-methylphenol	13u	12u	15u	13u	11u	15u	8u	8u	9u	9u	13u	12u	11u	12u	10u	12u
4,6 Dinitro-2-methylphenol	59u	55u	66u	58u	50u	65u	35u	37u	38u	39u	57u	53u	47u	55u	45u	51u
Benzoic Acid	<u>450u</u>	<u>790J</u>	<u>300J</u>	<u>320J</u>	<u>140J</u>	<u>330J</u>	<u>150J</u>	<u>130J</u>	<u>150J</u>	<u>44J</u>	<u>260J</u>	<u>210J</u>	<u>190J</u>	<u>260J</u>	<u>320J</u>	<u>530J</u>

- + = 0-2cm
- ++ = 2-5cm
- * = Historical data (Tetra Tech, 1985.)
- ** = Archived sample collected 3/15/84 by Tetra Tech, Inc. as part of the Commencement Bay Nearshore Tidelands Remedial Investigation. Re-analyzed 2/20/87 as part of the present study.
- = No data
- u = Not detected at detection limit shown.
- J = Estimated concentration
- = Compound detected

TOC concentrations ranged from 2.8 to 7.9 percent. Compared to data from the Commencement Bay Nearshore/Tideflats Remedial Investigation, these concentrations are elevated by approximately a factor of two, which indicates that the areas sampled are more organically enriched than other parts of Commencement Bay previously sampled. Wood waste was apparent in all samples.

Grain size analysis showed that sediments collected in Hylebos and St. Paul Waterways were composed primarily of silt (62um to 4um) while sand (2mm to 62um) was the predominant fraction in Blair sediments.

In general, the results of organic acid extractables analyses were unremarkable despite achievement of reasonably good detection limits. No phenolic compounds were detected in Hylebos or Blair Waterways sediments. The only compound detected was benzoic acid which ranged from estimated concentrations of 140 to 790 ug/kg dw and 44 to 150 ug/kg dw, respectively. Benzoic acid is a ubiquitous compound which occurs in nature in both free and combined forms. As an example, most berries contain appreciable amounts (Merck, 1983). Three phenolic compounds--phenol, 2-methylphenol, and 4-methylphenol--were detected in St. Paul Waterway. 2-methylphenol and 4-methylphenol concentrations were fairly consistent in all samples, ranging from estimated concentrations of 25 to 36 ug/kg dw and 350 to 570 ug/kg dw respectively. Benzoic acid was also detected in all samples. Estimated concentrations of benzoic acid were from 190 to 260 ug/kg dw.

To place the results from the present study in perspective, Table 5 summarizes concentrations of phenol, 2-methylphenol, 4-methylphenol, and benzoic acid found in Hylebos, Blair, and St. Paul Waterways and Carr Inlet surface sediments during Commencement Bay Nearshore/Tideflats Remedial Investigation (Tetra Tech, 1985).

Phenol, 4-methylphenol, 2-methylphenol, and benzoic acid were commonly detected in Hylebos, Blair, and St. Paul Waterways. With the exception of 2-methylphenol, these compounds were also routinely detected in Carr Inlet, the reference station selected for the study. Although detection limits differ slightly from the present study, comparison of the two data sets gives no evidence that 4-methylphenol concentrations under log rafting areas in Hylebos and Blair are atypical with respect to other parts of these waterways. While somewhat elevated levels of 4-methylphenol were seen in St. Paul Waterway sediments in both investigations, concentration gradients point to the Simpson pulp and paper mill discharge rather than wood waste from log rafts as the likely source.

CONCLUSIONS

- o Based on the available data, no clear correlation is evident between elevated levels of 4-methylphenol and the presence of wood waste debris in subtidal sediments of the areas studied.

Table 5. Summary of phenol, 2-methylphenol, 4-methylphenol, and benzoic acid concentrations [median (range)] in Hylebos, Blair, and St. Paul Waterways and Carr Inlet surface sediments collected March, 1984, by Tetra Tech, Inc. as part of the Commencement Bay Nearshore/Tideflats Remedial Investigation (concentrations reported in ug/kg dry weight).

Location	Phenol	2-Methylphenol	4-methylphenol	Benzoic Acid
Hylebos Waterway (n=38)	110(10u-2100)	10u(10u-53)	69(10u-520)	25u(25u-670)
Blair Waterway (n=22)	140(10B-550)	12(10u-52)	180(48-660)	250(25u-8000)
St. Paul Inner Waterway (n=3)	130Z(25Z-160Z)	35(10u-100)	390(250-1900)	25u(25u-630)
" Outer* " (n=3)	240Z(110Z-1700Z)	10u(10u-40u)	2600(890-96,000)	25u(25u-100u)
Carr Inlet (n=4)	30(10u-62)	10u(10u)	18(10u-32)	210(25u-430)

u = not detected at detection limit shown

* = adjacent to Simpson pulp mill outfall

B = Value corrected for blank contributions down to the detection limit.

Z = Value corrected for blank; resulting value still exceeds the detection limit.

- o TOC concentrations, ORP measurements, and visual observations indicate that sediments under the log rafting areas sampled are both organically enriched and reducing in nature.

RECOMMENDATIONS

If further work is undertaken related to sediment levels of 4-methylphenol in inner Commencement Bay, this work should be focused on the area around the Simpson pulp and paper mill outfall in outer St. Paul Waterway.

REFERENCES

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