CHEMICAL CONTAMINANTS IN SURFACE RUNOFF FROM THE ABANDONED CASCADE POLE (OLYMPIA) WOOD TREATING FACILITY

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ABSTRACT

Surface runoff from the abandoned Cascade Pole Company wood treatment plant in Olympia, Washington, was analyzed for EPA priority pollutant organics, metals (Arsenic, Copper, Zinc), polychlorinated dibenzodioxins (CDDs) and dibenzofurans (CDFs). In addition, runoff samples were subjected to bioassays with *Daphnia pulex* and *Salmonella* bacteria (Ames Test).

Results of these analyses indicate that copper in all discharges and pentachlorophenol concentrations in two of the discharges exceeded EPA criteria for the protection of saltwater aquatic life. Concentrations of most other contaminants were generally low. A high potential exists that CDDs and CDFs could be accumulating in marine sediments and organisms adjacent to the site. Bioassay results indicate that surface runoff was non-toxic to *Daphnia pulex* and non-mutagenic as measured by the Ames Test. Runoff calculations suggest that as much as 85-90% of precipitation at the site infiltrates.

INTRODUCTION

The Cascade Pole Company (CPC) site is located one mile north of downtown Olympia on a small peninsula that extends into lower Budd Inlet in southern Puget Sound (see Figure 1). The property, which is owned by the Port of Olympia, has been the site of wood preserving operations since 1939. Utility poles were preserved with creosote until 1957 when CPC began leasing the site and operating the treatment facility until 1986, using creasote and pentachlorophenol (PCP) in aromatic oil for preservatives (Coots, 1989).

Currently the facility has been demolished and the site is undergoing remediation. Substantial creosote and PCP contamination of ground water at the CPC site was first documented in 1983 (AGI, 1984). Subsequent investigations by the Washington State Department of Ecology (Ecology), the Port of Olympia, and CPC have also identified contaminants of concern in a variety of media both on and adjacent to the site. As a result of these investigations, Ecology, the Port of Olympia, and CPC have entered into a consent decree under the Model Toxics Control Act to facilitate remedial action at the site (Ecology, et al., 1990).

During negotiations for the consent decree, Ecology determined that a stormwater investigation of surface water discharges from the CPC site during the 1989-1990 wet season would help expedite remediation at the site. Ecology's Toxics Cleanup Program (TCP), therefore, requested the Toxics Investigations and Ground Water Monitoring Section to conduct a stormwater characterization study with the following objectives:

- Determine if surface water discharges from the CPC site contribute to off-site migration of contaminants.
- If detected, estimate contaminant loadings leaving the site and potential impacts on the receiving environment.

The information generated from this study will be used to determine the necessity for interim stormwater control measures at the site and assist in design of subsequent remediation/feasibility studies being conducted by the principal responsible parties. In addition, data from the current study was used to estimate infiltration at the site.

METHODS

Sample Collection - To characterize surface water discharges at the CPC site, two rounds of sampling were conducted--the first occurred on March 9 and the second April 25, 1990. Locations of all discharges sampled during this study are shown in Figure 1. In addition, detailed descriptions of their locations are listed in Appendix A1.

Sampling events were timed to occur during a low tide period following sufficient rainfall to produce overland flow at the site. Daily rainfall totals for the period of March 1 - May 24, 1990, at the CPC site are shown in Figure 2. On-site meteorological data was collected with

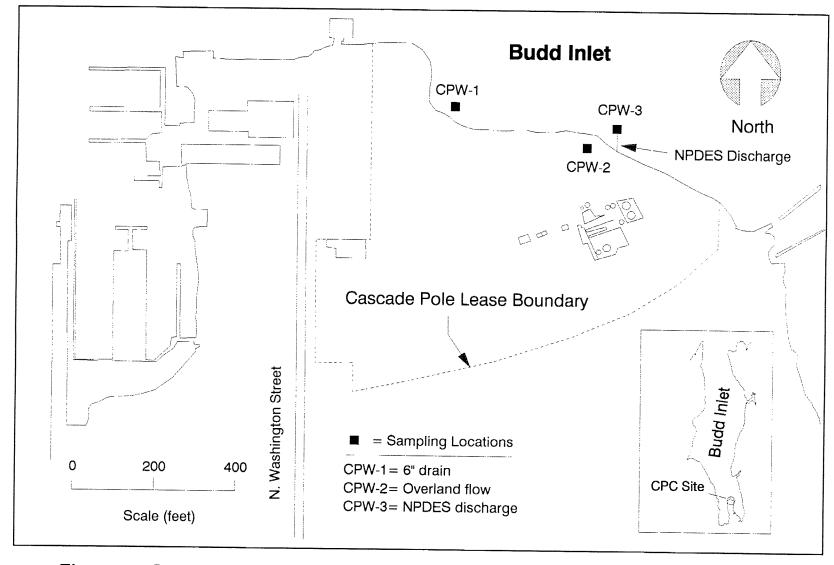


Figure 1: Sampling locations for Cascade Pole stormwater investigation.

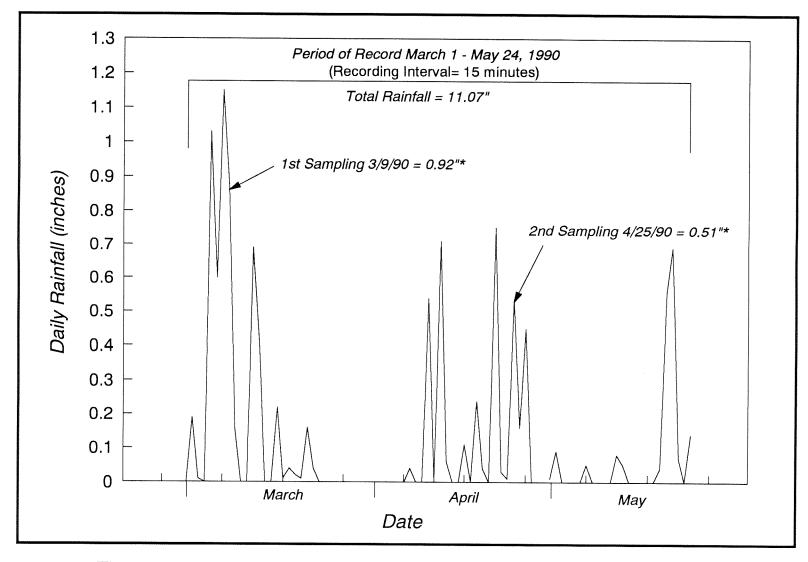


Figure 2: Daily Rainfall Totals for Cascade Pole Site 3/1 - 5/24, 1990.

(*=Rainfall total based on 24 hour total preceeding start of sample collection.)

a Unidata Model No. 6505D weather station and Model No. 6003A data logger in conjunction with a Sierra Misco Model No. 2500 tipping bucket rain gauge.

All stormwater samples were collected directly from the discharges by grab compositing three equal aliquots, into appropriate sample containers, over a period of approximately 1-2 hours. The only exception to this procedure was that overland flow at CPW-2 was channelized into a 6-inch diameter stainless steel pipe prior to being sampled. Sample containers and preservatives used in this study are summarized in Appendix A2. Aliquots for dissolved metals determinations were filtered in the field through 0.4 um polycarbonate membrane (Nucleopore) filters using an all glass and teflon vacuum filtration system. Ecology chain-of-custody procedures were followed for all sampling events (Huntamer, 1986). Copies of the chain-of-custody forms are included in Appendix A3.

Analysis and Quality Assurance - The chemical analyses, analytical methods, and laboratories used in this study are listed in Table 1. Target analytes and associated detection limits are summarized in Appendix B1. Accuracy and precision of the data set was assessed by analysis of transport, transfer, filter and method blanks, internal standards, surrogate spikes, duplicate matrix spikes, duplicate field samples, and standard reference materials (SRM). Volatiles, semivolatiles, and herbicides data were reviewed by Dickey Huntamer of the Ecology/EPA Manchester Laboratory. Polychlorinated dibenzodioxin (CDD) and dibenzofuran (CDF) results were reviewed by William Luksemburg of Alta Analytical Laboratories, El Dorado Hills, California. Blank results for metals and organics, matrix spike results for metals, and the organics data reviews are included in Appendix B.

Results of analysis of SRMs for metals are shown in Table 2. Chromium, copper, and zinc results were in good agreement with certified values (+/-6% of certified range) in SRM 1643B, indicating the analysis was accurate. Arsenic values are not certified in SRM 1643B. However, matrix spike recoveries for arsenic (97-102%, Appendix B4) indicate this analysis was also accurate. Due to blank contamination, chromium for all collections and dissolved zinc for the April 25 collection are not reported.

Table 2: Results of Analysis of Certified Reference Material for Water (ug/l).

	NBS 1643b									
	Certified	Manch	ester Result							
Element	Range	3/9/90	4/25/90							
Arsenic	(49)	48.0	56.7							
Chromium	18.6+/-0.4	17.3	17.3							
Copper	21.9+/-0.4	20.3	20.9							
Zinc	66+/-2	69.6	67.4							

NBS-1643b-Trace Elements in Water, National Bureau of Standards

()= Value is not certified

Table 1: Summary of Analytical Methods for Cascade Pole Stormwater Investigation.

Analysis	Method	Reference	Laboratory
Conventionals			
Flow	Bucket and Stopwatch	_	Field
Temperature	Thermometer (#212)	APHA, 1985	rr .
pH	pH meter (#423)	"	rr .
Specific Conductance	Conductance meter (#205)	"	n .
Total Sulfide	Titrimetric (#376.1)	EPA, 1983	n
Total Suspended Solids	Gravimetric (#160.2)	"	Ecology/EPA Manchester Lab
Total Organic Carbon	Persulfate/UV (#505)	"	Manchester, Wa.
Total Hardness	EDTA Titrimetric (#130.2)	"	n n
Ammonia	Automated Phenate (#350.1)	EPA, 1983	ıı ıı
Metals (Total Recoverable)	· ,		
Arsenic	GFAA (#206.2)	EPA, 1983	" "
Chromium	GFAA (#218.2)	"	n n
Copper, Zinc	ICP (#200.7)	<i>II</i>	n n
Organics			
Volatiles	GC/MS Purge and Trap (#624)	EPA, 1984	n n
Semivolatiles	GC/MS (modified #625)	"	n n
Pentachlorophenol	GC/ECD (modified #615)	EPA, 1982	ıı ıı
Dioxins/Furans	High Resolution GC/MS (#8290)	EPA, 1986	Triangle Labs Durham, NC.
Bioassays	-	•	<u> =,</u>
Daphnia Pulex	48 hour Acute	EPA, 1985	Ecology/EPA Manchester Lab
Ames	Salmonella/Microsome (chronic)	Ames, 1985	Microbiological Associates
		Muron, 1983	Rockville, MD.

With regard to organics analyses, holding times to extraction and analysis, matrix spike recoveries and precision, surrogate recoveries and blank results were found to be acceptable (except as noted below) and within prescribed limits of the EPA Contract Laboratory Program where applicable.

Volatiles - Acetone and methylene chloride, two common contaminants, were detected at low levels in laboratory blanks. In addition, 1,2,3-trichlorobenzene and naphthalene were also detected in laboratory blanks. The reported data set was not compromised by this blank contamination. The two matrix spikes had low surrogate recoveries for three of the four spiking compounds, ranging from 3-13% below CLP limits. These results are also not expected to alter the reported data set.

Semivolatiles - Surrogate spike recoveries for D-5 phenol and matrix spike results for benzo(b)fluoranthene were outside CLP limits for the April sample set.

Herbicides - During analysis of the March, samples the matrix spike solution was inadvertently left out of Sample No. 108082. Although the matrix spike duplicate was spiked, the spiking levels of PCP were too low (0.05 ug/L) to distinguish the spike from the PCP already present in the sample (40 ug/L). A similar situation occurred for the April collection where the original samples contained approximately 100 times more PCP than the amount of PCP spiked into the sample. Consequently, laboratory precision data is missing for PCP for both sample collections. However, as discussed below, precision estimates expressed as relative percent difference (RPD - range as percent of mean) calculated from blind field duplicates (RPD = 7-30%) suggest that sampling methods and laboratory analysis were not significant sources of data variability.

Dioxin/Furans - Isotopic abundance ratios were outside acceptable limits in two samples for the following congeners: Sample No. 108080 (13c-HeptaCDF); and Sample No. 108082 (13C-HexaCDF, 13C-HeptaCDF). Consequently, the reported concentrations have been flagged as estimates. Results for Sample No. 108088 are not reported due to method blank contamination. In addition, 2,3,7,8-TetraCDD (TCDD) is not reported and OctaCDD (OCDD) is qualified in Sample No. 108084 due to method blank contamination.

Precision estimates calculated from detected compounds in blind field duplicates were within RPD = \pm 1-30% for most target analytes. This suggests that sampling methods and laboratory analyses were not significant contributors to data variability for most analytes. Slightly lower precision (RPD = \pm 1-40%) was achieved for ammonia and total suspended solids (TSS) during the March collection, which may be a function of the low sample concentrations (ammonia = 0.02-0.03 ug/L and TSS = 2-3 mg/L). Overall precision (sampling \pm 1 laboratory) for CDD/CDF analysis was somewhat poorer than the other organics being approximately RPD = \pm 1-70% for most congeners. Again, this is probably a function of the low sample concentrations.

RESULTS AND DISCUSSION

The results of conventionals, metals and biological analyses of stormwater samples are summarized in Table 3.

Average flow rates from the site measured during the two sampling periods ranged from 0.9 (CPW-3) to 10.3 (CPW-3) gallons per minute (gpm). In general, surface water discharges at the CPC site can be characterized as having low suspended solids (2-4 mg/L), specific conductivities (78-180 umhos/cm), total hardness (34-57 mg/L) and ammonia (0.01u - 0.07 mg/L) levels; nearly neutral pH (6.7-7.6); and high concentrations of total organic carbon (8.1-14.7 mg/L). An exception to this general characterization of site runoff was discharge at CPW-1 which had high conductivities (11000-27200 umhos/cm), total hardness (1100-3600 mg/L), and very high total organic carbon (21.3-21.4 mg/L) concentrations. In addition, pH was slightly acidic during the April collection. The causes and significance of the unusual character of the CPW-1 discharge are not fully explained by the available information. Two possibilities are incomplete flushing of tidal water from the drain prior to sampling and/or the presence of wood waste debris in the upland drainage basin.

Total recoverable metals concentrations in the discharges were: arsenic (1.0u-5.6 ug/L); copper (6.3j-24 ug/L); and zinc (5.0u-56 ug/L). The highest concentrations of copper and zinc were measured in CPW-3 (NPDES discharge). Dissolved metals constituted a substantial portion of the total recoverable metals present in the discharges.

Toxicity of the discharges was evaluated with the use of two bioassays: Daphnia pulex, which is an acute freshwater bioassay that measures percent survival of Daphnia after 48 hours of exposure to the sample; and the Ames Test which is a chronic assay that evaluates the mutagenic potential of the sample using Salmonella bacteria. Results of the Daphnia bioassay indicate that the discharges were essentially non-toxic to Daphnia with the exception of CPW-1 which had 85% mortality. It was later discovered that the salinity of CPW-1 was 5 o/oo (o/oo - parts per thousand), considerably higher than might ordinarily be expected in a stormwater runoff sample. Consequently, a control was prepared to reflect the salinity of the sample. Forty-seven percent mortality was measured in the salinity control at the end of 48 hours. CPW-1 was retested on April 25, again using salinity controls that matched the sample. One-hundred percent mortality was obtained in both the sample and salinity controls. These data indicate that much of the toxicity observed for CPW-1 can be attributed to salinity effects. All discharges exhibited a negative response for mutagenic activity as measured by the Ames Test.

The results of volatile and semivolatile organics analyses of CPC stormwater samples are summarized in Table 4. Tentatively identified compounds are shown in Appendix C.

In general, concentrations of volatile and semivolatile organics were low in stormwater runoff from the site during both collection periods. Six target volatile compounds, primarily alkyl-substituted benzenes, were detected in CPW-3 (NPDES discharge). An additional twenty-three volatile organics were tentatively identified in this discharge. Alkyl-substituted benzenes, and indenes represented the bulk of the tentatively identified volatiles compounds (Appendix Table C1).

Table 3: Results of Conventionals, Metals and Biological Analyses of Cascade Pole Stormwater Samples Collected by Ecology March - April 1990.

Station		CPW-1		CPW-2			CPW-3	
Sample No.	10-8080	17-8091	10-8082	17-8093	10-8084	10-8090	17-8095	17-8097
Date	3/9/90	4/25/90	3/9/90	4/25/90	3/9/90	3/9/90	4/25/90	4/25/90
Time	1035-1255	0935-1115	1135-1330	0920-1030	1115-1305	Dup.	0950-1100	Dup.
Mean Flow (gpm)	4.0	6.4	0.9	0.9	10.3		6.3	
Temperature (°C)	7.7	11.5	6.8	12.7	6.0	_	10.7	_
pH (s.u.)	6.9	5.9	7.4	7.2	7.6	_	6.7	_
Spec. Cond. (umhos/cm)	11000	27200	78	160	180	_	180	_
Ammonia-N (mg/l)	0.04	0.03	0.01u	0.01	0.02	0.03	0.07	0.06
TSS (mg/l)	3	10	4	4	3	2	3	3
Total Hardness (mg/l)	1100	3600	38	57	36	34	42	48
Sulfide (mg/l)	1u	1u	1u	1u	1u	1u	1u	1u
TOC (mg/l)	21.3	21.4	8.6	17.2	8.3	8.1	14.7	14.4
Metals-1 (ug/l)								
Arsenic								
Total	5.6	2.7j	1.9j	2.3j	1.0u	1.0u	1.0u	1.4j
Dissolved	6.1	2.6j	2.2j	2.7j	1.0u	****	1.1j	
Chromium							·	
Total	*	*	*	*	*	*	*	*
Dissolved	*	*	*	*	*	*	*	*
Copper		İ						
Total	6.3j	10	11	17	23	24	21	19
Dissolved	2.5j	*	7.2j	15b	15	_	15b	_
Zinc								
Total	2 5j	5.0u	16j	5.0u	31	36	56	53.4
Dissolved	17j	*	7.5j	*	30j	_	*	-
Bioassay			_		•			
Daphnia pulex (%)-2	15	0	95	_	95		***	*****
Ames-3	Negative	_	Negative	_	Negative		***	_

⁻⁼Not analyzed

u=Not detected at detection limit shown

j=Estimated concentration

b=Also detected in blank at low levels relative to sample

^{*=}Not reported due to blank contamination (see appendix B1)

¹⁼Total recoverable metal

²⁼Percent Survival, 48 hour static test

³⁼Results as positive or negative response for mutagenic activity

Table 4: Summary of Organics Analyses of Cascade Pole Stormwater Samples Collected by Ecology March-April, 1990 (ug/l),

Station		CPW-1		CPW-2			CPW-3	
Sample No.	10-8080	17-8091	10-8082	17-8093	10-8084	10-8090	1 7-809 5	17-8097
Date	3/9/90	4/25/90	3/9/90	4/25/90	3/9/90	3/9/90	4/25/90	4/25/90
Time	1035-1255	0935-1115	1135-1330	0920-1030	1115-1305	Dup.	0950-1100	Dup.
Volatile Organics								
1,2,4-trimethylbenzene	-	1 u	_	10	-	-	2.0	2.0
1,3,5-trimethylbenzene	-	1 u	_	1 u	_	-	0. 9 j	0. 8 j
lsopropylbenzene	-	1u	_	1 u	-	-	0.2j	0.2j
Ethylbenzene	-	1 u	-	1u	-	-	0.3j	0.3j
Sec-butylbenzene	-	1u	-	1u	-	-	1 u	0.07j
Total xylenes		1u	-	1u	-	-	0. 8 j	0.Bj
Semivolatile Organics								
Acenaphthene	0.1j	0.1j	1.0u	0.3u	9.0	8.0	3.0	3.0
Acenaphthylene	0.8u	0.01j	1.0u	0.1j	0. 4 j	0.5j	1.0	1.0
Naphthalene	0.8u	0.07j	1.0u	0.3ช	0.8u	0. 8 u	0.2u	0.2u
Flourene	0. 8 u	0.03j	1.0u	0.3u	2.0	1.0	0.2u	0.2u
Anthracene	0.0 8 j	0.08j	0.4j	1.0	1.0	0.9	2.0	2.0
Phenanthrene	0. 8 u	0.02j	1.0u	0.3u	0.8u	0.8u	0.2u	0.2u
Sum LPAH	0.2j	0.3j	0.4j	1.1j	12 <u>j</u>	10j	6.0	6.0
Flouranthene	0.8u	0. 06 j	1.0u	0.3u	4.0	5.0	1.0	2.0
Benzo (a) anthracene	0.8u	0.2u	1.0u	0.2j	0.5j	0.7j	0.6	0.5
Pyrene	0.8u	0.07j	1.0u	0. 2 j	4.0	4.0	0.9	1.0
Chrysene	0.8u	0.2u	1.0u	0. 2 j	0.7j	0.9	0.4	0.5
Benzo (b) flouranthene	0.8u	0.2u	0.3j	0.3u	0. 8 j	0.9	0.6	0.7
Benzo (k) fluoranthene	0.8u	0.2u	1.0u	0.3u	0.8u	0. 8 u	0.5	0.6
Benzo (a) pyrene	0. 8 u	0.2u	1.0u	0.3u	0.8u	0. B u	0.4	0.2u
Sum HPAH		0.1j	0.3j	0. 6 j	10j	12j	4.4	5.3
Dibenzofuran	0.8u	0. 03 j	1.0u	0.3u	3.0	2.0	0.3	0.4
Carbazole	0. 8 u	0.2u	1.0u	0.3u	0.4j	0.8u	0.2u	0.20
Bis(2-ethylhexyl)phthalate	5.0u	0.4u	1.0u	3. 0 b	0.8u	0.8u	0.2u	1.0u
1-methylnaphthalene	0.8u	0.04j	1.0u	0.3u	0.8u	0.8u	0.2u	0.2u
2-methylnaphthalene	0.8u	0.01j	1.0u	0.3u	0.8u	0.8u	0.2u	0.2u
2-methylphenol	0.8u	0. 02 j	1.0u	0.3u	0.8u	0.Bu	0.2u	0.2u
4-methylphenol	0.8u	0.03j	1.0u	0.3u	0.8u	0.8u	0.2u	0.2u
2,4-dimethylphenol	0.8u	0.04j	1.0u	0.3u	0.8u	0. 8 u	0.2u	0.2u
Pentachlorophenol	4 u	m	m	m	m	m	m	m
Herbicides				:				
Pentachlorophenol	0.2	0.1	40	12	49	36	52	56
2,3,4,5-tetrachlorophenol	0.05	0.03	1.2	0.7	3.8	3.2	3.5	3.1

⁻⁼Not analyzed

n=Presumptive evidence of material

u=Not detected at detection limit shown

b=Also detected in blank at low levels relative to sample (see appendix B3)

j=Estimated concentration

m=Detected and confirmed by GC/MS but not quantified

Concentrations of target semivolatile organics (primarily polynuclear aromatic hydrocarbons (PAH)) were typically less than 1 ug/L in most discharges with the exception of CPW-3. Total LPAH and HPAH concentrations in CPW-3 ranged from 6.0-12j ug/L and 4.4-12j ug/L respectively. Similar concentrations of LPAH (2j ug/L) and HPAH (8j ug/L) were measured in the NPDES outfall in 1985 when the plant was operational (Johnson, 1985).

Forty-one semivolatile organics were also tentatively identified in the discharges sampled. Again, as was the case for volatiles, most were detected in the NPDES outfall. The majority of tentatively identified semivolatile compounds (Appendix Table C1) were alkyl-substituted benzenes and naphthalenes, and indenes.

Two chlorophenols, PCP and 2,3,4,5-tetrachlorophenol, were present at detectable levels in all the discharges sampled. Concentrations ranged from 0.1-56 ug/L for PCP and 0.03-3.8 ug/L for 2,3,4,5-tetrachlorophenol. The highest concentrations for both compounds were measured in discharge CPW-3 (NPDES outfall). For comparison, PCP was detected at 1700 ug/L in the NPDES outfall when the plant was operational (Johnson, 1985).

Results of CDD and CDF analysis of stormwater samples from the CPC site are shown in Table 5. Concentrations are reported in units of ng/L (parts per trillion). Detectable levels of at least two or more CDD and CDF congeners were present in all samples analyzed. The most acutely toxic form, TCDD, was not detected in any of the discharges sampled. Only a trace amount (0.008 ng/L) of 2,3,7,8-TetraCDF (TCDF) was measured in one sample of a duplicate set from the NPDES outfall. Concentrations of other CDD and CDF congeners (penta - octa) were typically less than 1 ng/L, except for HeptaCDD 0.34-17.2 ng/L, OCDD 4.5-248 ng/L and OctaCDF (OCDF) 0.1u-7.2 ng/L.

Significant sources of dioxins and furans in the environment include: the use of PCP as a wood preservative; municipal incinerators; and pulp and paper mills which use chlorine in the bleaching process (Boddington, et al., 1990). All of these sources produce complex mixtures which contain both CDDs and CDFs as impurities. PCP typically contains a mixture of hexa, hepta and octaCDDs and CDFs (Boddington, et al., 1990). The predominant congeners identified in stormwater runoff from the CPC site were hexa, hepta, and octa CDD and CDF. The simultaneous detection of PCP and the characteristic suite of CDD and CDF congeners in CPC runoff is compelling evidence that the source of these contaminants is related to the historical use of PCP as a wood preservative at the site.

Pollutant loadings for selected chemicals detected in surface water discharges from the CPC site are summarized in Table 6. Pollutant loadings measured during the present study were low, generally 2-3 grams/day or less for most chemicals. Loadings for individual discharges were similar during both the March and April sampling events. Calculated total loadings (in grams/day) from the site averaged over the two collection periods were as follows: arsenic (0.1 g/d); copper (1 g/d); zinc (3 g/d); LPAH (0.4 g/d); HPAH (0.4 g/d); and PCP (2 g/d). In most instances greater than or equal to 70 percent of the total pollutant loadings measured can be attributed to CPW-3 (NPDES outfall).

Table 5: Results of Chlorinated Dioxins and Furans Analysis of Cascade Pole Stormwater Samples Collected by Ecology March 9, 1990 (ng/l).

Station		CPW-1	CPW-2		CPW-3
Sample I	No.	10-8080	10-8082	10-8084	10-8090
Time		1035-1255	1135–1330	1115–1305	Dup
TEF	Chlorinated Dioxins				
1	2378-TCDD	0.01u	0.01u		0.005u
0.5	12378-PeCDD	0.01u	0.04	0.02	0.02e
0.1	123478-HxCDD	0.008u	0.08	0.09	0.04
0.1	123678-HxCDD	0.01u	0.46	0.45	0.38
0.1	123789-HxCDD	0.01u	0.18	0.24	0.11
0.01	1234678-HpCDD	0.34	17.2	10.8	13.8
0.001	OCDD	4.5	248	111*	196
	Total Dioxins=	4.8	270	120	210e
	Chlorinated Furans				
0.1	2378-TCDF	0.008u	0.01u	0.008	0.005u
0.05	12378-PeCDF	0.008u	0.01u	0.02e	0.01e
	23478-PeCDF	0.01u	0.01u	0.03	0.01e
0.1	123478-HxCDF	0.005u	0.03e	0.08	0.04
0.1	123678-HxCDF	0.005u	0.03e	0.04	0.02
0.1	234678-HxCDF	0.008u	0.05j	0.05	0.04
0.1	123789-HxCDF	0.01u	0.02uj	0.003u	0.02
0.01	1234678-HpCDF	0.03j	0.89j	0.83	0.75
0.01	1234789-HpCDF	0.02uj	0.03uj	0.09	0.03
0.001	OCDF	0.1u	5.5	3.8	7.2
	Total Furans=	0.0003j	6.5e	4.9e	8.1e
	Total TEQs=	0.01j	0.5e	0.4e	0.4e

u=Not detected at detection limit shown

e=Estimated maximum possible concentration

j=Estimated concentration

⁻⁼Not reported due to blank contamination

TEF=Toxicity equivalency factor (Barnes et al, 1989)

TEQs=Toxicity equivalents, estimated toxicity relative to 2,3,7,8-TCDD

^{*=}Also detected in blank at low levels relative to sample

Table 6: Summary of Pollutant Loadings for Cascade Pole Stormwater Investigation (grams/day).

Station		CPW-1		CPW-2		CPW-3	Total Load		
Date	3/9/90	4/25/90	3/9/90	4/25/90	3/9/90	4/25/90	3/9/90	4/25/90	
Metals-1						-		.,_0,00	
Arsenic	0.1	0.09	0.007	0.009j		0.04j	0.1	0.1j	
Copper	0.1j	0.3	0.04	0.06	1	0.7	1 i	1	
Zinc	0.6		0.06	_	2	2	3	2	
Organics							_		
LPAH	0.005j	0.01j	0.002j	0.004j	0.6j	0.2	0.6j	0.2j	
HPAH	_	0.003j	0.001j	0.002	0.6j	0.2	0.6j	0.2j	
Pentachlorophenol	0.005	0.003	0.2	0.05	2 ๋	2	2	2	

¹⁻Based on total recoverable metals concentration

ij=Estimated Load

⁻⁼ Compound was not detected in discharge

Table 7 compares concentrations of selected chemicals detected in stormwater discharges from the CPC site to EPA criteria for protection of saltwater aquatic life (EPA, 1986). In general, these data indicate that copper in all discharges and PCP concentrations in CPW-2 and CPW-3 exceeded EPA criteria for the protection of saltwater aquatic life. It is anticipated that during high tide periods, adequate dilution (approximately 2-8 times) would be available to reduce copper and PCP concentrations in the receiving environment to acceptable levels. However, during low tide periods, intertidal organisms would be exposed to full strength runoff which could produce adverse biological impacts.

Presently, numerical criteria to assess CDD and CDF contamination only exist for TCDD. However, EPA has recommended an interim procedure for estimating risks associated with exposure to mixtures of CDD and CDFs (Bellin and Barnes, 1986). Toxicity equivalency factors (TEFs) are used to convert concentrations of individual CDD and CDF congeners to equivalent concentrations of TCDD. Each of the congener concentrations is multiplied by the appropriate TEF and results summed to give toxicity equivalents (TEQs). Table 5 contains a listing of the most recent TEFs adopted by EPA (Barnes *et al.*, 1989) and shows the resulting TEQs for the CPC runoff samples. It should be noted that EPA cautions that the TEF approach is interim, needs additional data, and should ultimately be replaced with a more direct biological assay. Based on the TEQ approach, runoff samples from the CPC site have an estimated toxicity potential of 0.01 to 0.4 ng/L.

The data presented here, in conjunction with the fact that the major sinks for CDDs and CDFs in the aquatic environment are sediments and biota (Palmer et al., 1988), indicates that additional congener-specific testing should be performed for CDDs and CDFs in marine sediments and organisms adjacent to the CPC site. In addition, biological sampling should focus on organisms (possibly crustacea) that have a high potential to accumulate these compounds, based on a review of previous sampling efforts in Puget Sound and coastal regions of Washington (Albright, 1990).

To evaluate the degree to which rainfall results in surface runoff or by way of infiltration recharges ground water below the site, discharge flows measured during the two sampling events were compared to the total rate of precipitation to the site during these events. Total precipitation input rates were calculated using on-site precipitation data for the 24-hour period preceding the start of sampling and drainage basin area for the site obtained from the CPC site plan map submitted as part of their shoreline substantial development permit application (AGI, 1990). The following formula was then applied to the data:

$$I = (1 - \frac{R}{P})100$$

where I = Infiltration as a percent of total precipitation (%)

R = Total site surface runoff averaged over the sampling period (MGD)

P = Precipitation input rate to site (MGD)

Results of these calculations indicate that surface runoff from the site measured on March 9 and April 25, 1990, accounted for approximately 10% and 15%, respectively, of the total precipi-

Table 7: Comparison of Selected Compounds in Stormwater Discharges from the Cascade Pole Site to available Water Quality Criteria (units= ug/l, unless otherwise specified).

Station	CI	PW-1	CF	PW-2	С	PW-3	Marine(1)		
Date	3/9/90	4/25/90	3/9/90	4/25/90	3/9/90	4/25/90	Acute	Chronic	
Metals(2)								······································	
Copper	6.3j	10	11	17	24*	20*	2.9	2.9	
Zinc	25j	_	16j	_	34*	55*	95	86	
Organics			•						
Total PNA's	0.2j	0.4j	0.7j	1.7j	22j*	11*	300	+	
Pentachlorophenol	0.2	0.1	40	12	43*	54*	13	7.9	

(1)=EPA, 1986 "Quality Criteria for Water"

(2)=Total recoverable metal

*=Reported as mean of duplicate analysis

+= No criteria available

j=Estimated concentration

e=Estimated maximum possible concentration

-=Compound was not detected in discharge

=Concentration measured in discharge would require dilution to meet criteria in receiving water

tation input to the drainage basin. Ignoring evaporation (which during the sampling periods would have been inconsequential) this results in a calculated infiltration rate of 85-90%. This is in good agreement with the total infiltration estimate of 85% reported for the site during wet weather (October to April) by Applied Geotechnology (AGI, 1986). The relatively low ratio of runoff to precipitation is largely due to the flat topography of the site coupled with moderately permeable soils.

SUMMARY

The major findings of this study can be summarized as follows:

- Copper in all discharges (6.3j-24 ug/L) and pentachlorophenol in CPW-2 (12-40 ug/L) and CPW-3 (36-56 ug/L) exceeded EPA criteria levels considered protective of marine life. Concentrations of most other target chemicals (metals and organics) were generally low in the discharges tested.
- Results of dioxin and furan analyses indicate that there is a substantial potential that these compounds are accumulating in marine sediments and organisms near the site.
- Bioassays indicate surface water from the site was non-toxic to *Daphnia pulex* and non-mutagenic as measured by the Ames Test.
- The NPDES outfall accounted for greater than or equal to 70% of the pollutant loadings in surface runoff from the site during the present study.
- Runoff calculations suggest that approximately 85-90% of precipitation at the site infiltrates.

RECOMMENDATIONS

- Eliminate the discharge of untreated stormwater from the NPDES outfall and overland flow in the vicinity of CPW-2.
- Conduct congener specific dioxin and furan sampling of marine sediments and organisms in the nearshore receiving environment around the CPC site. Biological sampling should target organisms (possibly crustacea) that have a high potential to accumulate these compounds.
- Investigate the importance of infiltrating precipitation as a mechanism for off-site migration of contaminants.

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APPENDIX A

SAMPLE COLLECTION/DOCUMENTATION

Appendix A1: Descriptions for Sampling Points, Cascade Pole Stormwater Investigation.

Station No.	Description
CPW-1	6 inch corrugated metal pipe, intertidal, 15 ft north of riprap bulkhead, west end of property
CPW-2	Overland flow 100 ft west of NPDES outfall, above ordinary high water line
CPW-3	NPDES Outfall, intertidal

Appendix A2: Containers and preservatives for the Cascade Pole Stormwater Investigation.

Analysis	Container	Preservative
TOC	2oz polyethylene	1ml HNO3, cool 4°C
Ammonia	4oz polyethylene	0.5ml H2SO4, cool 4°C
Metals	I-Chem 1qt polyethylene cubitainers	1ml HNO3, cool 4°C
Volatile Organics	I-Chem 40ml glass vials w/teflon septum	2 drops HCL, cool 4°C
Semivolatile Organics	I-Chem 1gal glass w/teflon lined lids	cool 4°C
Pentachlorophenol	I-Chem 1/2gal glass w/teflon lined lids	cool 4°C
Dioxin\Furans	I-Chem 1qt amber glass w/teflon lined lids	cool 4°C
Daphnia pulex	I-Chem 1/2gal glass w/teflon lined lids	cool 4°C
Ames Test	I-Chem 1qt amber glass w/teflon lined lids	cool 4°C

I-Chem Hayward, Ca.: cleaning protocol; metals-series 200, organics\bioassay-series 300.

Appendix A3: Chain-of-Custody Tracking Forms for Cascade Pole Stormwater Investigations.

Report No. 1 = March Sampling

Report No. 2 = April Sampling

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APPENDIX B

SAMPLE ANALYSIS/QUALITY ASSURANCE

Appendix B1: List of Target Metal and Organic Compounds and Associated Detection Limits for Cascade Pole Stormwater Investigation.

	Detection	n	Detection
Compound	Limit	Compound	Limit
Metals (ug/l)		Volatiles-cont.	
Arsenic	1.0	1,1,2,2-Tetrachloroethane	1
Chromium	0.2	1,1,1,2-Tetrachloroethane	1
Copper	2.0	Toluene	1
Zinc	5.0	Chlorobenzene	1
		Ethylbenzene	1
Volatiles (ug/l)		Ethenylbenzene	1
Chloromethane	1	Bromobenzene	1
Dichlorodifluoromethane	1	1,2,3-Trichloropropane	1
Bromomethane	1	2-Chlorotoluene	1
Vinyl Chloride	1	4-Chlorotoluene	1
Chloroethane	1	Total Xylenes	1
Trichlorofluoromethane	1	1,2,4-Trimethylbenzene	1
Methylene Chloride	1	Tert-Butylbenzene	1
Acetone	1	1,3,5-Trimethbenzene	1
Carbon Disulfide	1	Sec-Butylbenzene	1
1,1-Dichloroethene	1	p-IsopropyItoluene	1
1,1-Dichloroethane	1	Butylbenzene	1
Trans-1,2-Dichloroethene	1	DBCP	1
Cis-1,2-Dichloroethene	1	1,2,3-Trichlorobenzene	1
2,2-Dichloropropane	1	Isopropylbenzene	1
Bromochloromethane	1	Propylbenzene	1
Chloroform	1	1,3-Dichlorobenzene	1
1,2-Dichloroethane	1	1,4-Dichlorobenzene	1
2-Butanone	1	1,2-Dichlorobenzene	1
1,1,1-Trichloroethane	1	1,2,4-Trichlorobenzene	1
Carbon Tetrachloride	1	Naphthalene	1
1,1-Dichloropropene	1	Hexachlorobutadiene	1
Vinyl Acetate	1		•
Bromodichloromethane	1	Semivolatiles (ug/l)	
1,2-Dichloropropane	1	Phenol	0.2-1.0
Dibromomethane	1	Bis(2-Chloroethyl)ether	0.2-1.0
Trans-1,3-Dichloropropene	1	o-Chlorophenol	0.2-1.0
Trichloroethene	1	1,3-Dichlorobenzene	0.2-1.0
Dibromochloromethane	1	1,4-Dichlorobenzene	0.2-1.0
1,2-Dibromoethane	1	Benzyl Alcohol	0.2-1.0
1,1,2-Trichloroethane	1	1,2-Dichlorobenzene	0.2-1.0
1,3-Dichloropropane	1	2-Methylphenol	0.2-1.0
Benzene	1	Bis(2–Chloroisopropyl)ether	0.2-1.0
Cis-1,3-Dichloropropene	1	4–Methylphenol	0.2-1.0
Bromoform	1	. Modifyiphonoi	0.2-1.0
2-Hexanone	1		
4-Methyl-2-Pentanone	1		
Tetrachloroethene	1		

Appendix B1: continued.

	Detection		Detection
Compound	Limit	Compound	Limit
Semivolatiles-cont. (ug/l)		Semivolatiles-cont.	
N-Nitroso-di-n-propylamine	0.2–1.0	3,3'-Dichlorobenzidine	0.2–1.0
Hexachloroethane	0.2–1.0	Benzo(a)anthracene	0.2-1.0
Nitrobenzene	0.2-1.0	Bis(2-ethylhexyl)phthalate	0.4-5.0
Isophorone	0.2–1.0	Chrysene	0.2–1.0
2–Nitrophenol	0.2-1.0	Di-n-octylphthalate	0.2-1.0
2,4-Dimethylphenol	0.2-1.0	Benzo(b)fluoranthene	0.2-1.0
Benzoic Acid	1.0-7.0	Benzo(k)fluoranthene	0.2-1.0
Bis(2-Chloroethoxyl)methane	0.2-1.0	Benzo(a)pyrene	0.2-1.0
2,4-Dichlorophenol	0.2-1.0	Indeno(1,2,3-cd)pyrene	0.2-1.0
1,2,4-Trichlorophenol	0.2-1.0	Dibenzo(a,h)anthracene	0.2-1.0
Naphthalene	0.2-1.0	Benzo(ghi)perylene	0.2-1.0
4-Chloroaniline	0.2-1.0		
Hexachlorobutadiene	0.2-1.0	Herbicides (ug/l)	
4-Chloro-3-Methylphenol	0.2-1.0	2-4-D	0.9-1.0
2-Methylnaphthalene	0.2-1.0	2,4-DB	0.37-4.2
1-methylnaphthalene	0.2-1.0	2,4,5-T	0.04-0.42
Hexachlorocyclopentadiene	0.4-3.0	2,4,5-TB	0.04-0.42
2,4,6-Trichlorophenol	0.2-1.0	2,4,5-TP	0.04-0.42
2,4,5-Trichlorophenol	1.0-7.0	MCPA	9.0–100
2-Chloronaphthalene	0.2-1.0	MCPP	9.0–100
2–Nitroaniline	1.0-7.0	МСРВ	9.0–100
Dimethylphthalate	1.0-7.0	Pentachlorophenol	0.01
Acenaphthylene	0.2-1.0	2,3,4,5-Tetrachlorophenol	0.015
3-Nitroaniline	1.0-7.0	Dicamba	0.04-0.42
Acenaphthene	0.2-1.0	Bromoxynil	0.04-0.42
2,4-Dinitrophenol	1.0-7.0	loxynil	0.04-0.42
4-Nitrophenol	1.0-4.0	Dinoseb	0.04-0.42
Dibenzofuran	0.2–1.0	Picloram	0.04-0.42
2,4-Dinitrotoluene	0.2-1.0	Holoram	0.04-0.42
2,6-Dinitrotoluene		Dioxins/Furans (ng/l)	
Diethylphthalate	0.2-1.0	2378-TCDD	0.005-0.01
4-Chlorophenyl-phenylether	0.2-1.0	12378-PeCDD	0.003-0.01
Fluorene	0.2-1.0	123478-HxCDD	0.008
4-Nitroaniline	1.0-7.0	123678-HxCDD	0.008-0.01
4,6-Dinitro-2-methylphenol	1.0-7.0	123789-HxCDD	
N-Nitrosodiphenylamine	0.2-1.0	1234678-HpCDD	0.008-0.01
4-Bromophenyl-phenylether	0.2-1.0	OCDD	0.005
Hexachlorobenzene	0.2-1.0	2378-TCDF	0.02
Pentachlorophenol	4.0		0.005-0.00
Phenanthrene	4.0 0.2–1.0	12378-PeCDF	0.008
Anthracene	0.2-1.0	23478-PeCDF	0.01
Carbazole		123478-HxCDF	0.005
	0.2-1.0	123678-HxCDF	0.005
Di-n-Butylphthalate	0.2-1.0	234678-HxCDF	0.008
Fluoranthene	0.2-1.0	123789-HxCDF	0.01
Pyrene	0.2-1.0	1234678-HpCDF	0.01
Retene	0.2-1.0	1234789-HpCDF	0.02
Butylbenzlphthalate	0.2-1.0	OCDF	0.1

Appendix B2: Summary of Metals-1 Analysis of Blank Samples for Cascade Pole Investigation (ug/l).

Blank Type	Tran	Transport		tion	Method		
Date	3/90	4/90	3/90	4/90	3/90	4/90	
Sample No.	10-8088	17-8100	10-8089	17–8101	_	_	
Arsenic	1.0u	1.0u	1.0u	1.0u	1.0u	1.0u	
Chromium	0.4j	0.2u	0.3j	0.2u	0.2u	0.6j	
Copper	2.0u	2.0u	2.0u	2.3j	2.0u	2.0u	
Zinc	5.0u	5.0u	5.0u	54	5.0u	5.0u	

¹⁻Total recoverable metals

Appendix B3: Summary of Organics Analysis of Blank Samples for Cascade Pole Investigation (ug/l).

Blank Type	Transp	oort	Metho	od
Date	3/90	4/90	3/90	4/90
Sample No.	10-8088	17-8100	_	_
Volatiles				
Methylene Chloride	_	1.0u	_	2
Acetone		1.0u	-	2
1,2,3-trichlorobenzene	_	1.0u	_	0.2j
Naphthalene	_	2	_	0.6j
Tentative ID Volatiles				
1-bromo-3-fluorobenzene		ND	-	69j
3-chloro-1-propenylbenzene	_	ND	-	0.4j
1,2 dimethylnaphthalene	_	2.6jn		ND
1,8 dimethylnaphthalene	_	2.4jn	_	ND
1-methylene-1H-indene	· _	ND	_	0.8j
1-ethylidene-1H-indene	_	0.8jn		ND
Nonanal	_	ND		2.4jn
Decanal	_	ND	_	4.9jn
Semivolatiles				
Phenol	0.8u	0.2u	0.07j	0.3j
Naphthalene	0.8u	0.01j	0.007j	1.0u
N-nitrosodiphenylamine	0.8u	0.2u	0.1j	0.9j
Diethylphthalate	0.8u	0.2u	0.01j	0.07j
Di-n-butylphthalate	0.8u	0.2u	0.05j	0.2j
Di-n-octylphthalate	0.8u	0.2u	0.2j	1.0u
Bis (2EH) phthalate	0.8u	0.2u	0.2j	0.4j
Tentative ID Semivolatiles				
2,6 bis (1,1 dimethyl) phenol	ND	ND	ND	1.6jn
1-fluoro-2-methoxy benzene	ND	ND	ND	0.5jn
2-cyclohexen-1-ol	ND	ND	ND	1.0jn
2-cyclohexen-1-one	ND	ND	ND	1.4jn
Hexadecanoic acid	ND	ND	ND	0.4jn
Bis (2-ethyl) hexadecanoic acid	ND	ND	ND	0.5jn
Herbicides				
Pentachlorophenol	0.04u	0.01u	0.2u	0.01u
2,3,4,5-Tetrachlorophenol	0.04u	0.02u	0.2u	0.02u

⁻⁼Not analyzed

j=Estimated concentration

u=Not detected at detection limit shown

j=Estimated concentration

ND=Not detected

Appendix B4: Summary of Duplicate Spike Results for Metals and Herbicides Analysis, Cascade Pole Stormwater Investigation (expressed as percent recovery).

Date		3/9/90			4/25/90	
Sample	MS	MSD	RPD	MS	MSD	RPD
Metals						
Arsenic	100	97	3	100	102	2
Chromium	90	90	0	113	112	1
Copper	106	106	0	107	107	0
Zinc	121	106	13	97	97	0

Appendix B5: Case Narratives/Quality Assurance Reviews of Organics Data for Cascade Pole Stormwater Investigation.

Report No. 1 = Organics data for March 9, 1990, collection

Report No. 2 = Dioxin/Furan data for March 9, 1990, collection

Report No. 3 = Organics data for April 25, 1990, collection

MANCHESTER ENVIRONMENTAL LABORATORY

7411 Beach Drive SE, Port Orchard Washington 98366

CASE NARRATIVE

May 24, 1990

Subject:

Cascade Pole - Stormwater I

Samples:

90 - 108080, -108082, -108084, -108088, -108090

Case No. DOE-407R

By:

Dickey D. Huntamer

Chemist - Organics Unit

SEMIVOLATILE ORGANICS

ANALYTICAL METHODS:

Semivolatile water samples were extracted with methylene chloride using the Manchester modification of the EPA CLP procedure with capillary GC/MS analysis of the sample extracts. All CLP QA/QC procedures were performed on the samples. Low detection limits were achieved by extracting approximately three liters of sample and concentrating the final extract to 0.5 mL for analysis.

HOLDING TIMES:

All sample extraction and analysis holding times were met. Samples were extracted within the seven day holding time and extracts were analyzed within the 40 day extract holding time.

CALIDI	E HOL	DIMO	TIMES
NAMPI	+ H()	DINCT	LIMES

Sample	Collect	Received	Extract	Analysis	Holdin	g Times
	Date	Date	Date	Date	Extr.	Anal.
108080	3/9	3/12	3/15	4/3	6	19
108082	3/9	3/12	3/15	4/3	6	19
108084	3/9	3/12	3/15	4/4	6	20
108088	3/9	3/12	3/15	4/4	6	20
108090	3/9	3/12	3/15	4/4	6	20
108082Y	3/9	3/12	3/15	4/4	6	20
108082Z	3/9	3/12	3/15	4/4	6	20

BLANKS:

No significant blank contamination was detected.

SURROGATES:

All surrogate spike recoveries were within normal limits for CLP water recoveries except for 2-Fluorophenol in the matrix spike duplicate (108082**Z**) where the recovery exceeded the CLP limit of 100% by only one percent.

MATRIX SPIKE AND MATRIX SPIKE DUPLICATE:

Matrix spikes compounds were added at one-fifth the normal spiking concentration of 50 ug to more closely approximate the low detection limits requested. No significant problems were encountered with recovering the matrix spike compounds at this level (3-5 ug/L). Although no matrix spike recovery limits have been established at this low level, spike recoveries were generally within the normal CLP recovery range found at higher matrix spike levels.

SPECIAL ANALYTICAL PROBLEMS:

No analytical problems were encountered in the analysis. The low detection limits were achieved by extracting 2.5 to 3 liters of sample and concentrating the extract to 0.5 mL prior to analysis. One unusual item was the presence of anthracene without the corresponding detection of phenanthrene. It will be interesting to see if the results of the second sampling follow this pattern.

The relatively high levels of Pentachlorophenol (PCP) in some of the samples permitted confirmation of its presence in the GC/ECD analysis by GC/MS. The semivolatile analysis report reflects the confirmation of the Herbicide analysis by reporting PCP with the "M" qualifier. The "M" qualifier means PCP was detected and confirmed but was not quantified using GC/MS.

VOLATILE ORGANICS

Volatile Organic Analysis (VOA) was cancelled on this sample set by the Project Officer when sample holding times could not be met. Resampling for VOA was scheduled for the second sampling event.

HERBICIDES

ANALYTICAL METHODS:

Extraction and analysis was accomplished following Manchester Lab modified EPA Method 615 for Herbicides and Pentachlorophenol (PCP), Tetrachlorophenol and Trichlorophenol.

BLANKS:

No significant blank contamination was found.

SURROGATES:

No surrogate recovery limits have been established for this method. Surrogate recoveries for this sample set ranged from 77 to 93 % for 2,4,6-Tribromophenol. The matrix spike 108082W had no surrogate recovery since the surrogate compound was not added to the sample.

HOLDING TIMES:

All sample extraction and analysis holding times were met. Samples were extracted within the seven day holding time and extracts were analyzed within the 40 day extract holding time.

	SAMPLE HOLDING TIMES					
Sample	Collect Date	Received Date	Extract Date	Analysis Date	Holding Times	
					Extr.	Anal
108080	3/9	3/12	3/15	3/30	6	15
108082	3/9	3/12	3/15	3/30	6	15
108084	3/9	3/12	3/15	3/30	6	15
108088	3/9	3/12	3/15	3/30	6	15
108090	3/9	3/12	3/15	3/30	6	15
108082 W	3/9	3/12	3/15	4/4	6	20
108082X	3/9	3/12	3/15	4/4	6	20

MATRIX SPIKE AND MATRIX SPIKE DUPLICATE:

The matrix spike solution was inadvertently left out of 108082W. Although the matrix spike duplicate was spiked only three out of the five spike compounds were distinguishable from the native materials. The other two compounds, Pentachlorophenol (PCP) and Dicamba had matrix interferences and no recoveries were reported. This failure to distinguish spiked PCP from native PCP is not surprising since the sample contained approximately 40 ug/L of native PCP and only .05 ug spiked PCP.

SPECIAL ANALYTICAL PROBLEMS:

No significant analytical problems were encountered other than the high PCP concentrations found in some of the samples. Samples 108082, 108084 and 108090 with 40.1, 48.7 and 36.0 ug/L PCP respectively were significantly higher in PCP than expected and in fact the concentrations were high enough to be confirmed by GC/MS. The unfortunate choice of sample 108082, which contained 40.1 ug/L PCP, as the matrix spike resulted in failure to obtain meaningful PCP recovery data for that matrix spike.

DATA QUALIFIER CODES:

- U The material was analyzed for, but was not detected. The associated numerical value is the sample quantitation limit.
- J The associated numerical value is an estimated quantity.
- R The data are unusable (compound may or may not be present). Resampling and reanalysis is necessary for verification.
- NAR No Analytical Result.
- M The compound was detected and confirmed but was not quantitated.



August 16, 1990

Stuart Magoon Washington State Department of Ecology P.O. Box 307 Manchester, WA 98353

Dear Mr. Magoon,

This is the final report on the review of data for your Cascade Pole project. Five water samples were sent to Triangle Laboratories, Inc. (TLI) for analysis of Cl₄-Cl₈ dioxins and furans plus confirmation of 2,3,7,8-TCDF using EPA Method 8290. Acceptable results were reported for three of the samples (10-1080, 10-8082, 10-8090). Sample 10-1088 was reextracted because of excessive losses of the 13C labeled internal standards. Sample 10-1084 was apparently re-extracted because of high recoveries of the internal standards and high detection limits.

On August 1, 1990 the raw data packet was received at Alta Analytical Laboratory. The following items were missing from the data packet:

- 1. Raw data was not provided for the original analysis of 10-1084 and 10-1088.
- 2. Initial calibration data, continuing calibration data, GC column performance data, window defining mixes, and resolution documentation was not provided for the reextracted samples. Presumably this was because the data was not usable due to blank and sample contamination.
- 3. Sample data sheets indicate that the ICAL date was 4/9/90. No ICAL data was received for 4/9/90. The actual ICAL file used was 4/8/90. This data was provided.

For the data that was received special notice should be given to the following items:

- 1. Method blank for 10-1080, 10-1082 and 10-1090. Recoveries of all the internal standards were <40%. The signal to noise ratio was >10:1 on all the internal standards. While EPA Method 8290 does not specifically require re-extraction of samples associated with a method blank that has low internal standard recoveries this may be an indication of analytical difficulties.
- 2. Sample 10-1080. The recoveries of 13C-2,3,7,8-TCDD, 13C-2,3,7,8-TCDF and OCDD were <20%. The signal to noise ratio was >10:1. The isotopic abundance

Alta Analytical Laboratory Inc.



ratio for 13C-1,2,3,4,6,7,8-HpCDF was outside of the acceptable range. Section 9.1.4.4 of 8290 states that corrective action should be taken if isotope abundance ratios for the 13C labeled internal standards are out of the acceptable range. It is unclear from the data provided what, if any, corrective action was taken. The results reported for the hepta-furans should be considered estimates.

- 3. Sample 10-1082. Recoveries of all 13C labeled internal standards was less than 40%. 13C-TCDD, 13C-TCDF, 13C-PeCDF, 13C-PeCDD, and OCDD were 10% or less. The signal to noise ratio was >10:1 on each of these internal standards. The isotopic abundance ratios for 13C-HxCDF and 13C-HpCDF are outside of the acceptable range. It is unclear from the data provided if any corrective action was taken. The results for the hexa-furans and hepta-furans should be considered extimates only.
- 4. Sample 10-1090. Recoveries of 13C-TCDD, 13C-TCDF, 13C-PeCDD, 13C-PeCDF, 13C-HpCDD and 13C-OCDD are less than 40%. The signal to noise was > 10:1. These results are acceptable as reported.
- 5. Sample 10-1088. According to the TLI narrative the original sample had little or no recovery of the 13C internal standards and was re-extracted. The method blank associated with the sample showed very high levels of 2,3,7,8-TCDD and detectable levels of other dioxins and furans. The results provided for this sample should be considered highly unreliable. Since TLI used all of the sample in the extraction and subsequent re-extraction no reliable data can be provided for this sample. This area should be re-sampled if possible.
- 6. Sample 10-1084. It appears that this sample was re-extracted because the original sample had high recoveries of the internal standards and high detection limits. The method blank associated with the re-extraction had background levels of 2,3,7,8-TCDD and OCDD. The same level of 2,3,7,8-TCDD was present in the sample. If the re-extraction data was written up properly, and 2,3,7,8-TCDD given a EMPC of .030 ppt, this sample could be a reasonable duplicate of sample 10-8090. However, because of the blank contamination this data should be considered highly unreliable.

Low internal standard recoveries associated with the blank and samples 10-1080, 10-1082, and 10-1090 occurred in the sample cleanups rather than the extraction. Since the reextraction of samples 10-1084 and 10-1088 did not have low recoveries it can be concluded that the problem was not associated with the matrix. Since there is no reliable data for the duplicate sample, no conclusions can be made regarding the precision of the data.

The following items were evaluated and found to be within the scope of the QA/QC requirements of Method 8290 for samples 10-1080, 10-1082, and 10-1090:

1. The initial calibration of both instruments met all the requirements including: resolution, column performance checks, isotopic abundance ratios, signal-to-noise ratios, and the %RSD was less than 20%.

- 2. The continuing calibrations were within the limits set by Method 8290. Documentation of resolution was present and within the limits, CPSMs showed adequate separation of the 2,3,7,8-isomer from the others, RRFs were within 20% of the initial calibration and isotopic abundance ratios were within the limits.
- 3. With the exception listed above the method blanks met the requirements of EPA Method 8290.
- 4. With the exceptions listed above the isotopic abundance ratios and signal-to-noise ratio criteria were correct for all the samples and standards.

Thank you for the opportunity to work with Washington State Department of Ecology. If you have dioxin analysis projects in the future I would appreciate the chance to bid on them. I am also enclosing all of the raw data I received from Triangle for this project. If there are any further questions regarding this report, please do not hesitate to contact me at (916)-933-1640.

Sincerely,

William J. Luksemburg

Director of HRMS Services

MANCHESTER ENVIRONMENTAL LABORATORY

7411 Beach Drive SE, Port Orchard Washington 98366

CASE NARRATIVE

August 9, 1990

Subject:

Cascade Pole - Stormwater II

Samples:

90 - 178091, -178093, - 178095, -178097 and -178100.

Case No. DOE-407R

By:

Dickey D. Huntamer

Chemist - Organics Unit

SEMIVOLATILE ORGANICS

ANALYTICAL METHODS:

Semivolatile water samples were extracted with methylene chloride using the Manchester modification of the EPA CLP procedure with capillary GC/MS analysis of the sample extracts. All CLP QA/QC procedures were performed on the samples. Low detection limits were achieved by extracting approximately three liters of sample and concentrating the final extract to 0.5 mL for analysis.

HOLDING TIMES:

All sample extraction and analysis holding times were met. Samples were extracted within the seven day holding time and extracts were analyzed within the 40 day extract holding time.

SAMPLE HOLDING TIMES

Sample	Collect	Received	Extract	Analysis	Holding	g Times
. •	Date	Date	Date	Date	Extr.	Anal.
178091	4/25	4/26	4/30	5/23	5	23
178093	4/25	4/26	4/30	5/24	5	24
178095	4/25	4/26	4/30	5/24	5	24
178097	4/25	4/26	4/30	5/24	5	24
178100	4/25	4/26	4/30	5/24	5	24
178093 Y	4/25	4/26	4/30	5/24	5	24
178093 Z	4/25	4/26	4/30	5/24	5	24

BLANKS:

No significant blank contamination was detected.

SURROGATES:

All surrogate spike recoveries were within normal limits for CLP water recoveries except for d₅-Phenol in the dilution of sample 178093D where the surrogate was not detected. The remaining surrogates were within CLP limits.

MATRIX SPIKE AND MATRIX SPIKE DUPLICATE:

Matrix spikes compounds were added at one-fifth the normal spiking concentration of 50 ug to more closely approximate the low detection limits requested. No significant problems were encountered with recovering the matrix spike compounds at this level (3-5 ug/L). Although no matrix spike recovery limits have been established at this low level, spike recoveries were generally within the normal CLP recovery range found at higher matrix spike levels.

The Matrix Spike/Matrix Spike Duplicate (MS/MSD) Relative Percent Difference (RPD) for Benzo(b)fluoranthene at 41% exceeded the CLP limit. The RPDs for the remaining Polynuclear Aromatic Hydrocarbons (PAH) were within CLP guidelines.

SPECIAL ANALYTICAL PROBLEMS:

No analytical problems were encountered in the analysis. In the previous analysis one unusual item was the presence of anthracene without the corresponding detection of phenanthrene as is typically seen in environmental samples. This pattern repeated itself on the second sample set. Only anthracene was detected, except for sample 178091 in which 0.02J ug/L phenanthrene was detected but it was still less than the anthracene (0.08J ug/L).

The relatively high levels of Pentachlorophenol (PCP) in some of the samples permitted confirmation of its presence in the GC/ECD analysis by GC/MS. The semivolatile analysis report reflects the confirmation of the Herbicide analysis by reporting PCP with the "M" qualifier. The "M" qualifier means PCP was detected and confirmed but was not quantified using GC/MS.

VOLATILE ORGANICS

ANALYTICAL METHODS:

Volatile organic compounds were analyzed using Manchester modification of the EPA CLP purge-trap procedure with capillary GC/MS analysis. Normal CLP QA/QC procedures were performed on the samples.

BLANKS:

Low levels of the common laboratory solvents Acetone and methylene chloride were detected in the laboratory blanks BW0117 and BW0117D. In addition 1,2,3 -Trichlorobenzene and Naphthalene were also detected. The EPA 5 times rule was applied to all target compounds which were found in the blank. Compounds that were found in the sample and in the blank were considered real and not the result of contamination if the levels in the sample are greater than or equal to five times the amount of compounds in the associated method blank.

SURROGATES:

Surrogate recoveries were within CLP limits for all of the samples except for d 8-Toluene in sample 178091 which was 4% below the CLP limit. The two matrix spikes had low surrogate recoveries for three out of the four surrogate compounds. Only BFB was within limits, the others ranged from 3 to 13 percent below the CLP limits. No surrogates were added to the duplicate blank BW0117D and consequently no surrogate recoveries are reported.

HOLDING TIMES:

All samples were analyzed within the recommended 14 day holding time for water samples.

Sample	Collect	Received	Analysis	Holding Times	
	<u>Date</u>	Date	Date	Anal.	
178091	4/25	4/26	4/27	2	
178093	4/25	4/26	4/27	2	
178095	4/25	4/26	4/27	2	
178097	4/25	4/26	4/27	2	
178100	4/25	4/26	4/27	2	
178091 Y	4/25	4/26	5/1	6	
178091 Z	4/25	4/26	5/1	6	

SPECIAL ANALYTICAL PROBLEMS:

High levels of Naphthalene were detected in 178093 and 178097, 83 and 78 ug/L respectively. The Naphthalene was not detected in the corresponding semivolatile analysis at a quantitation limit of 0.2U ug/L. A review of the data indicated that a small amount of Naphthalene was present in sample 178093 but it was not reported since it was below 0.2 ug/L. The VOA GC/MS data was also reviewed and the results are summarized in the attached memo from Greg Perez, "Cascade Pole Stormwater Project". The available data indicates that the VOA samples may have been contaminated prior to arrival at the laboratory and that the Naphthalene is not native to the sample. This is supported by the 1H-Indene compounds detected as Tentatively Identified Compounds (TIC) in the semivolatile and VOA analysis which had essentially the same concentration in both fractions and the fact that the second duplicate VOA vial, 178093, when reanalyzed one month after the original analysis showed no naphthalene, whereas the second vial for 178095 had 71 ug/L Naphthalene. The high levels of Naphthalene also do not match the much lower levels of the other PAHs found in the sample which also corresponds to the first sampling event.

HERBICIDES

ANALYTICAL METHODS:

Extraction and analysis was accomplished following Manchester Lab modified EPA Method 615 for Herbicides and Pentachlorophenol (PCP), Tetrachlorophenol and Trichlorophenol.

BLANKS:

No significant blank contamination was found.

SURROGATES:

No surrogate recovery limits have been established for this method. Surrogate recoveries for this sample set ranged from 68% to 87% for 2,4,6-Tribromophenol. The surrogate in sample178093 was diluted out due to the high levels of PCP and Tetrachlorophenol.

HOLDING TIMES:

All sample extraction and analysis holding times were met. Samples were extracted within the seven day holding time and extracts were analyzed within the 40 day extract holding time.

		SAMPLE HOLDING TIMES_						
Sample	Collect	Received	Extract	Analysis	Holding Times			
	Date	Date	Date	Date	Extr.	Anal.		
178091	4/25	4/26	5/1	6/8	5	39		
178093	4/25	4/26	5/1	6/8	5	39		
178095	4/25	4/26	5/1	6/8	5	39		
178097	4/25	4/26	5/1	6/8	5	39		
178100	4/25	4/26	5/1	6/8	5	39		
178093 Y	4/25	4/26	5/1	6/8	5	39		
17809 3Z	4/25	4/26	5/1	6/8	5	39		

MATRIX SPIKE AND MATRIX SPIKE DUPLICATE:

The low level PCP matrix spike was indistinguishable from the native PCP in sample 178093 due to the high native levels of PCP. Consequently matrix spike recoveries could not be determined. This failure to distinguish spiked PCP from native PCP is not surprising since the sample contained over 100 times more native PCP than spiked PCP.

SPECIAL ANALYTICAL PROBLEMS:

No significant analytical problems were encountered other than the high PCP concentrations found in some of the samples which reflects the results of the first analysis. Samples 178093, 178095 and 178097 with 12.0, 52.1 and 55.5 ug/L PCP respectively were high enough in PCP that they were confirmed by GC/MS. The unfortunate choice of sample 178093, which contained 12.0 ug/L PCP, as the matrix spike resulted in failure to obtain meaningful PCP recovery and precision data.

DATA QUALIFIER CODES:

U - The material was analyzed for, but was not detected. The associated numerical value is the sample quantitation limit.

J - The associated numerical value is an estimated quantity.

R - The data are unusable (compound may or may not be present). Resampling and reanalysis is necessary for verification.

NAR - No Analytical Result.

M - The compound was detected and confirmed but was not quantitated.



STATE OF WASHINGTON

DEPARTMENT OF ECOLOGY

Post Office Box 307 • Manchester, Washington 98353-0346 • (206) 895-4740

August 2, 1990

TO:

Dick Huntamer

FROM:

Greg Perez

SUBJECT:

Cascade Pole Stormwater Project:

Sample Numbers 90178091, 90178093, 90178095, 90178097,

90178100

These five samples were analyzed for volatiles and semi-volatiles. A discrepancy has been noted between the two fractions. Naphthalene was verified in the volatile fraction of samples 095 and 097. It was not found in the semivolatile fraction of these two samples.

This is remarkable as naphthalene is more appropriately analyzed as a semivolatile and therefore should have been seen in the BNA fraction. Laboratory contamination is unlikely for several reasons.

The VOA method blank showed less than 1 ppb naphthalene background. Sample 095 contained 83 $\mu g/L$ and 097 contained 78 $\mu g/L$. Sample 093, analyzed just prior to 095 had none and 100 (the transport blank), had a trace which may be attributed to carryover from the previous samples.

This data was confirmed by the reanalysis of the samples 093 and 095 a month later. These two samples were reshot in late May, (the original analysis was in late April) in order to resolve a problem with low level background contamination in Sample 093. Sample 095 was reshot as a reference. Naphthalene was confirmed in the second vial of 095 at a level of 71 μ g/L. Sample 093 showed no naphthalene.

Comparing the VOA with the BNA data, Roy Araki and I found tentative compounds which were identified in both fractions: 1H-indene and 1H-indene, 2,3,-dihydro. These compounds are similar in structure to naphthalene, elute just before it and can generally be expected to behave in a similar fashion. The concentrations found in the two fractions correlated remarkably closely.

Dick Huntamer August 2, 1990 Page 2

The BNA analysis uses d10-naphthalene as a surrogate. Recoveries for this were normal. If naphthalene losses had occurred, it would be expected that this surrogate would have displayed low recoveries.

It is hard to believe in the face of these facts that the naphthalene is native to the sample. If it was it should have shown up in the BNA fraction.

I have no explanation for this occurrence, but I am certain it is not due to an analytical error. The April analysis if backed up by the second analysis in May.

GP:mb

cc: Bill Kammin

APPENDIX C

TENTATIVELY IDENTIFIED COMPOUNDS

Appendix C1:Tentatively Identified Organics in Cascade Pole Stormwater Samples Collected by Ecology March - April, 1990.

Station		CPW-1		CPW-2		CPW-3		
Sample No.	10-8080	17-8091	10-8082	17-8093	10-8084	10-8090	17-8095	17-8097
Date	3/9/90	4/25/90	3/9/90	4/25/90	3/9/90	Dup.	4/25/90	Dup.
Time	1035-1255	0935-1115	1135-1330	0920-1030	1115-1305	_	0950-1100	-
Tentatively Identified in Volatiles Fraction								
Benzofuran	_	МD		ИD		_	0.3jn	ND
7-methyl benzofuran	_	ND	_	ND	_	_	1.4jn	0.4jn
Tert-butylbenzene	-	ND	-	ND	_	_	ND	2.1jn
Isopropylbenzene		ND	_	ND	-	_	ND	0.6jn
1-methyl-1-propenyl benzene		DN	_	ND	_	_	2.4jn	ND
1-ethyl-3-methylbenzene	***	ND		ND	_	_	ND	0.9jn
1-ethynyl-4-methylbenzene	_	ND		ND	-	_	2.2jn	1.9jn
1-ethyl-2,4-dimethyl benzene		ND	_	ND	_	_	1.6jn	ND
4-ethyl-1,2-dimethylbenzene		ИD		ND	-	_	0.8jn	ND
1,2,3-trimethylbenzene	_	ND	_	ND	_	_	2.1jn	ND
1,2,4,5-tetramethylbenzene	-	ND	_	ND	-	-	ND	1.5jn
1-ethylidene-1H-indene	-	ND	_	ND		***	8.7jnb	7.6jnb
2,3-dihydro-1-methyl-1H-indene	_	ND		ND		-	0.9jn	1.3jn
2,3-dihydro-4-methyl-1H-indene		ND	_	ND	_	_	1.1jn	1.0jn
2,3-dihydro-5-methyl-1H-indene	-	ND)	_	ND	_	-	ND	1.4jn
2,3-dihydro-1,6-D-1H-indene	-	ND	_	ПD	_	_	1.2jn	ND
1,2,3,4-tetrahydro-naphthalene	-	ND	_	ND	_	_	1.2jn	1.1jn
p-isopropyltoluene	_	ND		ND	-	_	0.6jn	0.6jn
Benzo (b) thiophene		ND	_	ND	_	_	1.5jn	ND
3-phenyl-2-propenal		ND	_	ND	_	_	0.5jn	1.2jn
Indan		ND		ND	-	_	9.2jn	9.1jn
5,6-dimethyl indan	_	ND		ND	_	_	ND	1.1jn
1-(3-methylphenyl) ethanone	-	ND	-	ND	-		ND	0.7jn
Tentatively Identified in Semivolatiles Fract	ion							
2-methyl-1-butenyl benzene	ND	ND	ND	ND	ND	ND	0.6jn	ND
1,3-dimethyl-5(1-methyl) benzene	ИD	ND	ND	ND	ND	ИD	0.4jn	0.4jn
Diethylmethyl benzene	ND	ND	ND	ND	ND	ND	0.3jn	0.3jn
1-ethyl-2-methyl benzene	ND	ND	ND	ND	0.5jn	ND	ND	ND
1-ethyl-2,3 dimethyl benzene	ND	ND	ND	ND	0.9jn	ND	ND	NE
2-ethyl-1,4-dimethyl benzene	ND	ND	ND	ND	ND	0.9jn	ND	ND
1,3-diethyl benzene	ND	ND	ND	ND	ND	ND	0.09jn	ND
1-ethenyl-2-methyl benzene	ND	ND	ND	ND	0.7jn	ND	ND	NE
1-ethenyl-3-ethyl benzene	ND	ND	ND	ND	ND	ND	0.8jn	0.7jr
1,2,3-trimethylbenzene	ND	ND	ND	ND	ND	ND	0.2jn	0.2jn

⁻⁼Not analyzed

n=Presumptive evidence of material

b=Also detected in blank at low levels relative to sample

ND=Not detection at unspecified detection limit

j=Estimated concentration

Appendix C1: Continued (ug/l).

Station		CPW-1		CPW-2			CPW-3	
Sample No.	10-8080	17-8091	10-8082	17-8093	10-8084	10-8090	17-8095	17-8097
Date	3/9/90	4/25/90	3/9/90	4/25/90	3/9/90	Dup.	4/25/90	Dup.
Time	10351255	0935-1115	1135-1330	0920-1030	1115-1305	-	0950-1100	·_
Tentatively Identified in Semivolatiles Frac	ction							
1,3,5-trimethylbenzene	ND	ND	ND	ND	0.9jn	0.9jn	0.3jn	0.3jn
1,2,3,4-tetramethyl benzene	ND	ND	ND	ND	1.0jn	ND	ND	ND
Pentamethyl benzene	ND	ND	ND	ND	ND	ND	0.9jn	0.7jn
1H-indene	ND	ND	ND	ND	ND	ND	1.2jn	1.1jn
1-methyl-1H-indene	ND	ND	ИD	ND	ND	ND	0.6jn	ND
2,3-dihydro-1,2-D-1H-indene	ND	ND	ND	ND	ND	ND	0.3jn	ND
2,3-dihydro-1,6-D-1H-indene	ND	ND	ND	ND	ND	ND	0.3jn	0.2jn
2,3-dihydro-1-methyl-1H-indene	ND	ND	ND	ND	1.7jn	1.8jn	ND	ND
2,3-dihydro-4-methyl-1H-indene	ИD	ND	ND	ИD	ND	2.0jn	ND	ND
2,3-dihydro-4,7-D-1H-indene	ND	ND	ND	ND	1.4jn	ND	ND	0.6jn
2,3-dihydro-1,4,7-1H-indene	ND	ND	ND	ND	1.3jn	ND	ND	ND
2,3-dihydro-4,5,7-1H-indene	ND	ND	ND	ND	ND	ND	0.4jn	ND
2,3-dihydro-1H-inden-1-one	ND	ND	ND	ND	8.9jn	9.8jn	3.1jn	2.8jn
2,3-dihydro-1H-inden-1-ol	ND	ND	ND	ND	ND	ND	ND	0.8jn
4-chlorocyclohexanol	ND	0.1jn	ND	ND	ND	ND	ND	ND
1,2-dimethyl naphthalene	ND	ND	ND	ИD	1.1jn	ND	ND	ND
2,3-dimethyl naphthalene	ND	ND	ND	ND	2.0jn	ND	ND	ND
1,3,6-trimethyl naphthalene	ND	ND	ND	ND	0.9jn	ND	ND	ND
1,2,3,4-tetrahydro-naphthalene	ND	ND	ND	ND	ND	ND	ND	0.3jn
1-(2-propenyl) naphthalene	ND	ND	ND	ИD	ИD	ND	0.8jn	0.7jn
1,8-naphthalenedimethanol	ND	ND	ND	ND	ND	ND	ND	2.7jn
2.3.4.6-tetrachlorophenol	ND	ND	ND	ND	ND	ND	2.9jn	ND
2,3,5,6-tetrachlorophenol	ND	ND	ND	ND	ND	ND	ND	2.2)n
1,4-benzodioxin	ND	ND	ND	ND	ND	ND	0.6jn	0.6jn
7-methyl-benzofuran	ND	ND	ND	ND	ND	ND	ND	1.4jn
Benzo (b) thiophene	ND	ND	ND	ND)	1.2jn	ND	3.4jn	3.6jn
Tetradecanoic Acid	ND	0.2jn	ND	ND	ND	ND	ND	ND
3-phenyl-2-propenoic acid	ND	ND	ND	ND	ND	ND	1.5jn	ND
1-(3-methylphenyl) ethanone	ND	ND	ND	ND	ND	ND	0.20jn	ND
Indan	ND	ND 1	ND	ND	ND	ND	0.2jn	0.3jn
Molecular sulfur	ND	1.5jn	ND	ND	ND	ND	ND	ND

⁻⁼Not analyzed

ND=Not detection at unspecified detection limit

j=Estimated concentration

n=Presumptive evidence of material

b=Also detected in blank at low levels relative to sample