

Lower Duwamish Waterway Remedial Investigation

TECHNICAL MEMORANDUM: 2009/2010 SURFACE SEDIMENT SAMPLING RESULTS FOR DIOXINS AND FURANS AND OTHER CHEMICALS FINAL

For Submittal to:

The U.S. Environmental Protection Agency Region 10 Seattle, WA

The Washington State Department of Ecology Northwest Regional Office Bellevue, WA

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Acronyms					
Acronym	Definition				
сРАН	carcinogenic polycyclic aromatic hydrocarbon				
dw dry weight					
EPA US Environmental Protection Agency					
HxCDF	hexachlorodibenzofuran				
J-qualifier	estimated concentration				
LDW	Lower Duwamish Waterway				
LDWG	Lower Duwamish Waterway Group				
MS	matrix spike				
NAD83	North American Datum of 1983				
QAPP	quality assurance project plan				
РАН	polycyclic aromatic hydrocarbon				
РСВ	polychlorinated biphenyl				
RPD	relative percent difference				
QC	quality control				
RL	reporting limit				
RM	river mile				
TEQ	toxic equivalent				
SMS	Washington State Sediment Management Standards				
SQS	sediment quality standard				
U-qualifier	not detected at given concentration				

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1 Introduction

This technical memorandum presents chemistry results for surface sediment samples collected from 47 locations in the Lower Duwamish Waterway (LDW) in December 2009 and January 2010. The primary objective of the sampling was to supplement the existing dioxin and furan data for the LDW. Data from this study will be used in the feasibility study to help understand the spatial distribution of dioxins and furans in the LDW, to help identify the area of potential concern for remediation, and to help identify an appropriate range of remedial action levels. Sampling was conducted according to the objectives and methods presented in the surface sediment quality assurance project plan (QAPP) (Windward 2005), the surface sediment QAPP addendum (Windward 2009), and the follow-up memorandum (Windward 2010). This technical memorandum consists of a brief summary of the field sampling effort and results from the chemical analyses.

2 Field Sampling Summary and Deviations

In accordance with the QAPP (Windward 2005), the QAPP addendum (Windward 2009), and the follow-up memorandum (Windward 2010), 13 samples were collected from beach play exposure areas, and 34 samples were collected from other locations in the LDW (Table 1; Map 1). Six of the beach play exposure area samples were collected as composite samples using methods described in a follow-up memorandum (Windward 2010) to the QAPP addendum (Windward 2009).¹ The remaining 7 beach samples and 34 samples from other locations were collected as discrete grab samples, as described in the QAPP addendum. All discrete grab samples, except those from two locations (LDW-SS520 and LDW-SS547), were collected on December 15, 16, and 17, 2009. The six composite beach samples and the two remaining discrete grab samples were collected on January 11, 12, and 13, 2010. Field notes, completed sediment collection forms, and chain-of-custody forms are presented in Attachment 2.

¹ The beach composite samples at these six locations (LDW-SS502, LDW-SS503, LDW-SS529, LDW-SS531, LDW-SS533, and LDW-SS544) were composed of eight discrete grab samples collected from each beach area. The compositing of subsamples from each beach area was conducted at Analytical Resources, Inc., following their standard operating procedures, as approved by the US Environmental Protection Agency.



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Sampling		Target Location ^a Date (X) (Y)		Actual L	ocation ^a	Distance from	Depth Above (+) or Below (-)	
Location	Date			(X) (Y)		Target (m)	MLLW (ft)	
LDW-SS501	12/16/09	1267164	211254	1267109	211237	17.5	-12	
LDW-SS502	1/11/10	na	na	na	na	na	nd	
LDW-SS503	1/11/10	na	na	na	na	na	nd	
LDW-SS504	12/16/09	1266433	210638	1266433	210637	0.4	-50	
LDW-SS505	12/16/09	1267046	210623	1266992	210415	65.4	-18	
LDW-SS506	12/16/09	1266889	209889	1266882	209888	2.1	-26	
LDW-SS507 ^b	12/16/09	1266591	209082	1266590	209084	0.6	-34	
LDW-SS508	12/15/09	1267244	208449	1267256	208414	11.4	4	
LDW-SS509	12/15/09	1265896	208303	1265893	208313	3.2	6	
LDW-SS510	12/16/09	1267272	207564	1267267	207571	2.5	-32	
LDW-SS511	12/17/09	1268127	206756	1268130	206762	2.0	-28	
LDW-SS512	12/16/09	1267204	206499	1267199	206503	1.9	-8	
LDW-SS513	12/17/09	1268449	206550	1268462	206566	6.3	-12	
LDW-SS514	12/16/09	1266591	206442	1266590	206442	0.2	-4	
LDW-SS515	12/16/09	1268108	205990	1268107	205989	0.5	-10	
LDW-SS516	12/16/09	1268071	205142	1268068	205140	1.1	-36	
LDW-SS517	12/16/09	1268339	204985	1268340	204985	0.4	-14	
LDW-SS518	12/16/09	1268422	203897	1268422	203896	0.4	-36	
LDW-SS519	12/16/09	1268460	203398	1268501	203409	13.0	-34	
LDW-SS520	01/11/10	1269538	203298	1269537	203301	1.1	-12	
LDW-SS521	12/16/09	1268839	202847	1268841	202855	2.4	-32	
LDW-SS522	12/16/09	1270700	201639	1270703	201644	1.6	-12	
LDW-SS523 ^c	12/15/09	1269525	201243	1269533	201193	15.4	nd	
LDW-SS524	12/17/09	1270256	201060	1270233	201146	27.2	-16	
LDW-SS525	12/16/09	1270429	200277	1270444	200303	9.0	-2	
LDW-SS526	12/16/09	1270708	199995	1270659	200018	16.7	nd	
LDW-SS527 ^d	12/17/09	1271355	199940	1271351	199943	1.5	-8	
LDW-SS528	12/16/09	1273448	199166	1273475	199278	35.1	-6	
LDW-SS529	1/11/10	na	na	na	na	na	na	
LDW-SS530	12/15/09	1271937	198674	1271917	198658	7.9	nd	
LDW-SS531	1/12/10	na	na	na	na	na	na	
LDW-SS532	12/17/09	1273597	197751	1273597	197754	0.9	2	
LDW-SS533	1/12/10	na	na	na	na	na	na	
LDW-SS534	12/17/09	1273850	197251	1273849	197249	0.8	-18	
LDW-SS535	12/17/09	1274623	196836	1274605	196855	8.0	0	
LDW-SS536	12/17/09	1274834	196353	1274835	196351	0.7	-16	
LDW-SS537	12/17/09	1274924	196015	1274925	196014	0.4	nd	
LDW-SS538	12/17/09	1275532	195943	1275536	195947	1.8	-6	
LDW-SS539	12/17/09	1275628	195673	1275627	195675	0.8	-18	
LDW-SS540	12/17/09	1275568	195398	1275565	195403	1.8	2	
LDW-SS541	12/17/09	1275838	195145	1275840	195146	0.8	-14	
LDW-SS542	12/17/09	1275927	194186	1275930	194188	1.1	-4	

Table 1.Target and actual coordinates for LDW dioxin and furan sediment
sampling locations

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Sampling	Sampling		Target Location ^a		Actual Location ^a		Depth Above (+) or Below (-)	
Location	Date	(X)	(Y)	(X)	(Y)	Target (m)	MLLW (ft)	
LDW-SS543	12/17/09	1276850	191834	1276849	191839	1.4	-4	
LDW-SS544	1/12/10	na	na	na	na	na	na	
LDW-SS545	12/17/09	1277541	190499	1277543	190498	0.7	-8	
LDW-SS546	12/17/09	1278567	190208	1278586	190150	18.7	nd	
LDW-SS547	01/11/10	1277573	189993	1277573	190001	2.4	nd	

^a Coordinates reported in NAD83 horizontal datum; X and Y coordinates are in Washington State Plane N (US survey ft).

^b Field duplicate LDW-SS602-010 was collected at this location.

^c Field duplicate LDW SS601-010 was collected at this location.

^d Field duplicate LDW-SS603-010 was collected at this location.

LDW – Lower Duwamish Waterway

na – not applicable (these beach locations represent a composite of eight samples; sampled areas are shown on Map 1)

nd – no data (gap in bathymetry coverage or outside the bathymetry survey area)

NAD83 – North American Datum of 1983

The target depth for collection of all samples was 0-10 cm, with the exception of composite samples collected at three beach locations (LDW-SS503, LDW-SS529, and LDW-SS533), each of which had a target depth of 0-45 cm. The target depth was not reached at some of the subsample locations at these three beach locations because hard sediment substrate was encountered. The average depth for the eight subsamples collected at each of these three beach locations was 43 cm for LDW-SS503 (Beach 1), 41 cm for LDW-SS529 (Beach 6), and 43 cm for LDW-SS533 (Beach 5).

Field duplicate samples were collected and analyzed such that one duplicate analysis was conducted for every 20 analyses for each analyte, with the exception of dioxins and furans, which were not analyzed in field duplicate samples. Instead, results of laboratory duplicate samples were used to provide the measure of precision for dioxin and furan analyses in accordance with the QAPP addendum (Windward 2009).

Field deviations from the QAPP (Windward 2005), QAPP addendum (Windward 2009), and follow-up memorandum (Windward 2010) included modifications to the sampling locations and dates; data quality and sampling objectives were not affected. The field deviations were as follows:

- Nine discrete grab samples were each collected more than 10 m from their target locations. The rationale for the relocation of each of these samples is presented in Table 2, and the target and actual sampling locations are shown on Map 1.
- Many of the randomly selected subsample locations for the beach composite samples could not be sampled at the pre-selected target locations² because they

² Locations were determined by dividing the beach area into eight segments and randomly assigning a sampling location within each segment.



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were either under water or the substrate was rocky. New subsample locations were randomly selected, as necessary, in the field in coordination with and under the oversight of the US Environmental Protection Agency (EPA), as described in the field notes presented in Attachment 2.

- Two of the discrete grab samples were collected in January 2010 rather than in December 2009. LDW-SS547 was initially sampled in December, but the location was off-target because the target coordinates had been entered incorrectly by the boat captain. Therefore, LDW-SS547 was re-sampled at the target location in January. LDW-SS520 could not be sampled until January because the access agreement with the property owners had not been finalized in December.
- At beach composite location LDW-SS531, one of the subsamples was inadvertently left on the beach during the evening low-tide sampling on January 12, 2010. This subsample location was re-sampled the following morning at low tide.

Table 2. Locations where samples were collected > 10 m from their target coordinates

Sampling Location	Rationale
LDW-SS501	Location was moved 17 m west of the target location after six unsuccessful attempts were made. ^a
LDW-SS505	Location could not be sampled because it was within the Ash Grove Cement barge off- loading area, so the location was moved 65 m south. ^a
LDW-SS508	Location was moved 11 m so sample could be collected between the two outfalls. ^a
LDW-SS519	Sample was collected approximately 12 m from the target location because of a discrepancy in the boat location positioning system.
LDW-SS523	Location was moved 15 m so sample could be collected closer to the outfall. ^a
LDW-SS524	Location was moved 27 m north because a barge was situated at the target location. ^b
LDW-SS526	Location was moved 17 m so the sample could be collected closer to the outfall. ^a
LDW-SS528	Location was moved 35 m toward the head of Slip 4 based on a discussion between LDWG and EPA.
LDW-SS546	Target coordinates were on land, so the sampling location was moved 35 m from the target location to be near the outfall, $^{\rm b}$

^a Location modifications were made in coordination with EPA oversight at the time of sampling.

^b EPA was informed of sampling location modification immediately after sampling and had no objections. EPA – Environmental Protection Agency

EPA – Environmental Protection Agency

LDWG – Lower Duwamish Waterway Group



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3 Chemistry Results

All of the 47 grab and composite surface sediment samples were analyzed for dioxin and furan congeners, grain size, total organic carbon, and percent moisture. In addition, each of the 13 beach samples (both composites and grabs) was also analyzed for arsenic, polychlorinated biphenyls (PCBs) (as Aroclors), and polycyclic aromatic hydrocarbons (PAHs). PAHs were analyzed so that carcinogenic PAH³ (cPAH) toxic equivalents (TEQs) could be calculated. Dioxin and furan congener data were also used to calculate TEQs.⁴ The analytical results for all individual chemicals for each sample, including field duplicates, are presented in Attachment 1 and are available online.⁵ Laboratory report forms are presented in Attachment 4.

Dioxin and furan TEQs ranged from 0.341 to 74.5 ng/kg dry weight (dw) in the grab samples and from 1.71 to 8.99 ng/kg dw in the beach composite samples (Table 3 and Map 2). The highest dioxin and furan TEQ was in the grab sample collected from the northern end of Beach 2 (location LDW-SS509), just south of River Mile (RM) 0.5 on the west side of the LDW (Map 2). The highest arsenic, cPAH, and total PCB concentrations (93.8 mg/kg dw, 7,100 μ g/kg dw, and 860 μ g/kg dw, respectively) were detected in the beach composite sample collected at Beach 6 (location LDW-SS529), which is located near RM 2.8 on the east side of the LDW (Map 3). A total PCB concentration of 860 μ g/kg dw was also detected in the grab sample collected from Beach 5 (location LDW-SS530) near RM 2.7 on the west side of the LDW (Map 3). Map 4 shows the dioxin and furan data from the 2009/2010 sampling event, along with historical data from previous sampling events.

	Detection		Detected Concentration			
Chemical	Frequency	Unit	Minimum	Maximum	Mean	
Beach Composite Samples						
Arsenic	6/6	mg/kg dw	4.3	93.8	24	
cPAH TEQ	6/6	µg/kg dw	29 J	7,100 J	1,300	
Total PCBs ^a	6/6	µg/kg dw	21	860	230	
Dioxin/furan TEQ	6/6	ng/kg dw	1.71 J	8.99 J	4.26	

Table 3.	Summary statistics for human health risk driver chemicals in
	beach composite and grab surface sediment samples

⁴ Dioxin and furan TEQs were calculated as the sum of the products of individual dioxin and furan congeners and congener-specific toxicity equivalency factors from Van den Berg et al. (2006). One-half the reporting limit was used for non-detected congeners when calculating dioxin and furan TEQs.

⁵ Available at <u>http://www.ldwg.org</u>.



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³ Total cPAHs were calculated as the sum of the products of the seven individual cPAH compounds (benzo(a)anthracene, benzo(b)fluoranthene, benzo(a)pyrene, benzo(kfluoranthene, chrysene, dibenzo(a,h)anthracene, and indeno(1,2,3-cd)pyrene) and their compound-specific potency equivalency factors from California Environmental Protection Agency (1994). One-half the reporting limit was used for non-detected cPAH compounds when calculating total cPAHs.

	Detection		Detected Concentration			
Chemical	Frequency	Unit	Minimum	Maximum	Mean	
Grab Samples						
Arsenic	8/8	mg/kg dw	3.8	19.1	11	
cPAH TEQ	7/8	µg∕kg dw	37 J	4,400 J	1,200	
Total PCBs ^a	7/8	µg/kg dw	19.6	860	280	
Dioxin/furan TEQ	41/41	mg/kg dw	0.341 J	74.5 J	9.66	

^a For PCB Aroclors, the total PCB concentration represents the sum of detected concentrations of nine individual PCB Aroclors for a given sample. For samples in which none of the individual Aroclors were detected, the maximum RL for an individual PCB Aroclor in that sample was used as the concentration.

cPAH – carcinogenic polycyclic aromatic hydrocarbon dw – dry weight

PCB – polychlorinated biphenyl RL – reporting limit

J – estimated concentration

TEQ – toxic equivalent

In addition to the analytes discussed above, two samples (beach composite sample LDW-SS502 and grab sample LDW-SS527) were analyzed for the full suite of Washington State Sediment Management Standard (SMS) chemicals at the request of the Washington State Department of Ecology. There were no exceedances of the sediment quality standards (SQS) in either of these two samples.⁶ All data are presented in Attachment 1.

4 Data Validation Results

Independent third-party data validation was conducted by Laboratory Data Consultants, Inc. (LDC), following EPA guidance (EPA 1995, 2004, 2005, 2008), as described in Section 5.0 of the original QAPP (Windward 2005). There were no laboratory deviations to the methods outlined in the QAPP (Windward 2005), QAPP addendum (Windward 2009), or follow-up memorandum (Windward 2010).

All dioxin and furan data underwent full-level data validation. For all other analytical data, a minimum of 20% of samples or one sample per delivery group underwent full-level data validation. Summary-level validation was performed on the rest of the data using all the quality control (QC) forms submitted in the laboratory data package. All QAPP (Windward 2005) and QAPP addendum (Windward 2009) requirements for data validation were met.

Based on the information reviewed, the overall data quality was considered acceptable for all uses, as qualified. The data validation reports prepared by LDC (Attachment 3) include a summary of field duplicate results for detected SMS chemicals. Results for the sample and associated field duplicate are comparable and do not indicate any concerns for data usability. Data did not require qualification

⁶ Chemical concentrations in the composite sample LDW-SS502 were compared to the SQS only for informational purposes because SMS criteria are not applicable to large areas represented by composite samples.



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based on the rinsate blank results, which are included in the data validation reports. Issues that resulted in the qualification of data are summarized below. Detailed information regarding every qualified sample is presented in the data validation reports in Attachment 3.

- Two furan concentrations were J-qualified as estimated because of the high relative percent difference (RPD) between the concentration in the sample and that in its laboratory duplicate sample (i.e., 1,2,3,4,7,8-hexachlorodibenzofuran [HxCDF] in sample LDW-SS534-010 and 2,3,4,6,7,8-HxCDF in sample LDW-SS520-010) (see Table A-1-5 in Attachment 1).
- Three samples (LDW-SS502-010-comp, LDW-SS527-010, and LDW-SS603-010 [the field duplicate of LDW-SS527-010]) each had concentrations of 2,4-dinitrophenol, 3,3-dichlorobenzidine, 4-chloroaniline, aniline, hexachlorobenzene, hexachlorocyclopentadiene, and n-nitrosodiphenylamine, which were UJ-qualified because the associated calibration verification or laboratory control sample results were outside of QC limits.
- All detected concentrations of benzo(b)fluoranthene and benzo(k)fluoranthene were J-qualified as estimated because of a lack of resolution between the isomeric peaks. A total peak quantitation was performed, and the average concentration of the single peak was reported for both compounds.
- Fluoranthene in sample LDW-SS601-01 was J-qualified as estimated because the matrix spike (MS) recovery was above QC limits.
- All Aroclor 1268 concentrations were UJ-qualified because of the low response in the associated initial calibration verification samples.
- All antimony concentrations were J- or UJ-qualified because of low MS recovery (13%); the post-digestion spike concentrations were within QC limits.
- All nickel concentrations were J- or UJ-qualified because of high RPD between the concentrations of the sample and its laboratory duplicate sample.

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