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JOHN SPELLMAN
Governor

STATE OF WASHINGTON
DEPARTMENT OF ECOLOGY
7272 Cleanwater Lane, LU-11 • Olympia, Washington 98504-6811 • (206) 753-2353

MEMORANDUM
January 25, 1985

To: Jim Krull

From: Art Johnson AJ and Dale Norton D.D., Water Quality Investigations Section

Subject: Completion Report on WDOE Project 5 (Part 3) for the Commencement Bay Nearshore/Tideflats Remedial Investigation: Aromatic Hydrocarbons and Other Organic Compounds in Groundwater Beneath D Street Petroleum Storage Facilities and in Nearby City Waterway Sediments, April 1984

ABSTRACT

Petroleum, groundwater, and adjacent subtidal marine sediment at petroleum storage facilities near the mouth of City Waterway were analyzed for aromatic hydrocarbons and other organic priority pollutants. Petroleum constituents detected in groundwater were benzene, ethylbenzene, toluene, xylenes, naphthalene, 2-methylnaphthalene, phenanthrene, phenol, and cresols. Concentrations of specific aromatics ranged from 0.024 to 30 mg/L, single-ring compounds being present in the highest concentrations. Although petroleum has been seeping into the waterway from this site for a number of years, results of sediment analysis showed an aromatic hydrocarbon distribution dominated by four- and five-ring compounds which is characteristic of combustion sources, not petroleum. Concentrations of these high molecular weight aromatic hydrocarbons in sediment at the entrance to City Waterway and immediately adjacent to the petroleum storage facilities are the highest reported for the waterway.

INTRODUCTION

The Water Quality Investigations Section (WQIS) had responsibility for five projects† in the Commencement Bay Nearshore/Tideflats Remedial Investigation.

†WQIS projects:
- No. 1 - Assessment of Log Sort Yards as Metals Sources to Commencement Bay Waterways
- No. 2 - Metals in Hylebos Creek Drainage
- No. 3 - Point Source Monitoring
- No. 4 - Source Evaluation for Metals in Sitcum Waterway Sediments
- No. 5.1 - Priority Pollutants in City Waterway Storm Drains
- No. 5.2 - Metals in City Waterway Sediments
- No. 5.3 - Petroleum Compounds in D Street Groundwater and Adjacent City Waterway Sediment

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Project 5 involved investigating sources of contaminants to City Waterway. Part 3 of the project is reported here and describes the results of organics analyses of groundwater beneath the petroleum storage facilities along Tacoma's D Street and of marine sediments in City Waterway bordering the storage area. The objective of the investigation was to determine if these sediments have been contaminated by petroleum known to be entering City Waterway from this aquifer.

SITE DESCRIPTION

Figures 1 and 2 show the locations of the storage facilities at the mouth of City Waterway. Figure 3 is a photograph of the site taken from the waterway. Petroleum seepage into the waterway has been observed here for at least twelve years (Hart Crowser, 1982). Intercepter wells have been installed but have not alleviated the problem. Hart Crowser and Associates, Inc. concluded the following as a result of their 1982 hydrogeologic investigation:

> "Petroleum product seepage into the City Waterway from property owned by Globe Machine and Union Oil is being observed. Observation wells indicate product is moving on the water table surface within a silty fine sand unit, although product may also be moving along man-made, higher permeability zones such as sewer line pipe bedding. The direction of ground water flow and product migration is generally towards the City Waterway from a petroleum product storage area owned by Union, Mobil and Shell."
>
> "The specific source of product cannot be identified with the existing data. However, limited data on the types of product seepage and the ground water flow directions indicates differing sources. Chemical analyses indicate the Globe seepage to be predominantly unleaded gasoline from a source located within the southeast portion of the product storage area. Chemical analyses indicate the Union seepage to be leaded gasoline mixed with fuel oil from a source within the southwest portion of the storage area."

METHODS

Sampling

Groundwater was sampled April 6, 1984. The wells designated A and B in the Hart Crowser report and shown in Figure 5 were selected for sampling because of their proximity to the waterway and position relative to the path of groundwater movement. At each well, the distance from the top of the casing to the liquid surface was measured and the thickness of petroleum floating on the groundwater determined with an Oil Recovery Systems 12-inch surface sampler (see Figure 4).

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A petroleum sample was collected from well A with a Johnson UOP 1000 cc teflon well bailer previously cleaned with nanograde methylene chloride. The bailer was lowered through the surfacer layer, retrieved, and the groundwater drained from a valve at the bottom of the bailer. The remaining petroleum was transferred to an eight-ounce jar. Several grabs were composited to make one sample.

Groundwater samples were collected from both wells using a Geofilter Model No. 004 peristaltic pump with silastic tubing and a teflon sampling line. The sampling line was rinsed with nanograde methylene chloride before use. To reduce contamination from the petroleum surface layer, positive pressure was put on the sampling line while the intake was lowered. Once beneath the water surface, groundwater was pumped through the system for several minutes before sampling. Sample containers for groundwater were one-gallon glass jars.

Field blanks were prepared for the well bailer and pump system. A transport blank was carried through the survey. Blank water was prepared at the EPA/ WDOE laboratory in Manchester, Washington, by passing de-ionized water through activated carbon filters.

Samples of City Waterway sediment were collected from depths of 25 to 28 feet (mean lower low water) on April 4, 1984 using a 0.1 m^2 VanVeen grab. As shown in Figure 5, six samples were collected---three nearshore and three offshore--between the Union Oil dock and the south end of the oil boom deployed off Globe Machine. This is the portion of shoreline where product seepage can be seen.

The surface 2 cm layer from each grab was removed with a stainless steel spoon, placed in a one-gallon glass jar, and homogenized by stirring. Subsamples of this homogenate were transferred to separate one-pint glass jars for organics and conventional analyses. Separate subsamples were placed in 4 1/2-ounce polyethylene cups for percent solids analysis.

Containers used for samples to be analyzed for organics were cleaned with sequential rinses of detergent, HCl, HNO_3, distilled water, nanograde acetone, and nanograde methylene chloride, then dried at 350°F for twenty-four hours. All containers had teflon-lined lids. Samples were kept on ice after collection. Chain-of-custody procedures were followed.

Analysis

Groundwater and sediment samples for organics analysis were sent to Cal Analytical in Sacramento, California, an EPA contract laboratory, by air freight on the day of collection and extracted within five days. Analysis

was by GC/MS according to IFB contract no. WA-83-A093 and by EPA methods 608 and 612 for polychlorinated butadienes, polychlorinated biphenyls, and pesticides. Target compounds included all the EPA priority pollutants (except cyanide), tri- and tetrachlorobutadiene isomers, and the twenty compounds on EPA's "non-priority pollutant hazardous substances" list. Additional compounds were tentatively identified by computer match for twenty of the largest remaining peaks in each sample. No specific analyses were done for paraffins or naphthenes, two of the three major hydrocarbon components of petroleum. The third component, aromatics, is part of the priority pollutant analysis. The oil fraction from well A was analyzed for volatiles and polycyclic aromatic hydrocarbons (PAH) only, by a modified method described in Appendix I.

Conventional sediment analyses were done by a second EPA contractor, Rocky Mountain Laboratory, in Arvada, Colorado. Samples were shipped by air freight, as above. Analysis followed EPA/COE (1981), Procedures for Handling and Chemical Analysis of Sediment and Water Samples. Total organic carbon and nitrogen were done with a Perkin-Elmer elemental analyzer and grain size by the method of sieves and pipettes.

Sediment percent solids were determined at the WDOE Tumwater, Washington, laboratory according to Method 160.3 in EPA (1979) Methods for Chemical Analysis of Water and Wastes.

Quality Assurance (Q/A) - This investigation was conducted in accordance with a quality assurance program (WDOE, 1983) developed following requirements and guidelines set down in Final QA Program Plan for Commencement Bay Nearshore/Tideflats Remedial Investigation (Tetra Tech, 1983).

James Farr, Ecology and Environment, Inc., Seattle, Washington, did the Q/A review on the organics data. Internal standards and surrogate/matrix spikes were within EPA-accepted limits. Transport, bailer, and pump blanks analyzed as part of the groundwater collection contained traces of methylene chloride only, probably a contaminant from the washing procedure. Appendix II contains the complete data set as received from the reviewer, and shows all compounds included in the analysis and their respective detection limits.

A duplicate sediment sample was prepared in the field from the grab at station CW-5. The results of organics analysis of the duplicates are shown in Table 1.

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Table 1. Organics results for sediment duplicates (ug/Kg, dry weight).

Compound	CW-5	CW-5 (duplicate)	Compound	CW-5	CW-5 (duplicate)
ethylbenzene	5u	17m	benzo(k)fluoranthene	830m	880m
total xylenes	5u	66	benzo(b)fluoranthene	830m	880m
naphthalene	440m	440m	benzo(g,h,i)perylene	730m	830m
acenaphthylene	200m	300m	indeno(1,2,3-cd)pyrene	730m	630m
anthracene	470m	490m	tetrachloroethylene	78	83
phenanthrene	630m	630m	di-n-butylphthalate	3300	2100
chrysene	930m	1100	bis(2-ethylhexyl)phthalate	2800	2800
pyrene	1500	1900	PCB-1260	220m	1000u†
benzo(a)anthracene	1200	1500	beta-BHC	50m	25u
fluoranthene	1100	1400	delta-BHC	5m	25m
benzo(a)pyrene	1900	2300			

u = not detected at detection limit shown
m = detected but less than quantification limit shown
†high detection limit due to greater dilution of duplicate sample for PCB analysis

The conventional sediment data, other than percent solids, were reviewed by Robert Barrick, Tetra Tech, Inc., Bellevue, Washington, QA officer for the Commencement Bay project. Duplicate results are in Table 2.

Table 2. Conventionals results for sediment duplicates (%).

Parameter	CW-5	CW-5 (duplicate)
solids	43	42
total organic carbon	5.27	5.40
nitrogen	0.22	0.23
sand	16.99	16.49
silt	68.94	68.92
clay	14.02	14.57

The average of duplicate results is used in the report. All blank and duplicate organics data are in Appendix II.

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RESULTS

Field Observations

Water level elevations in wells A and B were 1/.11 and 1/.32 feet above mean lower low water, respectively. An oil layer 0.29 foot in thickness was floating on the water surface of well A; the oil in well B was 0.04 foot thick. Hart, Crowser (1982) reported 0.11 to 0.12 foot of oil in well A and 0.08 foot of oil in well B in 1982. Their high and low tide elevation measurement in well A indicated only a 0.07 foot change with tide. Soil borings showed wells A and B to be in a thin aquifer confined within a ten- to fifteen-foot thick layer of dredged sand underlain by silt.

Oil and Groundwater

Table 3 shows the results of groundwater analysis.

Six aromatic hydrocarbons and two ketones were quantified in the oil layer sample from well A. Single-ring compounds--benzene, ethylbenzene, toluene, and xylenes--were the major aromatic constituents. Concentrations ranged from 16,000 mg/L (benzene) to 65,000 mg/L (total xylenes). The two-ring compounds identified, naphthalene and 2-methylnaphthalene, were present at relatively much lower concentrations of 3,500 mg/L and 2,700 mg/L, respectively. A 200 mg/L detection limit for higher molecular weight polycyclic aromatic hydrocarbons (PAH) precluded their detection in oil. PAH of three rings or more occur in petroleum in the lower parts per million range (Pancirov, 1980). The ketones identified in the oil sample were 2-hexanone and 4-methylpentanone, both at 3,000 mg/L.

Methylbenzenes, methylnaphthalenes, hexadecane, dihydroindene, and 1-methylphenyl ethanone were also tentatively identified in the oil at concentrations estimated to range from 750 to 1300 mg/L.

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Table 3. Concentrations of petroleum-related compounds detected in WDOE samples of groundwater collected beneath D Street petroleum storage facilities on City Waterway, April 6, 1984.

Sample Location		Well A		Well B
		(oil fraction)	(water fraction)	(water fraction)
Time sampled		1150	1055-1140	1230-1235
Laboratory Sample Number		J3439	J3440	J3442
Compound		Concentration (mg/L)		
benzene		16,000	27	5.5
ethylbenzene		22,000	5.3	0.85
toluene		50,000	30	5.9
total xylenes		65,000	22	8.6
naphthalene		3,500	5.6	0.64
2-methyl naphthalene		2,700	2.1	0.26
phenanthrene		200u	0.15	0.024
2-hexanone		3,000	0.005u	0.005u
4-methylpentanone		3,000	0.005u	0.005u
phenol		N/A	0.34	0.092
2-methylphenol		N/A	0.17	0.052
4-methylphenol		N/A	0.28	0.072
2,4-dimethylphenol		N/A	0.28m	0.028
Tentatively Identified Compounds	CAS #	Estimated Concentration (mg/L)		
nonane	111-84-2	N/I	1.5	N/I
hexadecane	544-76-3	890	N/I	N/I
1,2,4-trimethylbenzene	95-63-6	850	9.1	0.63
1,2,3,5-tetramethylbenzene	527-53-7	930	N/I	N/I
1-ethyl-2-methylbenzene	611-14-3	980	7.5	0.58
1-ethyl-3-methylbenzene	620-14-4	N/I	18	N/I
2-ethyl-1,4-dimethylbenzene	1750-88-9	N/I	4.6	N/I
2-ethyl-1,4-dimethylbenzene (isomer)	1758-88-9	710	6.9	0.18
diethylbenzene	25340-17-4	N/I	3.8	N/I
propylbenzene	103-65-1	N/I	5.8	N/I
2-propenylbenzene	300-57-2	N/I	5.6	N/I
1-methyl-4-propylbenzene	1074-55-1	N/I	6.1	0.12
2,3-dihydro-1H-indene	496-11-7	750	3.2	0.48
1,2-dimethylnaphthalene	573-98-8	1,000	N/I	N/I
2,7-dimethylnaphthalene	582-16-1	930	N/I	N/I
1-methylphenylethanone	26444-19-9	1,300	N/I	N/I

u = not detected at detection limit shown
m = detected, but less than limit of quantification shown
N/A = not analyzed.

CAS # = Chemical Abstracts Registry.
N/I = Not identified.

The one- and two-ring aromatics identified in the oil were detected in water at three to four orders of magnitude lower concentrations. Phenanthrene, a three-ring PAH, was also detected in water from both wells. No other high molecular weight PAH were reported, although low detection limits, 1 to 5 ug/L, were employed.

The ketones identified in oil were not detected in the groundwater.

Phenol and three methylphenols (cresols) were measured at less than 1 mg/L in water from both wells. Phenols are constituents of oil(Clark, 1977), but were not included in the oil analysis.

Several of the methylbenzenes and dihydroindene tentatively identified in the oil were also among the compounds tentatively identified in water. Other compounds identified in water were nonane and propylbenzenes.

Water from well A had higher contaminant concentrations than well B.

Sediment

As shown in Table 4, City Waterway surface sediments adjacent to the petroleum storage facilities were sandy silt with organic carbon and nitrogen contents of 3.17 to 5.50 percent and 0.14 to 0.23 percent, respectively. Nearshore sediment had higher concentrations of carbon and nitrogen and were generally coarser than sediment farther offshore.

Table 4. Percent moisture, total organic carbon, nitrogen, and grain size of WDOE samples of City Waterway sediment collected off D Street petroleum storage facilities, April 4, 1984.

Sample Location	Union Dock		Globe Small Boat Dock		Globe Oil Boom	
	CW-1 (nearshore)	CW-2 (offshore)	CW-4 (nearshore)	CW-3 (offshore)	CW-5 (nearshore)	CW-6 (offshore)
Depth at MLLW (feet)	30	32	25	28	25	29
Solids (%)	43	52	47	43	43	41
Total Organic Carbon (%)	5.04	3.17	5.50	4.85	5.33	4.80
Nitrogen (%)	0.21	0.14	0.22	0.19	0.23	0.21
Sand (%)	20.51	24.26	35.94	25.62	16.74	15.78
Silt (%)	71.56	55.19	49.50	59.64	68.93	71.01
Clay (%)	3.85	20.56	14.52	14.70	14.30	9.10
Total (%)	95.92	100.01	99.96	99.96	99.97	95.89

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The organics data for sediment samples are summarized in Table 5 (aromatic hydrocarbons) and Table 6 (other organic priority pollutants). The aromatic hydrocarbon assemblage in all sediment samples, unlike that in oil and groundwater, was dominated by four- and five-ring compounds, of which pyrene was present at the highest concentrations--up to 5600 ug/Kg dry weight. Naphthalene was detected in all sediment samples but at concentrations too low to quantify. 2-methylnaphthalene was not detectable. Phenanthrene concentrations ranged from less than 370 ug/Kg to 3,000 ug/Kg. With the exception of possible traces of ethylbenzene and xylenes at station CW-5, not confirmed in the companion duplicate sample (see Table 1, QA section), none of the single-ring aromatics which were the major oil and groundwater constituents were found in sediment at a detection limit of 5 ug/Kg. The phenols and ketones identified in groundwater or oil were also not detected in sediment, but detection limits for phenols were very high (1000 ug/Kg) for sediment.

Table 5. Concentrations of polyaromatic hydrocarbons (PAH) detected in WDOE samples of City Waterway sediment collected off D Street petroleum storage facilities, April 4, 1984.

Sample Location	Union Dock		Globe Small Boat Dock		Globe Oil Boom	
	CW-1 (nearshore)	CW-2 (offshore)	CW-4 (nearshore)	CW-3 (offshore)	CW-5 (nearshore)	CW-6 (offshore)
Depth at MLLW (feet)	30	32	25	28	25	29
Time sampled	1015	1050	1130	1110	1150	1205
Laboratory sample number	J3447	J3448	J3450	J3449	J3451	J3453
Compound	Concentration (ug/Kg, dry weight)					
acenaphthene	200u	200u	200u	200u	200u	200u
naphthalene	500m	290m	510m	410m	440m	430m
2-methylnaphthalene	200u	200u	200u	200u	200u	200u
acenaphthylene	360m	220m	700m	320m	250m	200m
anthracene	630m	510m	1,600	550m	480m	380m
phenanthrene	1,900	370m	3,000	650m	680m	670m
fluorene	200u	200u	200u	200u	200u	200u
chrysene	1,900	810m	2,600	1,200	1,000	910m
pyrene	5,000	1,400	5,600	2,000	1,700	1,300
benzo(a)anthracene	2,300	950m	3,400	1,400	1,300	1,000
fluoranthene	4,200	950m	3,900	1,400	1,200	980m
benzo(a)pyrene	1,700	1,400	3,200	1,400	2,100	1,600
dibenzo(a,h)anthracene	200u	200u	200u	200u	200u	200u
total benzofluoranthenes	1,000	620m	1,300	650m	850m	820m
benzo(g,h,i)perylene	590m	400m	1,100	600m	780m	630m
indeno(1,2,3-cd)pyrene	590m	480m	1,200	600m	730m	630m
Total 2-3 ring PAH*	3,800	1,800	2,300	6,200	2,200	2,100
Total ≥4 ring PAH†	17,000	7,200	23,000	9,500	10,000	8,100
% organic carbon	5.04	3.17	5.50	4.85	5.33	4.80

u = Not detected at detection limit shown.
m = Detected, but less than quantification limit shown.
* = Acenaphthene through fluorene (excluding 2-methylnaphthalene).
† = Chrysene through indeno(1,2,3-cd)perylene.

NOTE: Total PAH calculated using detection and quantification limits.

No tentative identifications were reported for sediment analyses (also, apparently, a function of detection limit; see data in discussion).

Four other organic compounds unrelated to petroleum were detected in sediment, Table 6. Tetrachloroethylene was found in all but one sample with concentrations ranging from 35 to 61 ug/Kg. Phthalates were detected in all samples. Two samples had PCB-1260, but at concentrations too low to quantify.

Table 6. Concentrations of organic priority pollutants (other than polyaromatic hydrocarbons) detected in WDOE samples of City Waterway sediment collected off D Street petroleum storage facilities, April 4, 1984.

Sample Location	Union Dock		Globe Small Boat Dock		Globe Oil Boom	
	CW-1 (nearshore)	CW-2 (offshore)	CW-4 (nearshore)	CW-3 (offshore)	CW-5 (nearshore)	CW-6 (offshore)
Depth at MLLW (feet)	30	32	25	28	25	29
Time sampled	1015	1050	1130	1110	1150	1205
Laboratory sample number	J3447	J3448	J3450	J3449	J3451	J3453
Compound	Concentration (ug/Kg, dry weight)					
tetrachloroethylene	61	5u	53	35	81	37
di-n-butylphthalate	230m	510m	2,700	5,100	2,700	540
bis(2-ethylhexyl)phthalate	2,200	1,100	1,900	2,600	2,800	2,500
PCB-1260	100u	100u	100u	190m	100u	240m

u = Not detected at detection limit shown.
m = Detected, but less than quantification limit shown.

DISCUSSION

The aromatics detected in groundwater during this survey are the same as reported in other field and laboratory investigations on fractionation of petroleum compounds into water (Zurcher, 1978; Boylan, 1971). Their presence is a function of solubility.

The sediment data show that the major groundwater contaminants, benzene and related single-ring compounds, are not being retained in substantial concentrations in City Waterway subtidal sediments near the D Street site. The question of the source of the polycyclic aromatic hydrocarbons (PAH) in these sediments hinges on the relative abundance of substituted (i.e., having attached methyl groups) PAH and their unsubstituted parent compounds. The major source materials for the PAH found in Puget Sound and other marine sediments are combustion products from burning fossil fuels and wood, and uncombusted petroleum products and coal (Barrick, 1982; LaFlamme, 1978; Brown, 1979). The PAH in petroleum and coal have a higher relative abundance of methylnaphthalenes and

methylphenanthrenes than unsubstituted naphthalene or phenanthrene. Combustion products are dominated by unsubstituted PAH of three or more rings (LaFlamme, 1978). The chromatograms in Figure 6 illustrate these two characteristic profiles. Table 7 has two examples from Puget Sound where sediment PAH distributions indicate different degrees of petroleum contamination.

Table 7. Examples of PAH distributions in Puget Sound sediments indicative of petroleum contamination.

Sample Location	Ediz Hook (intertidal)	Blair Waterway (subtidal)
Investigator	Brown (1979); NOAA	Riley (1981); Battelle
Compound	Concentration (ug/Kg, dry weight)	
naphthalene	3.0	2,434
2-methylnaphthalene	5.0	3,443
1-methylnaphthalene	1.6	631
biphenyl	0.74	573
2,6-dimethylnaphthalene	2.4	353
2,3,5-trimethylnaphthalene	1.7	19
fluorene	1.0	94
dibenzothiophene	2.5	86
phenanthrene	7.1	213
anthracene	0.54	82
1-methylphenanthrene	0.56	70
fluoranthene	0.58	36
pyrene	4.1	231
benzo(a)anthracene	0.61	333
chrysene	4.8	72
benzo(e)pyrene	ND	106
benzo(a)pyrene	ND	525
perylene	ND	221

ND = not detected

2-methylnaphthalene, the only substituted target compound in the present survey, was not detectable in the WDOE sediment samples. Tetra Tech, Inc. and NOAA have obtained PAH data, including several substituted PAH, for sediments near the D Street storage facilities. These data, in Tables 8 and 9, show the same predominance of unsubstituted four- and five-ring PAH and low relative concentrations of methylnaphthalenes and methylphenanthrenes seen in the WDOE data. The Tetra Tech data set includes phenols and cresols and indicates a peak for these compounds off the D Street site.

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Table 8. Tetra Tech, Inc. data on aromatic hydrocarbons and phenols in a mid-channel, City Waterway sediment transect off D Street petroleum storage facilities, March 1984.

Sample Location Station Number	N. of 11th St. Bridge CI-19	Off Globe Machine CI-20	Off Union Oil CI-21	Waterway Entrance CI-22
Compound	Concentration (ug/Kg, dry weight)			
acenaphthene	90	130	380	190
naphthalene	830	980	2,400	1,200
2-methylnaphthalene	320	360	890	460
acenaphthylene	140	190	650	330
anthracene	230	330	1,600	960
phenanthrene	510	670	2,700	1,500
fluorene	110	160	600	280
chrysene	490	640	1,500	1,300
pyrene	1,100	900	4,700	260
benzo(a)anthracene	370	500	1,900	1,300
fluoranthene	710	790	2,700	1,500
benzo(a)pyrene	590	670	2,400	1,200
dibenzo(a,h)anthracene	110	67	270	150
total benzofluoranthenes	1,500	690	4,400	2,800
benzo(g,h,i)perylene	290	260	640	380
indeno(1,2,3-cd)pyrene	290	240	670	410
Total 2-3 ring PAH*	1,900	2,500	8,300	4,500
Total ≥4 ring PAH†	5,500	4,800	19,000	12,000
phenol	200	1,200	20	30
2-methylphenol	37	43	35	38
4-methylphenol	240	230	330	150
2,4-dimethylphenol	10u	29	20u	10u
Tentatively Identified Compounds	Estimated Concentration (ug/Kg, dry weight)			
1,1'-biphenyl	120	42	60	
1-methyl-2-(1-methylethyl) benzene		250	32	60
1-methylphenanthrene	130		220	320
2-methylphenanthrene	76	220		180
1-methylpyrene	57	230	210	60
dibenzothiophene	37	110	60	70
retene	180	530		460
percent organic carbon	4.90	4.59	2.82	1.21

u = Not detected at detection limit shown.
* = Acenaphthene through fluorene (excluding 2-methylnaphthalene)
† = Chrysene through indeno(1,2,3-cd)pyrene
Source: Unpublished data provided to WDOE by T. Ginn and R. Barrick, Tetra Tech Inc., Bellevue WA.

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Table 9. NOAA data on aromatic hydrocarbons in sediment at City Waterway station 5-09031 immediately seaward of 11th Street Bridge.

Date	1979	1980	1981
Compound	Concentration (ug/Kg, dry weight)		
biphenyl	490	82	130
acenapthene	710	100	150
naphthalene	4,000	580	980
1-methylnaphthalene	720	120	180
2-methylnaphthalene	1,600	240	360
2,6-dimethylnaphthalene	820	150	210
2,3,5-trimethylnaphthalene	800	140	140
acenaphthalene	310	100	170
anthracene	2,200	140	690
phenanthrene	4,800	330	1,400
fluorene	810	160	290
chrysene	3,800	970	1,600
pyrene	10,000	1,800	3,900
benzo(a)anthracene	4,700	1,700	690
fluoranthene	6,100	1,200	2,200
benzo(a)pyrene	2,600	650	830
dibenzo(a,h)anthracene	NA	NA	NA
benzofluoranthenes	6,600	1,300	2,000
benzo(g,h,i)perylene	NA	NA	NA
indeno(1,2,3-cd)pyrene	1,300	350	260
benzothiophene	230	38	34
dibenzothiophene	220	120	170
percent organic carbon	5.17	3.3	2.9

N/A = Not analyzed.

Source: Malins et al., 1980 and 1982.

Each of three independently collected data sets fail to show substantial input of petroleum to sediment in this part of City Waterway. Most of the petroleum seeping into the waterway from the D Street site probably evaporates -- 75 percent of No. 2 fuel oil hydrocarbons and almost 100 percent of gasoline hydrocarbons are rapidly volatilized (National Academy of Sciences, 1975). Distillate fuels, unlike crude oil, have little tendency to form semi-solid globules (tar balls) which subsequently sink to the bottom and become incorporated in the sediments (National Academy of Sciences, 1975). Lack of direct evidence of fuel oil in subtidal sediments has been observed before in both real and experimental spills (Boehm, et al., 1982; and references therein).

Figure 7† incorporates the Tetra Tech and WDOE data to show the horizontal distribution of PAH in this part of City Waterway. The figure shows both low and high molecular weight PAH increase with proximity to the petroleum storage facilities and indicate that elevated levels of contaminants extend out to the waterway entrance. In Figure 8†, PAH concentrations are normalized to total organic carbon. The fact that the concentration gradients persist indicates the observed distribution is due to a local source and not simply a function of carbon content of the sediment (Barrick, 1984). The TOC normalized data suggest a greater relative degree of contamination in sediments at the entrance to the waterway than in those nearest petroleum seepage from the D Street site.

Possible sources of these compounds include debris from waterfront fires and creosote. Phenols are also constituents of creosote. Urban runoff is a less likely source because all major storm drains are south of the 11th Street bridge.

Table 10 summarizes the data presently available on PAH for all of City Waterway. The waterway entrance and D Street nearshore have the highest concentrations of high molecular weight PAH in the waterway. This area was last dredged in 1948 (Urabeck, 1984).

Table 10. Summary of Tetra Tech and WDOE data on PAH in City Waterway sediments (ppm).

Location of Stations	Head of WW to 11th St. Bridge	11th St. Bridge to mouth of WW	Offshore D Street Petroleum Storage Facilities	Nearshore D Street Petroleum Storage Facilities
Station Numbers	CI 1-18	CI 19-22	CW 1, 4, 5	CW 2, 3, 6
Investigator	Tetra Tech	Tetra Tech	WDOE	WDOE
Number of Samples	7	4	3	3
	Dry Weight Basis			
LMW PAH	4.0(2.7-8.8)	3.5(1.9-8.3)	2.1(1.8-2.3)	3.8(2.2-6.2)
HMW PAH	8.9(4.7-14)	8.7(4.8-19)	8.1(7.2-9.5)	17(10-23)
	TOC Basis			
LMW PAH	44(42-110)	180(39-370)	48(43-56)	75(42-110)
HMW PAH	150(75-220)	400(100-960)	190(170-230)	350(190-410)

median(range)

†Figure prepared by R. Feins, Tetra Tech, Inc.

Memo to Jim Krull
Completion Report on WDOE Project 5 (Part 3) for the Commencement Bay Nearshore/ Tideflats Remedial Investigation: Aromatic Hydrocarbons and Other Organic Compounds in Groundwater Beneath D Street Petroleum Storage Facilities and in Nearby City Waterway Sediments, April 1984

SUMMARY

The major findings of this investigation are as follows:

1. Substantial amounts of oil continue to be present in groundwater beneath the D Street storage facilities.

2. The major groundwater contaminants identified were the single-ring aromatic hydrocarbons benzene, ethylbenzene, toluene, and xylenes. Concentrations of individual compounds in water ranged up to 30 mg/L (toluene).

3. Phenol and several methylphenols (cresols) were also detected in the groundwater at less than 1 mg/L.

4. Adjacent City Waterway subtidal sediment did not contain detectable concentrations of benzene, ethylbenzene, toluene, or xylenes, but did have substantial concentrations of PAH from naphthalene to indeno(1,2,3-cd)-pyrene.

5. The low abundance of methylnaphthalenes and methylphenanthrenes relative to parent compounds and the absence of benzene and related compounds in these sediments indicate that petroleum from the D Street site is not being incorporated into City Waterway sediments in substantial amounts.

6. The predominance of unsubstituted high molecular weight PAH in these sediments indicates that PAH contamination in sediments is probably primarily due to a combustion source.

7. The PAH gradients observed in the surface sediments suggest the source is local and near the waterway entrance. Debris from waterfront fires and creosote are two possible sources.

8. Concentrations of high molecular weight PAH in sediments near the waterway entrance and adjacent to the D Street site are the highest reported in City Waterway.

AD:DN:cp

Attachments

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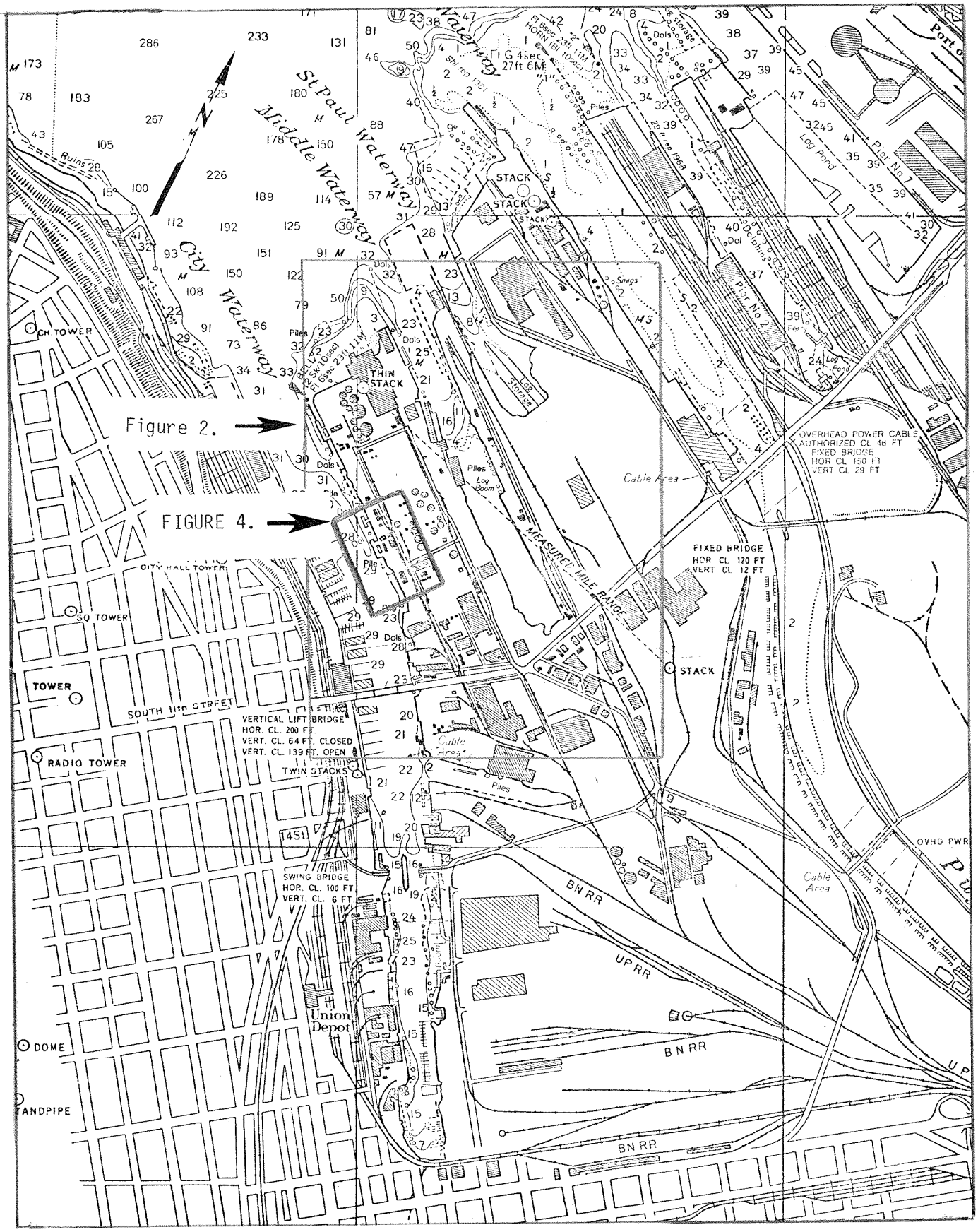


Figure 1. City Waterway showing survey area for WDOE investigation on aromatic hydrocarbons in groundwater beneath D Street petrolcum storage facilities and adjacent sediment, April 1984.

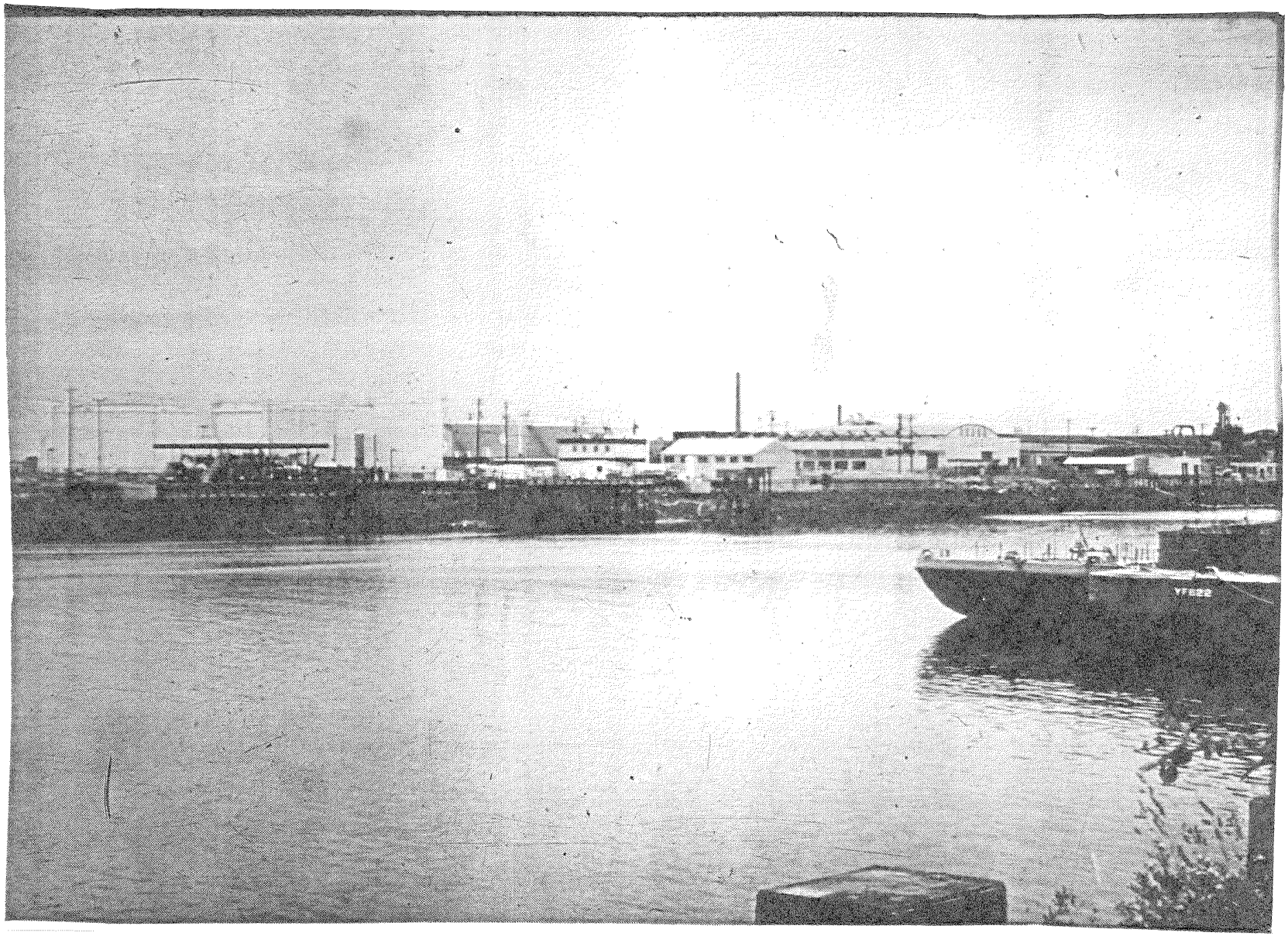


Figure 3. View of D Street petroleum storage facilities from City Waterway.

Figure 4. Sample of petroleum-contaminated groundwater from Well A, April 6, 1984.

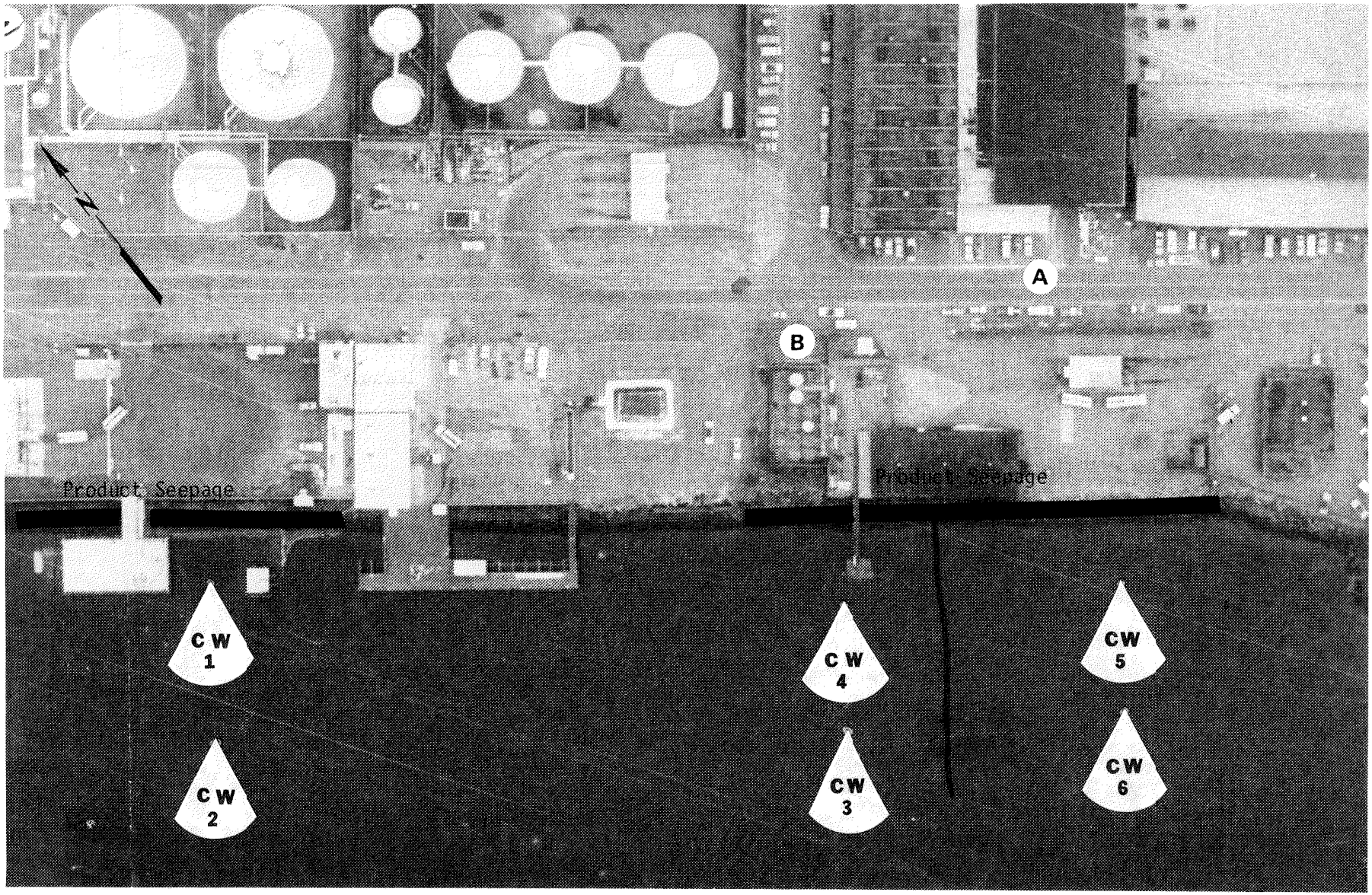
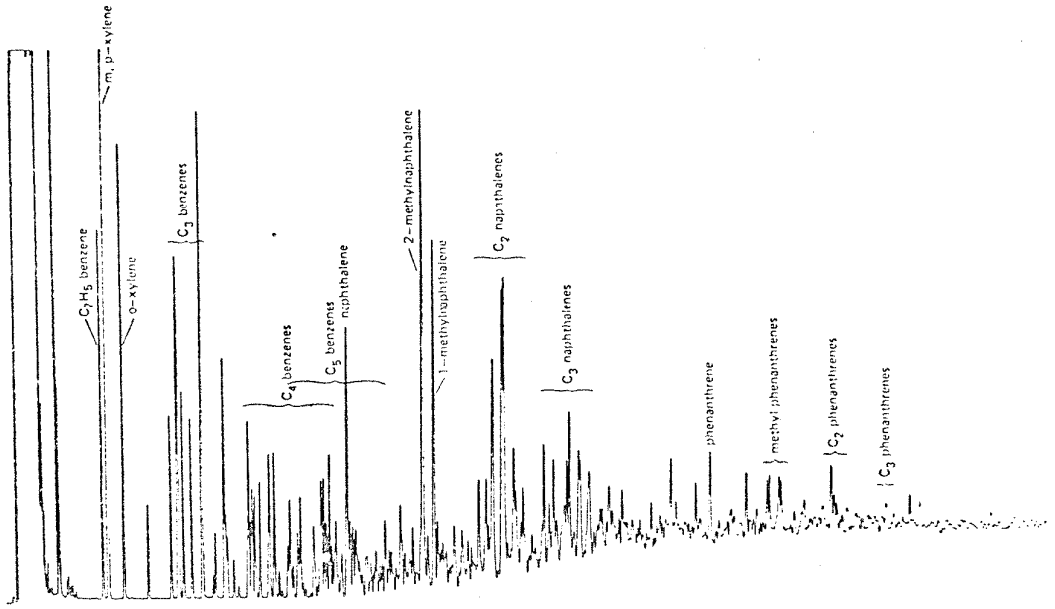


Figure 5. Groundwater (wells A and B) and sediment (CW1-CW6) sample locations for WDOE aromatic hydrocarbon investigation, April 1984.

1. Prudhoe Bay crude.



2. Duwamish River sediment.

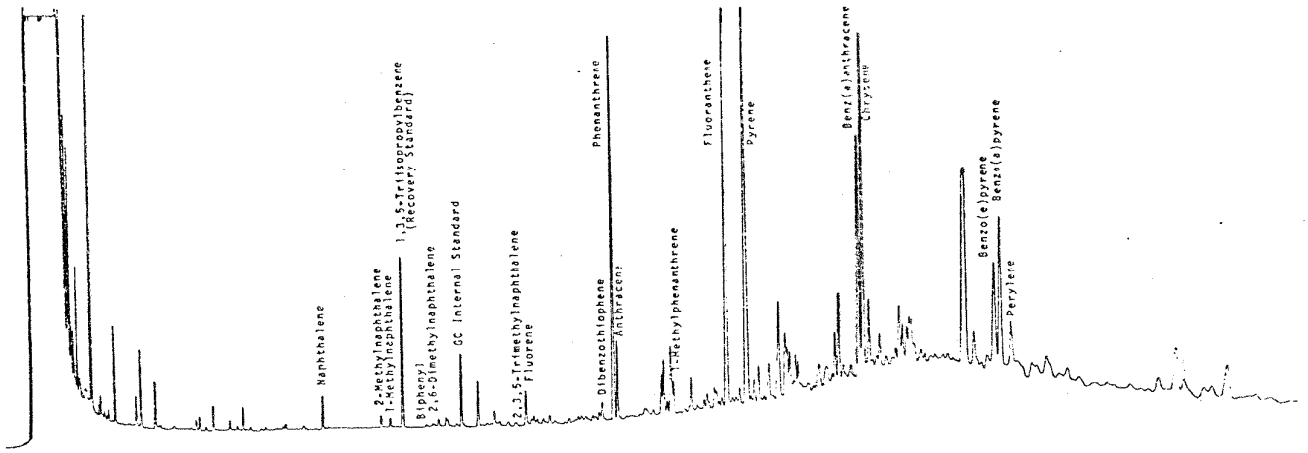


Figure 6. Gas chromatograms of aromatic hydrocarbons representative of petroleum (Prudhoe Bay crude) and combustion of fossil fuels (Duwamish River sediment). From Brown, et al. (1979).

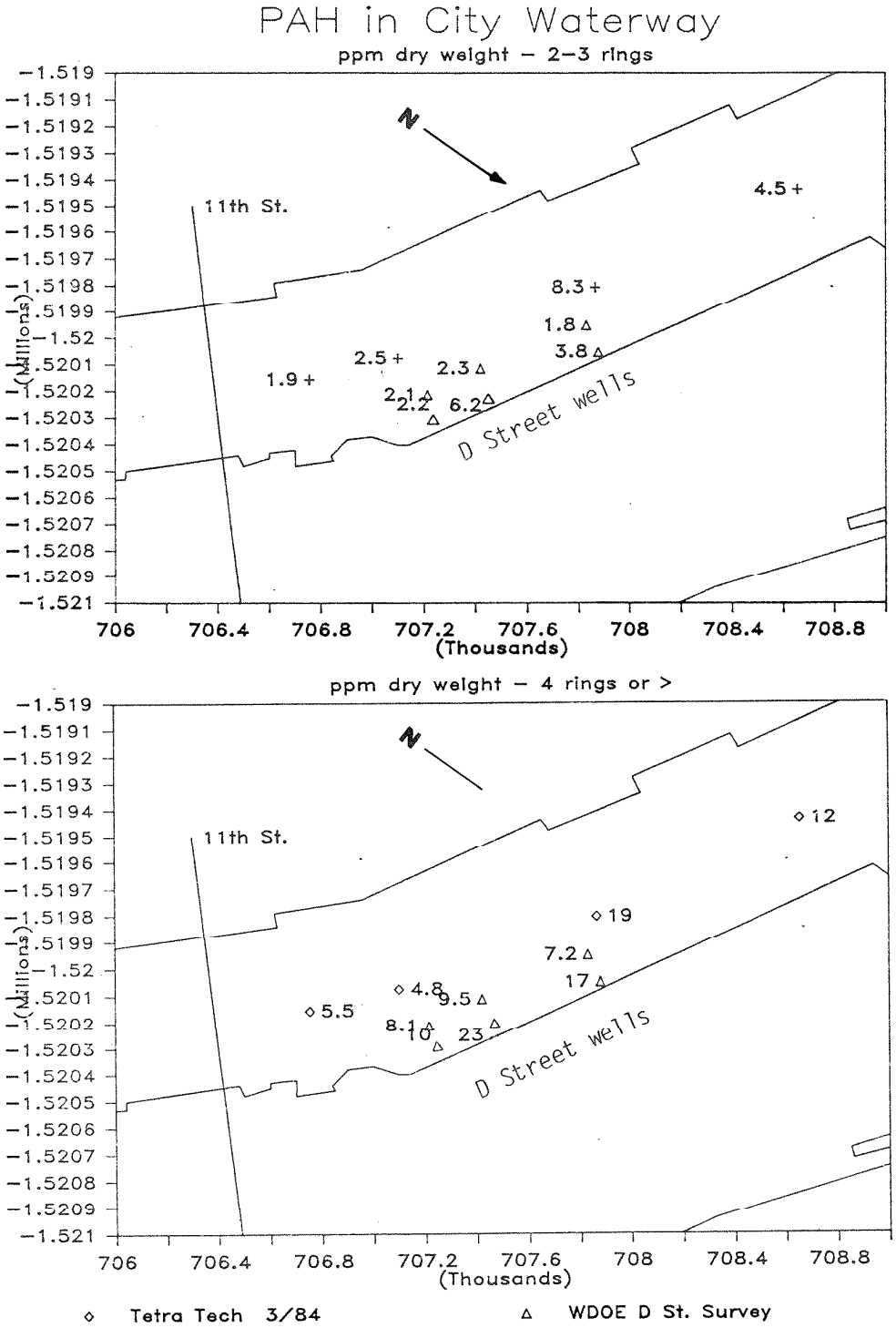


Figure 7. (state plane coordinates).

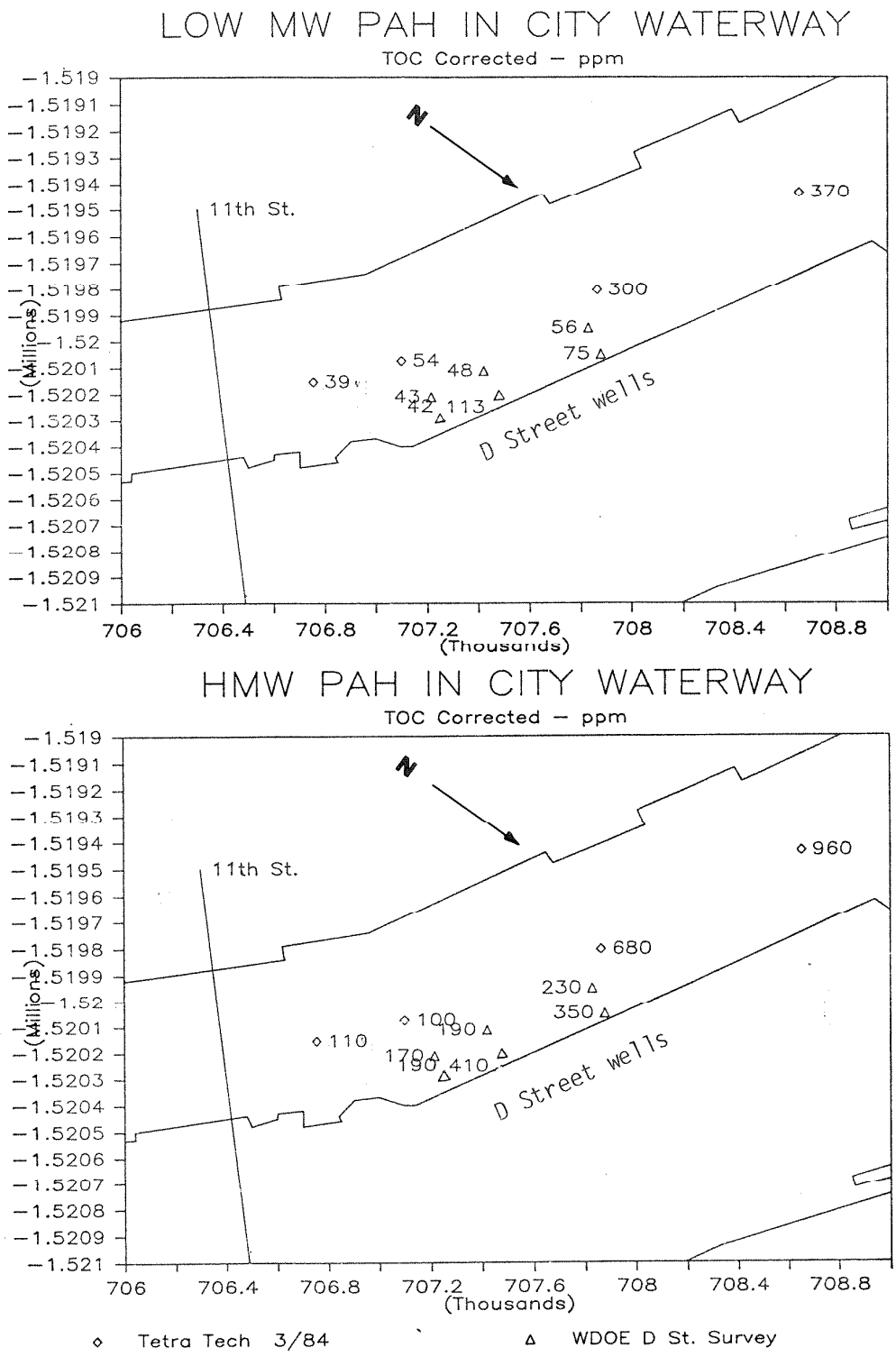


Figure 8 (state plane coordinates).