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POLYCYCLIC AROMATIC HYDROCARBON (PAH) AND DIOXIN/FURAN CONCENTRATIONS IN VANCOUVER HARBOUR SEDIMENTS JANUARY 1991

Data Report: DR91-07A

by

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REVIEW NOTICE

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INTRODUCTION

Goyette and Boyd (1989) reported selected benthic contaminants in Vancouver Harbour excluding polychlorinated dibenzo-para-dioxins and polychlorinated dibenzofurans (i.e. dioxins and furans). Due to fishery closures from dioxin and furan contamination in certain areas (Department of Fisheries and Oceans, 1989), there was a need to measure the levels of these compounds in Vancouver Harbour sediments to supplement the existing database.

The study located sampling sites near potential anthropogenic sources, past and present. Potential sources include anti-sapstain treatment and lumber storage areas, sawmills using chlorophenate treated lumber, ship building and repair operations, combined sewer overflows (CSO), stormwater, and combustion.

Polycyclic aromatic hydrocarbons (PAH) arise from some of the same sources. Sediment PAH levels were measured for relative comparison among sites. Goyette and Boyd (1989) also provides past PAH measures at some sites.

METHODS

Study Area:

The study area included False Creek, Vancouver Harbour between the First and Second narrows (Inner Harbour), Vancouver Harbour between Second Narrows and the Indian Arm/Port Moody Arm junction (Central Harbour), Port Moody Arm, and Indian Arm. Two relatively undisturbed sites in Indian Arm were selected to provide local reference data. Figure 1 locates the 24 sampling stations; Appendix I lists the station depths and coordinates.

Field Collections:

Sediment sampling took place January 23-24, 1991 deploying a ponar grab from a 21 foot motor boat. Taking 3 grabs per site, we collected the top 2 cm from each grab with a heat-treated stainless steel spoon, blended the 3 composites then split in two 125 ml heat-treated jars, one jar for dioxin/furan analysis and one for PAH. Samples were immediately stored on ice in coolers then frozen at -20°C until analyzed.

Laboratory Analysis:

<u>Dioxin and Furans</u> - Samples were analyzed as per Environment Canada Quality Assurance Guidelines (1989) for the following parameters:

TOTAL DIOXIN CONGENERS:		TOTAL FURAN CONGENERS:	
Tetrachlorodibenzodioxins	(T4CDD)	Tetrachlorodibenzofurans	(T4CDF)
Pentachlorodibenzodioxins	(P5CDD)	Pentachlorodibenzofurans	(P5CDF)
Hexachlorodibenzodioxins	(H6CDD)	Hexachlorodibenzofurans	(H6CDF)
Heptachlorodibenzodioxins	(H7CDD)	Heptachlorodibenzofurans	(H7CDF)
Octachlorodibenzodioxins	(O8CDD)	Octachlorodibenzofurans	(O8CDF)

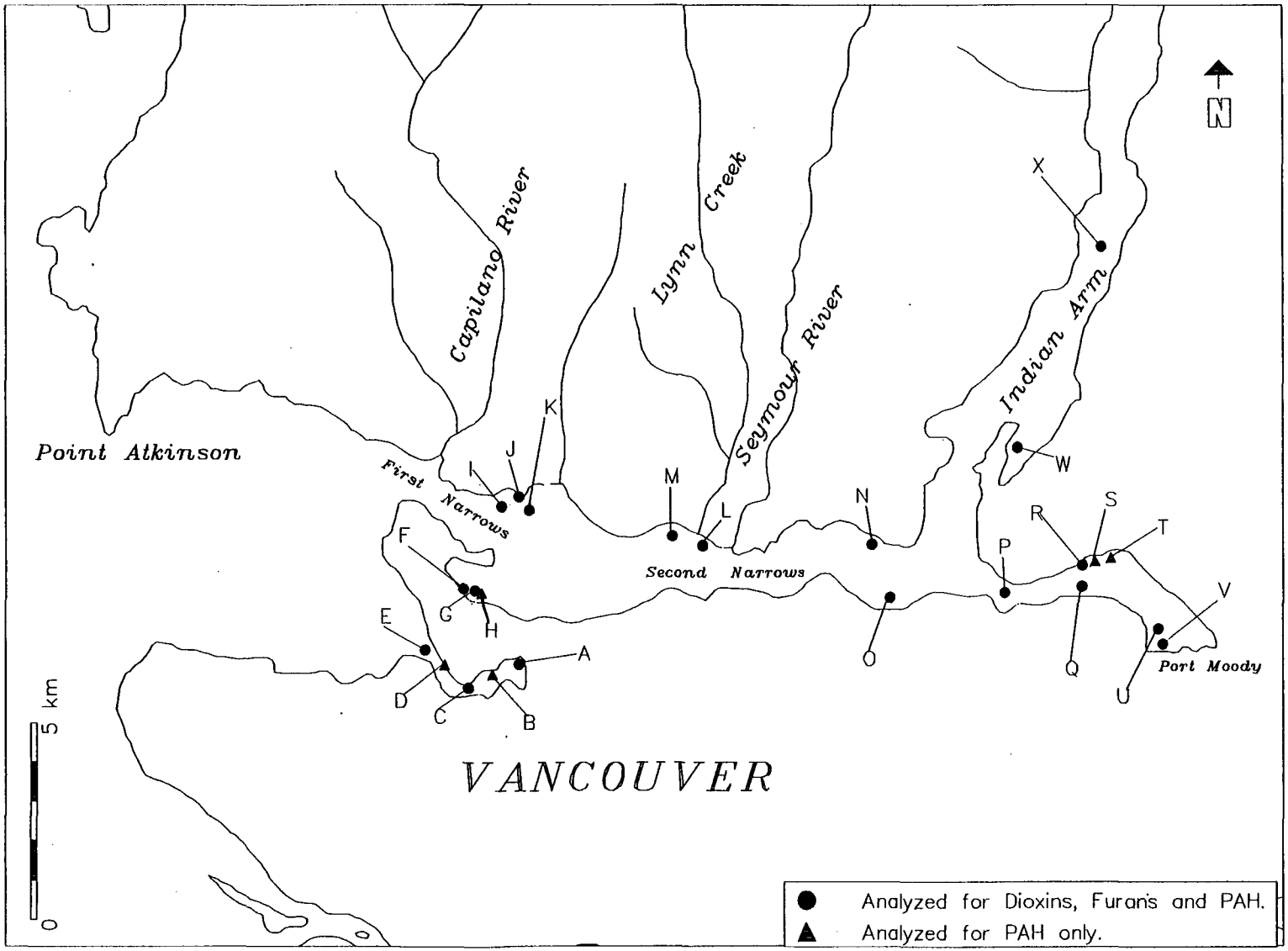

Figure 1 Sediment Sampling Station Locations in Vancouver Harbour - January 1991

Chemical analyses also included the following individual isomers:

DIOXINS	FURANS
2,3,7,8 T4CDD	2,3,7,8 T4CDF
1,2,3,7,8 P5CDD	1,2,3,7,8 P5CDF
1,2,3,4,7,8 H6CDD	2,3,4,7,8 P5CDF
1,2,3,6,7,8 H6CDD	1,2,3,4,7,8 H6CDF
1,2,3,7,8,9 H6CDD	1,2,3,6,7,8 H6CDF
1,2,3,4,6,7,8 H7CDD	2,3,4,6,7,8 H6CDF
	1,2,3,7,8,9 H6CDF
	1,2,3,4,6,7,8 H7CDF
	1,2,3,4,7,8,9 H7CDF

Sample analyses took place in February, 1991 except for Station K which remained frozen at -20°C until analyzed in March 1993 by the same laboratory. Blind splits formed ten percent of the sample submissions for external quality assurance and control (QA/QC). The laboratory duplicated 5 samples for internal QA/QC (Appendix II). Due to limited fundings, stations B, D, H, S, and T were not analyzed for dioxins and furans. The following summarizes the analytical technique (Seakem, 1990).

Samples were spiked with an aliquot of ^{13}C labelled internal standards (tetrachlorodioxin, tetrachlorofuran, pentachlorodioxin, hexachlorodioxin, heptachlorodioxin and octachlorodioxin) to assess instrument performance (Appendix III). The sediment was ground with anhydrous sodium sulfate and extracted in a soxhlet apparatus for 20 hours. The extract was subjected to a series of cleanups (washings with acid and base, column chromatorgraphy on layered silica, alumina, carbon then alumina again) then analyzed by capillary gas chromatography with mass spectrometric detection. Samples were analyzed by high resolution mass spectrometry except stations C, E, N, O, P, and W, run by low resolution mass spectrometry.

Polycyclic Aromatic Hydrocarbons (PAH) - All samples were submitted in early March and analyzed according to Environment Canada Quality Assurance Guidelines (1990). Target compounds included the following:

LOW MOLECULAR WEIGHT	HIGH MOLECULAR WEIGHT
naphthalene	fluoranthene
acenaphthylene	pyrene
acenaphthene	benzo(a)anthracene
fluorene	chyrsene
phenanthrene	benzo(b/k)fluoranthenes
anthracene	benzo(a)pyrene
	indeno(1,2,3-cd)pyrene
	dibenz(ah)anthracene
	benzo(ghi)perylene

In addition to internal QA/QC performed by the laboratory, we submitted 2 blind sample duplicates and a prepared reference standard from the NRCC HS series (4 parts HS-3 to 6 parts HS-4) for external QA/QC (Appendix IV). The analysts provided the following summary of analytical method (Seakem, 1991).

An aliquot of surrogate standard was added to a sediment sample placed in a round-bottom flask. It was refluxed with methanol, potassium hydroxide, and extracted water; the resulting digest was extracted with pentane. The combined pentane layers were washed, dried over anhydrous sodium sulphate, and concentrated in a Kuderna-Danish flask. The extract was loaded onto a silica gel column and eluted with first pentane then dichloromethane. The pentane fraction was discarded. The dichloromethane fraction, which contains the PAH, was concentrated to a small volume and transferred to a microvial.

An aliquot of recovery standard was added prior to analyzing the extract using a 3400 gas chromatograph (GC) with Finnigan Incos 50 mass spectrometer (MS) and a DG 10 Data system. The mass spectrometer was operated in the MID mode to increase sensitivity. The GC retention time and response factors were determined using a mixed calibration standard containing all target and surrogate compounds. Compounds were quantified by intergrated peak area relative to the peak area of the surrogate standard.

A procedural blank and certified reference sediment sample were analyzed with each sample batch. Twenty percent of the samples were duplicated for an internal lab comparison. The following surrogate standards were added to each sample:

napthalene d-8	chrysene d-12
acenaphthene d-10	perylene d-12
phenanthrene d-10	dibenzo(ah)anthracene d-14
pyrene d-10	benzo(ghi)perylene d-12

Recoveries, determined from the recovery standard added just prior to instrumental analysis, provided an overall indication of analysis quality (Appendix V).

Particle Size - This analysis was conducted using the sediment sample remaining from the PAH samples. The analysts employed the pipette method (Black, 1965) to determine particle size distribution using the following sieve sizes and classifications (Wentworth):

<0.063 mm	(-230 mesh)	silt and clay
<0.125 mm	(-120 mesh)	very fine sand
<0.25 mm	(- 60 mesh)	fine sand
<0.50 mm	(- 35 mesh)	medium sand
<1.0 mm	(- 18 mesh)	coarse sand
<2.0 mm	(- 10 mesh)	very coarse sand
>2.0 mm	(+ 10 mesh)	granule

RESULTS

Table 1 lists particle size distribution and median particle sizes for the 24 stations. Silts and clays predominated the sample types.

Tables 2 and 3 report the sediment dioxin and furan levels, respectively for 19 stations in Vancouver Harbour. Refer to Appendix II for comparison of QA/QC duplicates. Generally, both internal and external audits compare favourably

TABLE 1 PERCENT PARTICLE SIZE DISTRIBUTION AND MEDIAN PARTICLE SIZE.

STN	G	VCS	CS	MS	FS	VFS	S&C	Median Particle Size
FALSE CREEK								
A	0	0.6	1.6	4.8	9.6	7.7	75.7	silt and clay
B	0	0.1	0.3	1.0	2.5	4.2	91.9	silt and clay
C	-	-	-	-	-	-	-	silt and clay*
D	18.1	6.8	13.0	20.8	12.5	5.8	23.0	medium sand
E	0	1.0	6.6	17.8	21.0	12.0	41.6	very fine sand
INNER HARBOUR								
F	0	1.4	2.6	5.5	7.6	5.8	77.1	silt and clay
G	8.6	2.9	3.6	4.7	12.3	7.7	60.2	silt and clay
H	0	1.5	2.4	6.4	6.6	7.7	75.4	silt and clay
I	0	0.3	0.5	1.4	5.3	7.0	85.5	silt and clay
J	0	1.8	1.2	2.2	7.0	10.8	77.0	silt and clay
K	11.2	7.6	14.8	28.0	23.0	6.0	9.4	medium sand
L	1.2	3.1	11.2	59.1	22.1	1.1	2.2	medium sand
M	0	2.0	3.7	7.7	20.7	19.6	46.3	very fine sand
CENTRAL HARBOUR								
N	0.7	1.7	3.5	9.6	32.9	26.3	25.3	very fine sand
O	4.5	4.2	7.7	29.4	38.1	9.2	6.9	fine sand
PORT MOODY ARM								
P	0	5.0	trace	trace	trace	trace	95.0	silt and clay
Q	0	0.7	0.8	2.1	3.9	5.3	87.2	silt and clay
R	0	16.9	trace	trace	trace	trace	83.1	silt and clay
S	0	7.3	trace	trace	trace	trace	92.7	silt and clay
T	0.8	4.1	6.7	12.3	20.1	11.1	44.9	very fine sand
U	0	0.2	0.2	0.9	2.8	11.4	84.5	silt and clay
V	0	14.2	trace	trace	trace	trace	85.8	silt and clay
INDIAN ARM								
W	0	2.6	8.6	21.3	31.5	18.6	17.4	fine sand
X	0	2.0	trace	trace	trace	trace	98.0	silt and clay

Legend:			
G	granules	>2.0 mm	(+10 mesh)
VCS	very coarse sand	<2.0 mm	(-10 mesh)
CS	coarse sand	<1.0 mm	(-18 mesh)
MS	medium sand	<0.5 mm	(-35 mesh)
FS	fine sand	<0.25 mm	(-60 mesh)
VFS	very fine sand	<0.125 mm	(-120 mesh)
S&C	silt and clay	<0.063 mm	(-230 mesh)

* not analyzed due to insufficient sample; estimate based on similar field observations for stations A, B, & C.

trace - sample remaining after separating silts and clays was >.5 grams.

TABLE 2. POLYCHLORINATED DIBENZO-PARA-DIOXIN (PCDD) CONCENTRATIONS (pg/g dry weight) MEASURED IN THE SURFACE SEDIMENTS FROM VANCOUVER HARBOUR - JANUARY 1991.

	POLYCHLORINATED DIBENZO-PARA-DIOXINS (PCDD) (Concentrations in pg/g dry weight)										
AREA	TETRA		PENTA		HEXA				HEPTA		OCTA
STATION	2378 T4CDD	TOTAL T4CDD	12378 P5CDD	TOTAL P5CDD	123478 H6CDD	123678 H6CDD	123789 H6CDD	TOTAL H6CDD	1234678 H7CDD	TOTAL H7CDD	TOTAL O8CDD
FALSE CREEK											
A*	2.1 (0.1)	62 (0.1)	9.6 (0.1)	96 (0.1)	23 (0.3)	250 (0.3)	46 (0.3)	1300 (0.3)	1600 (0.4)	3800 (0.4)	8800 (0.6)
C	ND (1.5)	110 (1.5)	7.6 (2.3)	190 (2.3)	7.0 (2.4)	170 (2.4)	25 (2.4)	980 (2.4)	1000 (2.9)	2100 (2.9)	5200 (4.5)
E	ND (1.0)	3.7 (1.0)	ND (1.6)	ND (1.6)	ND (2.9)	18 (2.9)	ND (2.9)	120 (2.9)	140 (3.1)	300 (3.1)	710 (4.5)
INNER HARBOUR											
F*	82 (0.3)	880 (0.3)	620.0 (0.3)	3000 (0.3)	660 (0.8)	1600 (0.8)	1700 (0.8)	11000 (0.8)	15000 (0.8)	31000 (0.8)	110000 (97)
G*	NDR (0.1)	26 (0.1)	5.7 (0.1)	52 (0.1)	7.2 (0.2)	50 (0.2)	17 (0.2)	350 (0.2)	440 (0.4)	980 (0.4)	2500 (0.5)
I*	NDR (0.1)	15 (0.1)	4.4 (0.2)	34 (0.2)	8.2 (0.4)	85 (0.4)	17 (0.4)	410 (0.4)	670 (0.6)	1300 (0.6)	3400 (0.9)
J*	0.9 (0.1)	11 (0.1)	27.0 (0.2)	250 (0.2)	3.6 (0.5)	30 (0.5)	12 (0.5)	230 (0.5)	460 (0.8)	1200 (0.8)	2500 (1.1)
K*	0.1 (0.1)	1.5 (0.1)	0.4 (0.1)	2.3 (0.1)	0.6 (0.1)	3.7 (0.1)	0.9 (0.1)	22 (0.1)	31 (0.2)	62 (0.2)	180 (0.1)
L*	ND (0.2)	ND (0.2)	ND (0.2)	ND (0.2)	0.6 (0.3)	8.1 (0.3)	1.5 (0.3)	22 (0.3)	57 (0.2)	74 (0.2)	61 (0.2)
M*	NDR (0.1)	9.8 (0.1)	8.3 (0.1)	47 (0.1)	10 (0.3)	140 (0.3)	30 (0.3)	560 (0.3)	1300 (0.4)	2200 (0.4)	4900 (0.5)
CENTRAL HARB.											
N	ND (0.7)	2.9 (0.7)	ND (1.1)	ND (1.1)	ND (1.7)	12 (1.7)	3.3 (1.7)	59 (1.7)	110 (2.0)	220 (2.0)	650 (2.1)
O	ND (0.6)	ND (0.6)	ND (0.9)	ND (0.9)	ND (1.4)	4.4 (1.4)	ND (1.4)	27 (1.4)	60 (1.4)	170 (1.4)	350 (1.5)
PORT MOODY ARM											
P	ND (2.0)	12 (2.0)	ND (4.4)	12 (4.4)	ND (4.3)	74 (4.3)	18 (4.3)	380 (4.3)	540 (3.9)	990 (3.9)	2700 (3.9)
Q*	1.9 (0.1)	35 (0.1)	6.0 (0.3)	60 (0.3)	5.4 (0.5)	78 (0.5)	26 (0.5)	520 (0.5)	1000 (0.8)	2200 (0.8)	5900 (0.9)
R*	2.6 (0.1)	66 (0.1)	8.9 (0.2)	110 (0.2)	11 (0.3)	120 (0.3)	44 (0.3)	820 (0.3)	2200 (0.4)	5000 (0.4)	13000 (0.5)
U*	1.4 (0.2)	41 (0.2)	7.8 (0.3)	80 (0.3)	12 (0.7)	110 (0.7)	34 (0.7)	580 (0.7)	1300 (0.8)	2500 (0.8)	9000 (0.9)
V*	3.8 (0.2)	430 (0.2)	5.9 (0.2)	290 (0.2)	11 (0.2)	51 (0.2)	26 (0.2)	420 (0.2)	860 (0.4)	1700 (0.4)	5500 (0.3)
INDIAN ARM											
W	ND (1.0)	ND (1.0)	ND (1.7)	ND (1.7)	ND (2.4)	7.4 (2.4)	ND (2.4)	42 (2.4)	66 (4.6)	120 (4.6)	380 (4.1)
X*	1.2 (0.1)	19 (0.1)	6.0 (0.1)	54 (0.1)	5.4 (0.1)	100 (0.1)	25 (0.1)	590 (0.1)	610 (0.1)	1100 (0.1)	3000 (0.3)

ND - Not detected at the sample detection level, specified in brackets.

NDR - Peak detected at the right time but did not meet verification criteria therefore compound could not be confirmed.

* Samples analyzed by High Resolution Mass Spectrometry (HRMS); remaining samples were analyzed by Low Resolution Mass Spectrometry.

TABLE 3. POLYCHLORINATED DIBENZOFURAN (PCDF) CONCENTRATIONS (pg/g dry weight) MEASURED IN THE SURFACE SEDIMENTS FROM VANCOUVER HARBOUR - JANUARY 1991.

	POLYCHLORINATED DIBENZOFURANS (PCDF) (Concentrations in pg/g dry weight)														
AREA	TETRA		PENTA			HEXA					HEPTA			OCTA
STATION	2378 T4CDF	TOTAL T4CDF	12378 P5CDF	23478 P5CDF	TOTAL P5CDF	123478 H6CDF	123678 H6CDF	234678 H6CDF	123789 H6CDF	TOTAL H6CDF	1234678 H7CDF	1234789 H7CDF	TOTAL H7CDF	TOTAL O8CDF
FALSE CREEK														
A*	16 (0.1)	84 (0.1)	ND (0.1)	8.4 (0.1)	330 (0.1)	56 (0.2)	45 (0.2)	34 (0.2)	ND (0.2)	2500 (0.2)	1300 (0.3)	39 (0.3)	3600 (0.3)	1100 (0.4)
C	21 (1.0)	88 (1.0)	8.1 (1.4)	5.0 (1.4)	260 (1.4)	28 (1.8)	23 (1.8)	20 (1.8)	ND (1.8)	1400 (1.8)	1100 (2.0)	20 (2.0)	2600 (2.0)	830 (4.2)
E	6.8(0.7)	11 (0.7)	ND (1.0)	ND (1.0)	36 (1.0)	ND (2.7)	ND (2.7)	ND (2.7)	ND (2.7)	160 (2.7)	140 (2.5)	ND (2.5)	320 (2.5)	100 (4.2)
INNER HARBOUR														
F*	200 (0.1)	1300 (0.1)	46 (0.2)	56 (0.2)	1500 (0.2)	270 (0.6)	170 (0.6)	82 (0.6)	ND (0.6)	4100 (0.6)	2900 (0.7)	120 (0.7)	9800 (0.7)	9500 (0.9)
G*	16 (0.1)	60 (0.1)	2.6 (0.1)	3.6 (0.1)	95 (0.1)	11 (0.1)	7.6(0.1)	5.4(0.1)	ND (0.1)	330 (0.1)	200 (0.2)	6.5(0.2)	580 (0.2)	330 (0.4)
I*	16 (0.1)	64 (0.1)	2.1 (0.1)	4.2 (0.1)	170 (0.1)	17 (0.3)	12 (0.3)	8.4(0.3)	ND (0.3)	940 (0.3)	550 (0.5)	18 (0.5)	1600 (0.5)	590 (0.7)
J*	8.2(0.1)	35 (0.1)	15 (0.9)	ND (0.9)	590 (0.9)	7.0(0.3)	5.3(0.3)	4.5(0.3)	0.8(0.3)	230 (0.3)	160 (0.3)	4.3(0.3)	420 (0.3)	240 (0.5)
K*	2.0(0.2)	7.3(0.2)	0.3 (0.1)	0.4 (0.1)	8.4 (0.1)	1.1(0.1)	0.7(0.1)	0.6(0.1)	ND (0.1)	31 (0.1)	22 (0.3)	NDR(0.3)	58 (0.3)	25 (0.3)
L*	ND (0.2)	1.7(0.2)	ND (0.2)	ND (0.2)	10 (0.2)	1.5(0.2)	1.9(0.2)	1.8(0.2)	ND (0.2)	64 (0.2)	41 (0.2)	1.3(0.2)	93 (0.2)	ND (0.2)
M*	11 (0.1)	79 (0.1)	6.4 (0.1)	6.4 (0.1)	520 (0.1)	31 (0.2)	38 (0.2)	31 (0.2)	ND (0.2)	2100 (0.2)	1200 (0.4)	35 (3.4)	3200 (0.4)	1200 (0.4)
CENTRE HARB.														
N	4.0(0.6)	4.8(0.6)	ND (1.5)	ND (1.5)	17 (1.5)	ND (3.1)	ND (3.1)	ND (3.1)	ND (3.1)	70 (3.1)	63 (1.5)	ND (1.5)	160 (1.5)	90 (3.3)
O	1.5(0.5)	1.5(0.5)	ND (0.4)	ND (0.4)	5.9 (4.4)	ND (0.8)	ND (0.8)	ND (0.8)	ND (0.8)	22 (0.8)	19 (1.0)	ND (1.0)	48 (1.0)	23 (1.4)
PORT MOODY ARM														
P	14 (1.0)	41 (1.0)	ND (4.4)	ND (4.4)	110 (4.4)	16 (2.2)	11 (2.2)	4.6(2.2)	ND (2.2)	480 (2.2)	320 (2.5)	7.4(2.5)	830 (2.5)	310 (3.5)
Q *	18 (0.1)	76 (0.1)	3.0 (0.2)	4.8 (0.2)	130 (0.2)	19 (0.4)	9.5(0.4)	9.5(0.4)	ND (0.4)	510 (0.4)	340 (0.7)	9.3(0.7)	890 (0.7)	320 (0.8)
R *	15 (0.1)	84 (0.1)	4.8 (0.1)	6.7 (0.1)	180 (0.1)	28 (0.3)	13 (0.3)	12 (0.3)	ND (0.3)	720 (0.3)	380 (0.3)	12 (0.3)	1100 (0.3)	480 (0.5)
U *	11 (0.1)	95 (0.1)	5.6 (0.2)	ND (0.2)	300 (0.2)	29 (0.5)	16 (0.5)	13 (0.5)	ND (0.5)	810 (0.5)	320 (0.4)	8.7(0.4)	830 (0.4)	290 (0.5)
V *	35 (0.1)	230 (0.1)	6.7 (0.1)	6.5 (0.1)	170 (0.1)	18 (0.1)	7.6(0.1)	6.7(0.1)	ND (0.1)	350 (0.1)	180 (0.2)	NDR(0.2)	490 (0.2)	170 (0.3)
INDIAN ARM														
W	2.1(0.9)	2.1(0.9)	ND (0.8)	ND (0.8)	6.7 (0.8)	ND (1.6)	ND (1.6)	ND (1.6)	ND (1.6)	46 (1.6)	42 (2.7)	ND (2.7)	110 (2.7)	52 (5.1)
X*	22 (0.1)	64 (0.1)	5.1 (0.1)	4.4 (0.1)	130 (0.1)	18 (0.1)	12 (0.1)	11 (0.1)	ND (0.1)	640 (0.1)	490 (0.1)	ND (0.1)	1200 (0.1)	400 (0.3)

ND - Not detected at the sample detection level, specified in brackets.

NDR - Peak detected at the right time but did not meet verification criteria therefore compound could not be confirmed.

* Samples analyzed by High Resolution Mass Spectrometry (HRMS); remaining samples were analyzed by Low Resolution Mass Spectrometry.

with the exception of the external blind audit for Station C in the lower congeners. A rerun of the sample could not resolve the differences. Appendix III reports the surrogate standard recoveries for each sample. Mean surrogate recoveries ranged from 76-89%.

Table 4 reports the sediment PAH concentrations all 24 stations (Figure 1). Refer to Appendix IV for the results of QA/QC samples. Both internal and external audit samples show good comparison. Appendix V reports the surrogate standard recoveries for each sample.

DISCUSSION

Generally, the largest concentrations of dioxins were the highest congeners (i.e. T4CDD<P5CDD<H6CDD<H7CDD<O8CDD) (Table 2). The furans exhibited a similar increasing pattern except for the O8CDF. Total H7CDF and most total H6CDF levels exceeded total O8CDF (i.e. T4CDD<P5CDD<H6CDD<H7CDD>O8CDD) (Table 3).

Station F had the highest dioxin and furan concentrations and exceeded the other stations by about an order of magnitude (Tables 2 and 3). It also ranked highest for total PAH (117.38 μg/g) (Table 4). This site is situated near a decommissioned shipbuilding and repair facility.

Station A, located at the east end of False Creek, ranked second for total PAH levels (80.18 μg/g) as well as total H6CDD and the higher congener furans. In the past, this area supported much more industrial activity including coal gasification plants, sawmills, shingle mills and wood preservating operations.

Station R, located in Port Moody Arm had the second highest H7CDD and O8CDD levels (Table 2). Poor water circulation in the Arm, about 30% water exchange during each tidal cycle (Waldichuk, 1965), results in accumulated sediments.

Station V, also located in Port Moody Arm at the east end, had relatively high PAH levels where reported (Table 4). Note that interferences in the sample during the analyses prevented adequate recovery of the higher molecular weight PAH compounds therefore sample totals were underestimated. The T4CDD levels at this station were high by comparison (430 μg/g) but the other congeners were in the mid ranges similar to, for example, stations C, Q and U.

Finer particles tend to concentrate contaminants more easily than coarser particles due to a larger surface area (McLaren and Little 1987). The stations noted above all contained mainly silts and clays as did most of the samples (Table 1). Stations D, E, K, L, M, N, O, T & W contained coarser sediments, and tended to have lower concentrations of dioxins, furans and PAH (Tables 1-4). Station M was an exception. Its median particle size was very fine sand but it contained the most silt and clay (46.3%) of these 9 stations. In addition, a number of chemicals measured exceeded levels reported for stations that were predominantly silt and clay.

Dioxin and furan levels in one of the reference samples (Station X) exceeded expected values. This area could be influenced by sediments transported from outside sources or atmospheric deposition.

TABLE 4 POLYCYCLIC AROMATIC HYDROCARBON (PAH) CONCENTRATIONS (μg/g dry weight) MEASURED IN SURFACE SEDIMENTS FROM VANCOUVER HARBOUR - JANUARY 1991.

	LOW MOLECULAR WEIGHT PAH						HIGH MOLECULAR WEIGHT PAH											
AREA STATION	Naph tha lene	Ace naph thylene	Ace naph thene	Fluo rene	Phen anth rene	An thra cene	Fluor anth ene	Py rene	Benzo(a) anthra cene	Chry sene	Benzo(b) (k)fluo rene	Benzo (a) pyrene	Indeno (123-cd) pyrene	Dibenz (ah) anthr.	Benzo (ghi) peryl.	TOTAL LMW PAH	TOTAL HMW PAH	TOTAL PAH
FALSE CREEK																		
A	5.40	0.92	0.91	2.00	6.20	3.30	12.00	14.00	5.30	7.10	9.80	6.20	3.80	0.35	2.90	18.73	61.45	80.18
B	0.48	0.11	0.14	0.22	0.82	0.52	1.20	1.60	0.98	1.30	1.70	1.10	0.93	(0.17)*	0.77	2.29	9.58	11.87
C	0.73	0.24	0.24	0.34	0.99	0.63	1.20	1.50	0.64	0.86	1.30	0.80	0.77	0.11	0.62	3.17	7.80	10.97
D	0.11	0.04	0.03	0.10	0.45	(0.44)*	0.51	0.55	0.26	0.36	0.30	0.20	0.12	0.02	0.09	0.73	2.41	3.14
E	0.87	0.28	0.15	0.21	0.89	0.33	0.90	1.50	0.32	0.49	0.57	0.32	0.20	(0.044)*	0.20	2.73	4.50	7.23
INNER HARBOUR																		
F	1.30	0.70	3.10	3.50	9.50	3.70	23.00	18.00	7.70	13.00	15.00	7.00	6.50	0.58	4.80	21.80	95.58	117.38
G	0.30	0.09	0.20	0.32	1.50	0.49	2.30	2.80	0.77	1.40	1.90	0.84	0.65	0.12	0.51	2.90	11.29	14.19
H	0.17	0.06	0.11	0.19	0.84	0.43	2.50	2.50	0.73	1.50	1.30	0.60	0.50	(0.086)*	0.35	1.80	9.98	11.78
I	0.15	0.03	0.13	0.21	0.83	0.38	1.90	1.50	0.59	1.00	1.20	0.50	0.36	(0.071)*	0.29	1.73	7.34	9.07
J	1.30	0.05	1.60	1.60	9.10	2.20	11.00	8.60	3.60	5.40	6.40	3.00	2.20	0.40	1.50	15.85	42.10	57.95
K	0.05	0.004	0.02	0.03	0.16	0.05	0.22	0.22	0.13	0.17	0.20	0.10	0.07	0.01	0.05	0.31	1.17	1.48
L	0.02	(0.003)*	0.01	0.01	0.06	0.01	0.09	0.07	0.03	0.04	0.07	0.04	0.03	0.005	0.03	0.11	0.41	0.52
M	0.55	(0.010)*	0.19	0.44	1.30	0.54	2.60	2.30	1.00	1.40	1.60	0.66	0.38	0.08	0.35	3.02	10.37	13.39
CENTRAL HARB.																		
N	0.22	0.03	0.25	0.32	1.20	0.36	1.50	1.40	0.67	0.89	1.10	0.60	0.47	0.11	0.37	2.38	7.11	9.49
O	0.04	0.01	0.06	0.07	0.22	0.09	0.63	0.72	0.20	0.23	0.27	0.12	0.05	0.01	0.05	0.49	2.28	2.77
PORT MOODY ARM																		
P	0.20	0.07	0.06	0.10	0.40	0.15	0.57	0.64	0.26	0.44	0.66	0.31	0.27	0.05	0.29	0.98	3.49	4.47
Q	0.29	0.08	0.10	0.22	0.70	0.35	1.10	1.60	0.70	1.20	1.50	0.64	0.40	0.10	0.41	1.74	7.65	9.39
R	0.54	0.16	0.12	0.30	0.99	0.57	1.90	2.40	1.00	1.80	1.90	0.90	0.62	0.14	0.63	2.68	11.29	13.97
S	0.46	0.16	0.24	0.43	0.99	0.88	5.60	5.20	1.60	2.30	3.00	1.30	0.74	0.22	0.68	3.16	20.64	23.80
T	0.25	0.08	0.03	0.07	0.32	0.13	0.45	0.73	0.18	0.39	0.49	0.26	0.18	0.05	0.28	0.88	3.01	3.89
U	0.32	0.08	0.05	0.07	0.52	0.07	0.77	0.75	0.21	0.42	0.58	0.26	0.22	0.04	0.26	1.11	3.51	4.62
V**	16.00	3.70	1.00	0.64	6.80	0.41	7.70	(4.6)*	(.29)*	(.38)*	(.48)*	ND(.13)	NA	NA	NA	28.55	>7.70	>36.25
INDIAN ARM																		
W	0.02	0.01	0.002	ND(.01)	.03	0.01	0.05	0.06	0.02	0.03	0.06	0.02	0.02	(0.007)*	0.02	0.07	0.28	0.35
X	0.15	0.02	(.028)*	0.06	0.27	0.08	0.41	0.45	0.17	0.34	0.46	0.24	0.18	0.03	0.22	0.58	2.50	3.08

ND - Not detected (detection limit in brackets) NA - Not able to recover and analyze compound in the sample (interferences).

*Peak detected at right time but did not meet verification criteria, could not confirm compound. Quantity in brackets, not added in totals.

**This sample was reanalyzed several times. Although results were consistent, the surrogate recoveries for most compounds are low and lab was unable to quantitate all species due to the presence of interferring compounds.

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APPENDIX I - SAMPLING STATION DEPTHS AND COORDINATES.

AREA	STATION	DEPTH (metres)	LATITUDE	LONDGITUDE
False Creek	A	6	49°16.53'N	123°06.19'W
	B	8	49°16.32'N	123°06.94'W
	C	5	49°16.19'N	123°07.45'W
	D	8	49°16.45'N	123°08.05'W
	E	7	49°16.66'N	123°08.30'W
Inner Harbour	F	7	49°17.50'N	123°07.62'W
	G	9	49°17.48'N	123°07.36'W
	H	10	49°17.44'N	123°07.20'W
	I	13	49°18.73'N	123°06.62'W
	J	9	49°18.77'N	123°06.32'W
	K	15	49.18.61'N	123°06.08'W
	L	17	49°17.89'N	123°02.25'W
	L	13	49°17.91'N	123°02.32'W
	L	18	49°17.88'N	123°02.19'W
	M	11	49°18.23'N	123°02.75'W
Central Harbour	N	6	49°18.15'N	122°57.75'W
	O	12	49°17.37'N	122°57.68'W
Port Moody Arm	P	29	49°17.50'N	122°54.66'W
	Q	13	49°17.52'N	122°53.22'W
	R	10	49°18.00'N	122°53.02'W
	S	15	49°17.97'N	122°52.88'W
	T	7	49°17.95'N	122°52.70'W
	U	2	49°16.94'N	122°51.44'W
	V	5	49°16.92'N	122°51.20'W
Indian Arm	W	31	49°19.43'N	122°54.70'W
	X	205	49°22.20'N	122°52.75'W

APPENDIX II - RESULTS OF INTERNAL LABORATORY AND EXTERNAL BLIND AUDITS FOR DIOXIN AND FURAN ANALYSES

POLYCHLORINATED DIBENZO-PARA-DIOXIN (PCDD) - Concentrations in pg/g dry weight

STATION	TETRA		PENTA		HEXA				HEPTA		OCTA
	2378 T4CDD	TOTAL T4CDD	12378 P5CDD	TOTAL P5CDD	123478 H6CDD	123678 H6CDD	123789 H6CDD	TOTAL H6CDD	1234678 H7CDD	TOTAL H7CDD	TOTAL O8CDD
INTERNAL LABORATORY AUDITS											
A*	2.1 (0.1)	62 (0.1)	9.6 (0.1)	96 (0.1)	23 (0.3)	250 (0.3)	46 (0.3)	1300 (0.3)	1600 (0.4)	3800 (0.4)	8800 (0.6)
A*	2.2 (0.1)	55 (0.1)	13 (0.1)	130 (0.1)	21 (0.2)	220 (0.2)	36 (0.2)	1200 (0.2)	1800 (0.3)	3900 (0.3)	9300 (0.4)
V*	3.8 (0.2)	430 (0.2)	5.9 (0.2)	290 (0.2)	11 (0.2)	51 (0.2)	26 (0.2)	420 (0.2)	860 (0.4)	1700 (0.4)	5500 (0.3)
V*	3.2 (0.2)	370 (0.2)	6.3 (0.2)	210 (0.2)	9.1 (0.3)	59 (0.3)	22 (0.3)	490 (0.3)	790 (0.4)	1600 (0.4)	5400 (0.4)
W	ND (1.0)	ND (1.0)	ND (1.7)	ND (1.7)	ND (2.4)	7.4 (2.4)	ND (2.4)	42 (2.4)	66 (4.6)	120 (4.6)	380 (4.1)
W	ND (1.1)	ND (1.1)	ND (1.7)	ND (1.7)	ND (2.7)	6.1 (2.7)	ND (2.7)	34 (2.7)	66 (5.6)	120 (5.6)	400 (4.8)
EXTERNAL BLIND AUDITS											
C	ND (1.5)	110 (1.5)	7.6 (2.3)	190 (2.3)	7.0 (2.4)	170 (2.4)	25 (2.4)	980 (2.4)	1000 (2.9)	2100 (2.9)	5200 (4.5)
C	NDR (1.2)	10 (1.2)	NDR (1.7)	34 (1.7)	8.8 (1.9)	150 (1.9)	23 (1.9)	700 (1.9)	930 (2.3)	1900 (2.3)	4300 (3.3)
G*	NDR (0.1)	26 (0.1)	5.7 (0.1)	52 (0.1)	7.2 (0.2)	50 (0.2)	17 (0.2)	350 (0.2)	440 (0.4)	980 (0.4)	2500 (0.5)
G*	NDR (0.1)	20 (0.1)	5.2 (0.1)	42 (0.1)	5.0 (0.2)	45 (0.2)	15 (0.2)	300 (0.2)	410 (0.3)	910 (0.3)	2200 (0.3)

POLYCHLORINATED DIBENZOFURAN (PCDF) - Concentrations in pg/g dry weight

STATION	TETRA		PENTA			HEXA					HEPTA			OCTA
	2378 T4CDF	TOTAL T4CDF	12378 P5CDF	23478 P5CDF	TOTAL P5CDF	123478 H6CDF	123678 H6CDF	234678 H6CDF	123789 H6CDF	TOTAL H6CDF	1234678 H7CDF	1234789 H7CDF	TOTAL H7CDF	TOTAL O8CDF
INTERNAL LABORATORY AUDITS														
A*	16 (0.1)	84 (0.1)	ND (0.1)	8.4 (0.1)	330 (0.1)	56 (0.2)	45 (0.2)	34 (0.2)	ND (0.2)	2500 (0.2)	1300 (0.3)	39 (0.3)	3600 (0.3)	1100 (0.4)
A*	18 (0.1)	120 (0.1)	ND (0.1)	11 (0.1)	470 (0.1)	43 (0.2)	35 (0.2)	31 (0.2)	ND (0.2)	2200 (0.2)	1400 (0.3)	42 (0.3)	3900 (0.3)	1200 (0.3)
V*	35 (0.1)	230 (0.1)	6.7 (0.1)	6.5 (0.1)	170 (0.1)	18 (0.1)	7.6(0.1)	6.7(0.1)	ND (0.1)	350 (0.1)	180 (0.2)	NDR(0.2)	490 (0.2)	170 (0.3)
V*	37 (0.5)	250 (0.5)	8.4 (0.1)	5.8 (0.1)	160 (0.1)	20 (0.2)	8.4(0.2)	6.0(0.2)	ND (0.2)	360 (0.2)	170 (0.2)	ND (0.2)	430 (0.2)	180 (0.4)
W	2.1(0.9)	2.1(0.9)	ND (0.8)	ND (0.8)	6.7 (0.8)	ND (1.6)	ND (1.6)	ND (1.6)	ND (1.6)	46 (1.6)	42 (2.7)	ND (2.7)	110 (2.7)	52 (5.1)
W	2.5(0.9)	2.5(0.9)	ND (0.8)	ND (0.8)	7.6 (0.8)	ND (1.6)	ND (1.6)	ND (1.6)	ND (1.6)	41 (1.6)	48 (3.2)	ND (3.2)	110 (3.2)	47 (4.7)
EXTERNAL BLIND AUDITS														
C	21 (1.0)	88 (1.0)	8.1 (1.4)	5.0 (1.4)	260 (1.4)	28 (1.8)	23 (1.8)	20 (1.8)	ND (1.8)	1400 (1.8)	1100 (2.0)	20 (2.0)	2600 (2.0)	830 (4.2)
C	23 (1.1)	73 (1.1)	6.5 (1.1)	7.2 (1.1)	250 (1.1)	27 (1.4)	28 (1.4)	21 (1.4)	ND (1.4)	1400 (1.4)	1000 (2.1)	26 (2.1)	2400 (2.1)	650 (2.6)
G*	16 (0.1)	60 (0.1)	2.6 (0.1)	3.6 (0.1)	95 (0.1)	11 (0.1)	7.6(0.1)	5.4(0.1)	ND (0.1)	330 (0.1)	200 (0.2)	6.5(0.2)	580 (0.2)	330 (0.4)
G	19 (0.1)	72 (0.1)	ND (0.1)	3.2 (0.1)	89 (0.1)	10 (0.1)	6.4(0.1)	5.3(0.1)	ND (0.1)	270 (0.1)	190 (0.2)	5.4(0.2)	510 (0.2)	250 (0.2)

* Samples analyzed by High Resolution Mass Spectrometry (MS); remaining samples were analyzed by Low Resolution MS. ND - Not detected (detection limit).
NDR - Peak detected at the right time but did not meet verification criteria therefore compound could not be confirmed.

APPENDIX III SURROGATE STANDARD RECOVERY PERCENTAGES FOR POLYCHLORINATED DIBENZO-PARA-DIOXIN (PCDD) AND POLYCHLORINATED DIBENZOFURAN (PCDF) ANALYSIS.

	SURROGATE STANDARD RECOVERY (%)					
STN	^{13}C-T4CDD	^{13}C-T4CDF	^{13}C-P5CDD	^{13}C-H6CDD	^{13}C-H7CDD	^{13}C-O8CDD
A*	56	83	95	62	76	72
A*(DUP)	79	120	120	80	90	106
C	71	71	73	62	63	62
C (DUP)	88	78	87	80	79	90
E	74	77	75	67	66	66
F*	61	77	79	71	78	97
G*	78	120	110	81	89	86
G*(DUP)	82	110	120	95	94	100
I*	63	76	84	69	68	66
J*	89	100	90	89	99	98
K*	86	76	82	81	75	54
L*	81	85	81	86	79	71
M*	63	70	73	76	79	86
N	79	85	81	79	80	90
O	81	87	94	84	82	88
P	65	73	66	65	68	79
Q*	80	84	100	93	97	100
R*	77	89	92	85	100	100
U*	72	78	92	72	91	106
V*	86	90	90	94	100	120
V*(DUP)	64	69	89	68	81	89
W	81	80	90	77	73	73
W (DUP)	82	79	82	79	70	70
X*	75	77	90	84	81	87
n	24	24	24	24	24	24
Mean	76	85	89	78	82	86
S.D.	9	14	13	10	11	16
Max.	89	120	120	95	100	120
Min.	56	69	66	62	63	54

* Samples were analyzed by high resolution mass spectrometry; remaining samples were analyzed by low resolution mass spectrometry.

DUP - Samples replicated as part of QA/QC program. Refer to Appendix II for corresponding PCDD and PCDF values; refer to Table 1 for the remainder.

APPENDIX IV. RESULTS OF INTERNAL LABORATORY AND EXTERNAL BLIND AUDITS FOR POLYCYCLIC AROMATIC HYDROCARBON (PAH) ANALYSIS (μg/g dry weight).

	LOW MOLECULAR WEIGHT PAH						HIGH MOLECULAR WEIGHT PAH											
STATION	Naphthalene	Acenaphthylene	Acenaphthene	Fluorene	Phenanthrene	Anthracene	Fluoranthene	Pyrene	Benzo(a)anthracene	Chrysene	Benzo(b)(k)fluorene	Benzo(a)pyrene	Indeno(123-cd)pyrene	Dibenz(ah)anthr.	Benzo(ghi)peryl.	TOTAL LMW PAH	TOTAL HMW PAH	TOTAL PAH
INTERNAL LABORATORY AUDITS																		
C	0.73	0.24	0.24	0.34	0.99	0.63	1.20	1.50	0.64	0.86	1.30	0.80	0.77	0.11	0.62	3.17	7.80	10.97
C	0.73	0.16	0.18	0.24	0.97	0.46	1.30	1.80	0.81	1.10	1.70	0.88	0.61	0.13	0.52	2.74	8.85	11.59
D	0.11	0.04	0.03	0.10	0.45	NDR	0.51	0.55	0.26	0.36	0.30	0.20	0.12	0.02	0.09	0.73	2.41	3.14
D	0.20	0.03	NDR	0.10	0.37	0.19	0.49	0.58	0.22	0.26	0.38	0.23	0.18	0.03	0.13	0.89	2.50	3.39
F	1.30	0.70	3.10	3.50	9.50	3.70	23.00	18.00	7.70	13.00	15.00	7.00	6.50	0.58	4.80	21.80	95.58	116.75
F	1.20	0.31	2.60	2.80	7.40	2.70	18.00	15.00	6.50	11.00	12.00	5.60	5.30	NDR	3.90	17.01	77.30	94.31
P	0.20	0.07	0.06	0.10	0.40	0.15	0.57	0.64	0.26	0.44	0.66	0.31	0.27	0.05	0.29	0.98	3.49	4.47
P	0.25	0.06	0.06	0.10	0.47	0.18	0.62	0.65	0.27	0.39	0.66	0.36	0.33	0.05	0.31	1.12	3.64	4.76
R	0.54	0.16	0.12	0.30	0.99	0.57	1.90	2.40	1.00	1.80	1.90	0.90	0.62	0.14	0.63	2.68	11.29	13.97
R	0.63	0.20	0.20	0.36	1.30	0.72	2.00	2.60	1.20	1.60	2.20	1.00	0.64	0.20	0.67	3.41	12.11	15.52
HS-6(Lab)	4.50	0.24	0.22	0.51	3.25	1.10	3.23	2.83	1.68	2.48	4.60	1.90	2.45	0.43	1.85	9.82	21.45	31.27
HS-6(NRC)	4.10	0.19	0.23	0.47	3.05	1.13	3.54	2.99	1.84	2.05	4.25	2.24	1.95	0.49	1.78	9.17	21.13	30.30
EXTERNAL BLIND AUDITS																		
C	0.73	0.24	0.24	0.34	0.99	0.63	1.20	1.50	0.64	0.86	1.30	0.80	0.77	0.11	0.62	3.17	7.80	10.97
C	0.80	0.16	0.16	0.22	0.91	0.44	1.30	1.80	0.68	0.95	1.80	0.86	0.58	0.14	0.51	2.69	8.62	11.31
G	0.30	0.09	0.20	0.32	1.50	0.49	2.30	2.80	0.77	1.40	1.90	0.84	0.65	0.12	0.51	2.90	11.29	14.19
G	0.65	0.81	0.19	0.29	1.00	0.57	1.70	2.00	0.97	1.70	1.70	0.93	0.83	0.14	0.60	3.51	10.57	14.08
HS-3/4 (Lab)	3.70	0.17	1.70	4.00	25.00	3.00	23.00	14.00	4.80	5.60	6.50	2.30	2.20	0.40	1.70	37.57	60.50	98.07
HS-3/4 (NCR)	3.69	0.21	1.89	5.53	34.41	5.44	24.75	16.16	6.16	6.03	4.84	3.35	2.47	0.59	2.35	51.17	66.70	117.87

NDR Peak detected but did not meet quantification criteria. NDR values are as follows:
Station D anthracene 0.44, Station D acenaphthene 0.07, Station F dibenz(ah)anthracene 0.8. These are not included in the TOTALS.

HS6 National Research Council Standard Reference Material for PAH, NRC certified values compared to laboratory performance (LAB).

HS-3/4 Blend of NCR Standard Reference Material composed of 4 parts HS-3 to 6 parts HS-4. NCR certified values compared to LAB results.

APPENDIX V SURROGATE STANDARD RECOVERY PERCENTAGES FOR POLYCYCLIC AROMATIC HYDROCARBON (PAH) ANALYSIS.

	SURROGATE STANDARD RECOVERY (%)							
STN	Naphthalene d-8	Acenaphthene d-10	Phenanthrene d-10	Pyrene d-10	Chrysene d-12	Perylene d-12	Dibenz (ah) anthracene d-14	Benzo (ghi) perylene d-12
A	53	60	72	75	69	57	73	48
B	44	61	65	74	65	72	79	77
C	51	69	74	81	102	70	83	67
C(DUP)	44	63	63	63	53	38	21	25
C(DUP)	46	61	61	58	41	37	26	27
D	60	70	82	85	80	93	110	120
D(DUP)	47	60	77	83	111	83	98	83
E	47	75	72	69	74	62	68	74
F	52	54	67	70	48	87	100	69
F(DUP)	47	57	83	76	44	70	69	58
G	49	80	98	83	110	100	120	110
G(DUP)	44	69	88	73	95	93	87	100
H	51	82	95	86	121	109	116	105
I	56	80	85	90	82	96	96	91
J	40	72	71	74	110	110	99	119
K	50	69	70	84	100	97	100	110
L	36	52	74	65	38	50	66	68
M	58	75	64	66	79	43	36	30
N	62	73	80	88	89	88	95	84
O	67	76	77	84	83	76	80	73
P	60	71	71	81	86	74	72	68
P(DUP)	42	62	79	79	71	83	71	110
Q	62	72	78	88	93	77	69	70
R	51	70	54	85	89	75	66	60
R(DUP)	68	102	57	86	87	73	68	55
S	58	76	57	77	110	70	65	56
T	53	68	66	71	98	60	76	69
U	46	63	64	65	57	42	48	57
V	33	43	8	6	3	4	0	1
X	48	58	69	76	76	61	59	68

DUP - Samples replicated as part of QA/QC program. Refer to Appendix III for corresponding concentrations; refer to Table 2 for the remainder.

NOTE Spiked surrogate recoveries correspond to PAH compounds as follows:
naphthalene d-8: naphthalene
acenaphthene d-10: acenaphthylene, acenaphthene, fluorene.
phenanthrene d-10: phenanthrene, anthracene.
pyrene d-10: fluoranthene, pyrene.
chrysene d-12: benz(a)anthracene, chrysene.
perylene d-12: benzofluoranthene, benzo(a)pyrene
benzo(ghi)perylene d-12: indeno(1,2,3-cd)pyrene
dibenz(ah)anthracene d-14: dibenz(ah)anthracene
benzo(ghi)perylene d-12: benzo(ghi)perylene