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Sediment Sampling of Proposed Dredge Sites in the Confluence of the Snake and Clearwater Rivers

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January 1992

Prepared for the
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Pacific Northwest Laboratory
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**SEDIMENT SAMPLING OF PROPOSED
DREDGE SITES IN THE CONFLUENCE
OF THE SNAKE AND CLEARWATER RIVERS**

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SUMMARY

Battelle/Marine Sciences Laboratory (MSL) conducted this study for the U.S. Army Corps of Engineers (USACE), Walla Walla District. The purpose of the study was to measure the concentration of dioxins in sediment proposed to be dredged from the Lower Granite Reservoir near Lewiston, Idaho, and compare it to concentrations found at the reference sites.

The area to be dredged is immediately adjacent to and downstream from an effluent discharge pipe belonging to the Potlatch Corporation's pulp mill. Information provided by the Environmental Protection Agency (EPA) indicate the need to test for dioxins and furans in sediments of waters adjacent to and downstream of pulp mill effluents because of the by-product created through the chlorination process.

Thirty-three sampling stations were identified from which sediments were then collected using either a 4-in. vibratory-hammer coring device or a van Veen or Ponar grab sampler. All 33 sampling stations were composited and analyzed for total organic carbon and grain size. Nine of the 33 stations were also analyzed for dioxins and furans.

Grain-size results indicated the majority of sediments consisted of silty sands. A smaller number of samples consisted of sandy silts. All samples contained less than 15% clay with the exception of one, which contained approximately 20% clay. Total organic carbon concentrations for the Snake River sediment samples ranged from 0.08% to 2.91%, with the majority of samples above 1.0%.

Some chlorinated dioxin congeners were detected in all nine of the sediment samples analyzed for dioxins and furans. Concentrations in those samples ranged from approximately 2.2 pptr for total tetrachlorodibenzodioxin (TCDD) to 100 pptr for octachlorodibenzodioxin (OCDD). No samples showed concentrations of 2,3,7,8 TCDD at detection limits ranging from 0.34 pptr to 1.5 pptr. These ranges are within the target detection limit of 1 pptr. Chlorinated furans were detected in all samples ranging from 0.12 pptr (1,2,3,4,6,7,8 hexachlorodibenzofuran) to 9.9 pptr [octochlorodibenzofuran (OCDF)]. Chlorinated furan concentrations of 2,3,7,8 tetrachlorodibenzofuran (TCDF) ranged from 0.38 pptr to 5.6 pptr, with the higher concentration being that of the reference site. The higher concentration of TCDF for the

reference site may be related to grain size and its relatively high organic carbon concentration, a substance with which dioxin/furan materials are closely associated. Ranges for OCDD and OCDF were 8.7 to 150 and 0.48 pptr, respectively. According to EPA Method 8290, the presence of OCDD and OCDF is not considered a problem because of their ubiquitous nature.

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1.0 INTRODUCTION

The Lower Granite Reservoir is part of a larger waterway that provides slackwater navigation from the Pacific Ocean to the Lewiston, Idaho, area. The reservoir includes a levee system designed to protect large areas of industrial, commercial, and residential properties in the Lewiston area from inundation by waters impounded behind the Lower Granite Dam. The dam and reservoir also provide power generation capabilities and recreational opportunities.

Sediment accumulation in the Lower Granite Reservoir has reduced the designed capability of the Lewiston levee system for flood protection and has affected authorized navigation. Dredging this accumulated sediment at the confluence of the Snake and Clearwater rivers is one alternative being considered by the U.S. Army Corps of Engineers (USACE), Walla Walla District, to reduce sediment accumulation. If the dredging alternative is used, it could mean the annual disposal of 800,000 to 1,200,000 cubic yards of deposited sediment in downstream waters. Sediments from two previous dredging events have been disposed downstream of the confluence in deep and mid-depth disposal sites. Dredged material was also used to create an island near the disposal site. Based on the statements set forth in the Clean Water Act (33 U.S.C. 1341 and 1344), there must be adequate evaluation of water and sediment characteristics before dredging and disposal activities commence.

The area to be dredged is immediately adjacent to and downstream from an effluent discharge pipe belonging to the Potlatch Corporation's pulp mill; therefore, there is some concern that nearby sediments may be contaminated with dioxins and furans. The USACE asked the Battelle/Marine Sciences Laboratory (MSL),^(a) to perform a study to measure the concentration of dioxins in the sediment proposed for dredging and subsequently compare it to concentrations found at the reference site. This evaluation is necessary to obtain state water quality certification.

Information provided by the U.S. Environmental Protection Agency (EPA) indicate the need to test sediments for dioxins and furans when associated with pulp mill effluents because of the by-product created through the chlorination process. Effluent and sludge from holding tanks used by the Potlatch Corporation's pulp mill were found to contain concentrations of 71

(a) The Marine Sciences Laboratory is part of the Pacific Northwest Laboratory, which is operated for the U.S. Department of Energy by Battelle Memorial Institute.

to 79 parts per quadrillion (ppqd) and 79 parts per trillion (pptr) of 2,3,7,8 tetrachlorodibenzo-p-dioxin (2,3,7,8TCDD), respectively. This compound is one of the primary dioxins of concern. As a result of the recent concerns with dioxins/furans, a sampling program was designed by the MSL in conjunction with the USACE, Walla Walla District; USACE, North Pacific Division; and USACE's Waterways Experiment Station.

This report contains four sections. Section 2.0 details the methods used in the study, Section 3.0 presents the quality control summary and results, and Section 4.0 contains the reference cited.

2.0 METHODS

The field-sampling program designed jointly by the MSL and USACE included 11 transects (2 to 4 sampling sites per transect) and 2 additional reference sites (Figure 2.1). The reference sites were carefully chosen to ensure a lack of contamination by previously disposed dredged material.

The sites were positioned between Snake River Mile (RM 119.56 and 140.22, and Clearwater RM 0.28 and 0.53). Thirty-three stations were identified for sampling purposes (Tables 2.1 and 2.2). A 4-in.-diameter vibratory-hammer coring device, or a van Veen or Ponar grab sampler was used to collect sediment to the depth of the original river bed materials, where water depths ranged from 16 to 85 ft. Original river bed materials, typically cobble and gravel in consistency, were not included in the samples because chemical binding in large particle-size materials of non-organic nature is unlikely. Selected sediment cores (three per site) were collected from within the entire area proposed for dredging. Only material from the sample site most likely to contain dioxins (based on TOC content from previous sediment sampling events) and the two reference sites were analyzed for dioxins and furans. Bulk sediment, volatile solids, and TOC analyses were conducted on composited samples from all sampling stations (33 designated, plus 7 samples from composites of cores longer than 4 ft). Sediments remaining after compositing and subsampling for chemistry, were archived at 0°C.

2.1 FIELD SAMPLING

Sediment sampling occurred between October 25 and October 30, 1990. Collection of sediment samples was performed aboard a subcontracted derrick barge (supplied by Hickey Marine Enterprises) equipped with a spud anchoring system and positioned with a tug-boat (supplied by Tidewater Terminal Company). Test stations were determined by line-of-sight to land monuments. Range markers flagged with orange tape (by USACE personnel) were placed on both banks of the stream channel. The markers allowed the field crew to locate the transect line for each station. Individual stations within each transect were located using charts of the river bathymetry. Each river cross section provided information regarding distance in ft (from left to right bank looking downstream) of each sampling site and necessary core lengths based on the river stage for that day. Because the river stage was subject to

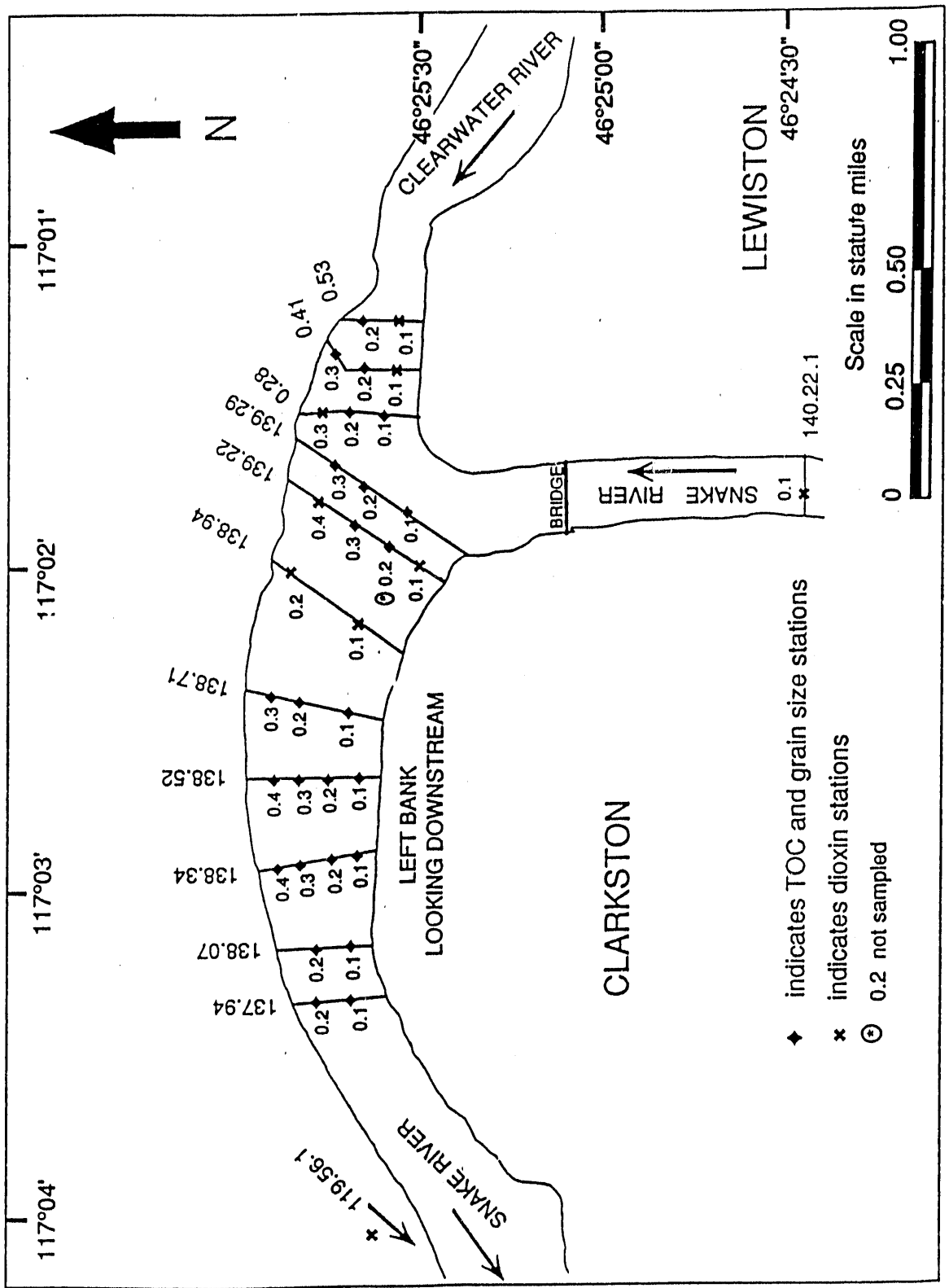


FIGURE 2.1. Snake River Sampling Stations

TABLE 2.1. Clearwater River Sampling Stations

| <u>Sampling Station</u> | <u>Replicate</u> | <u>Date</u> | <u>Water Depth</u> | <u>Core Length</u> | <u>Composite in 4-in. Sections</u> | <u>Dioxin Station</u> |
|-------------------------|------------------|-------------|--------------------|--------------------|------------------------------------|-----------------------|
| 0.53.1 | 1 | 10/26/90 | 19' | 2'0" | | |
| 0.53.1 | 2 | 10/26/90 | | 2'6" | | |
| 0.53.1 | 3 | 10/26/90 | | 2'6" | | |
| 0.53.1 | 1,2,3 | 10/26/90 | | | | DX |
| 0.53.2 | 1 | 10/26/90 | 33' | 1'6" | | |
| 0.53.2 | 2 | 10/26/90 | | 1'3" | | |
| 0.53.2 | 3 | 10/26/90 | | 1'3" | | |
| 0.41.1 | 1 | 10/26/90 | 22' | 4'0" | | |
| 0.41.1 | 2 | 10/26/90 | | 2'6" | | |
| 0.41.1 | 3 | 10/26/90 | | 3'0" | | |
| 0.41.1 | 1,2,3 | 10/26/90 | | | | DX |
| 0.41.2 | 1 | 10/26/90 | 24' | 1'0" | | |
| 0.41.2 | 2 | 10/26/90 | | 1'7" | | |
| 0.41.2 | 3 | 10/26/90 | | 1'6" | | |
| 0.41.3 | 1 | 10/26/90 | 26' | 1'10" | | |
| 0.41.3 | 2 | 10/26/90 | | 2'5" | | |
| 0.41.3 | 3 | 10/26/90 | | 2'2" | | |
| 0.28.1 | 1 | 10/26/90 | 23' | 5'2" | X | |
| 0.28.1 | 2 | 10/26/90 | | 6'2" | X | |
| 0.28.1 | 3 | 10/26/90 | | 5'2" | X | |
| 0.28.2 | 1 | 10/26/90 | 19' | 4'7" | X | |
| 0.28.2 | 2 | 10/26/90 | | 4'10" | X | |
| 0.28.2 | 3 | 10/26/90 | | 6'0" | X | |
| 0.28.3 | 1 | 10/26/90 | 21' | 4'11" | X | |
| 0.28.3 | 2 | 10/26/90 | | 4'7" | X | |
| 0.28.3 | 3 | 10/26/90 | | 8'0" | X | |
| 0.28.3 | 1,2,3 | 10/26/90 | | | | DX |

TABLE 2.2. Snake River Sampling Stations

| <u>Sampling Station</u> | <u>Replicate</u> | <u>Date</u> | <u>Water Depth</u> | <u>Core Length</u> | <u>Composite in 4" Sections</u> | <u>Dioxin Station</u> |
|-------------------------|------------------|-------------|--------------------|--------------------|---------------------------------|-----------------------|
| 139.29.1 | 1 | 10/27/90 | 22' | 2'2" | | |
| 139.29.1 | 2 | 10/27/90 | | 1'2" | | |
| 139.29.1 | 3 | 10/27/90 | | 10" | | |
| 139.29.2 | 1 | 10/27/90 | 21' | 3'0" | | |
| 139.29.2 | 2 | 10/27/90 | | 1'2" | | |
| 139.29.2 | 3 | 10/27/90 | | 2'7" | | |
| 139.29.3 | 1 | 10/27/90 | 21' | 2'2" | | |
| 139.29.3 | 2 | 10/27/90 | | 4'5" | X | |
| 139.29.3 | 3 | 10/27/90 | | 6'0" | X | |
| 139.22.1 | 1 | 10/27/90 | 25' | 2'11" | | |
| 139.22.1 | 2 | 10/27/90 | | 2'2" | | |
| 139.22.1 | 3 | 10/27/90 | | 1'3" | | |
| 139.22.1 | 1,2,3 | 10/27/90 | | | | DX (a) |
| 139.22.2 | 1 | 10/27/90 | 38' | No Sample (b) | | |
| 139.22.2 | 2 | 10/27/90 | | No Sample | | |
| 139.22.2 | 3 | 10/27/90 | | No Sample | | |
| 139.22.3 | 1 | 10/27/90 | 31' | 2'7" | | |
| 139.22.3 | 2 | 10/27/90 | | 3'4" | | |
| 139.22.3 | 3 | 10/27/90 | | 3'0" | | |
| 139.22.4 | 1 | 10/27/90 | 27' | 5'1" | X | |
| 139.22.4 | 2 | 10/27/90 | 5'9" | | X | |
| 139.22.4 | 3 | 10/27/90 | 5'7" | | X | |
| 139.22.4 | 1,2,3 | 10/27/90 | | | | DX |
| 138.94.1 | 1 | 10/28/90 | 24' | 4'2" | X | |
| 138.94.1 | 2 | 10/28/90 | 4'4" | | X | |
| 138.94.1 | 3 | 10/28/90 | 5'0" | | X | |
| 138.94.1 | 1,2,3 | 10/28/90 | | | | DX |
| 138.94.2 | 1 | 10/28/90 | 38' | 1'0" | | |
| 138.94.2 | 2 | 10/28/90 | | 1'6" | | |
| 138.94.2 | 3 | 10/28/90 | | 2'4" | | |
| 138.94.2 | 1,2,3 | 10/28/90 | | | | DX |

TABLE 2.2. (contd)

| <u>Sampling Station</u> | <u>Replicate</u> | <u>Date</u> | <u>Water Depth</u> | <u>Core Length</u> | <u>Composite in 4" Sections</u> | <u>Dioxin Station</u> |
|-------------------------|------------------|-------------|--------------------|--------------------|---------------------------------|-----------------------|
| 138.71.1 | 1 | 10/28/90 | 16' | 2'3" | | |
| 138.71.1 | 2 | 10/28/90 | | 2'3" | | |
| 138.71.1 | 3 | 10/28/90 | | 3'11" | | |
| 138.71.2 | 1 | 10/28/90 | 22' | 2'3" | | |
| 138.71.2 | 2 | 10/28/90 | | 4'0" | | |
| 138.71.2 | 3 | 10/28/90 | | 5'5" | X | |
| 138.71.3 | 1 | 10/28/90 | 26' | 2'5" | | |
| 138.71.3 | 2 | 10/28/90 | | 1'1" | | |
| 138.71.3 | 3 | 10/28/90 | | 2'7" | | |
| 138.52.1 | 1 | 10/28/90 | 21' | 3'0" | | |
| 138.52.1 | 2 | 10/28/90 | | 2'4" | | |
| 138.52.1 | 3 | 10/28/90 | | 3'4" | | |
| 138.52.2 | 1 | 10/28/90 | 21' | 2'1" | | |
| 138.52.2 | 2 | 10/28/90 | 26' | 1'5" | | |
| 138.52.2 | 3 | 10/28/90 | 24' | 2'2" | | |
| 138.52.3 | 1 | 10/28/90 | 24' | 2'1" | | |
| 138.52.3 | 2 | 10/28/90 | | 1'5" | | |
| 138.52.3 | 3 | 10/28/90 | | 2'2" | | |
| 138.52.4 | 1 | 10/28/90 | 30' | 10" | | |
| 138.52.4 | 2 | 10/28/90 | | 1'0" | | |
| 138.52.4 | 3 | 10/28/90 | | 1'10" | | |
| 138.34.1 | 1 | 10/29/90 | 23' | 2'3" | | |
| 138.34.1 | 2 | 10/29/90 | | 2'4" | | |
| 138.34.1 | 3 | 10/29/90 | | 2'7" | | |
| 138.34.2 | 1 | 10/29/90 | 23' | 2'3" | | |
| 138.34.2 | 2 | 10/29/90 | | 1'7" | | |
| 138.34.2 | 3 | 10/29/90 | | 1'5" | | |
| 138.34.3 | 1 | 10/29/90 | 23' | 1'6" | | |
| 138.34.3 | 2 | 10/29/90 | | 1'0" | | |
| 138.34.3 | 3 | 10/29/90 | | 1'6" | | |

TABLE 2.2. (contd)

| <u>Sampling Station</u> | <u>Replicate</u> | <u>Date</u> | <u>Water Depth</u> | <u>Core Length</u> | <u>Composite in 4" Sections</u> | <u>Dioxin Station</u> |
|-------------------------|------------------|-------------|--------------------|--------------------|---------------------------------|-----------------------|
| 138.34.4 | 1 | 10/29/90 | 29' | 1'4" | | |
| 138.34.4 | 2 | 10/29/90 | | 1'3" | | |
| 138.34.4 | 3 | 10/29/90 | | 1'11" | | |
| 138.07.1 | 1 | 10/29/90 | 27' | 2'1" | | |
| 138.07.1 | 2 | 10/29/90 | | 2'0" | | |
| 138.07.1 | 3 | 10/29/90 | | 1'3" | | |
| 138.07.2 | 1 | 10/29/90 | 31' | 1'2" | | |
| 138.07.2 | 2 | 10/29/90 | | 1'0" | | |
| 138.07.2 | 3 | 10/29/90 | | 8" | | |
| 137.94.1 | 1 | 10/29/90 | 30' | 1'7" | | |
| 137.94.1 | 2 | 10/29/90 | | 3'8" | | |
| 137.94.1 | 3 | 10/29/90 | | 2'5" | | |
| 137.94.2 | 1 | 10/29/90 | 33' | 1'1" | | |
| 137.94.2 | 2 | 10/29/90 | | 1'11" | | |
| 137.94.2 | 3 | 10/29/90 | | 1'10" | | |
| 119.56.1 | 1 | 10/30/90 | 85' | Ponar Grab | | |
| 119.56.1 | 1 | 10/30/90 | | van Veen Grab | | |
| 119.56.1 | 2 | 10/30/90 | | van Veen Grab | | |
| 119.56.1 | 3 | 10/30/90 | | van Veen Grab | | DX |
| 140.22.1 | 1 | 10/28/90 | 24' | Ponar Grab | | DX |

(a) DX indicates Dioxin Station.

(b) No sample taken because same water depth and sediment consistency as 139.22.1.
The remaining three buoys were spread out evenly over the channel.

change, water depths and core lengths were determined daily. Actual core lengths at each station ranged from 1.0 to 8.0 ft. After calculating water depths, MSL's 17-ft Boston Whaler was positioned along the transect line until it reached the appropriate distance from the left bank and the correct water depth (using a depth finder) as indicated on the sediment cross sections. Then, weighted buoys were released to indicate station position. To further identify the site, compass bearings were taken to easily recognized landmarks and recorded in the core logs.

A 4-in.-diameter vibratory-hammer coring device equipped with a steam-cleaned Lexan liner was lowered to the sediment surface and then hammered into the surface of the original river bed material. Actual core samples were collected down to the surface of the original river bed. Various methods were used to retain sediment in the core liner. For sandy and fine-grained sediments, a flapper valve was placed on the end of the core barrel to catch and hold sediments. Coarser, less cohesive sediments required the use of a core catcher and cutterhead. Three core samples were collected from each of 33 sites for a total of 93 cores. The remaining two sites required a van Veen grab for sediment collection. Pertinent information regarding sampling procedures was noted in core logs. Core samples were then capped and, if necessary, cut into 4-ft sections. Each core was labeled and stored at 4°C in a refrigerated container located on the barge. The cores were off-loaded nightly into a refrigerated truck and maintained at 4°C. After completion of the field work, each core was recorded on a chain-of-custody form and shipped to the MSL via a refrigerated truck.

Reference site Snake RM 140.22 was sampled with a Ponar grab sampler (0.06 m²); site Snake RM 119.56 was sampled using a van Veen (0.1m²). At site Snake RM 140.22, a Ponar grab sample was taken to determine if the sediment was suitable for coring. The sediment proved to be too fine and liquified for the vibratory-hammer sampler to retain cored sediment, consequently 4 gal of sediment was collected using the Ponar grab. The collected sediment was then composited and subsampled for chemistry. At site Snake RM 119.56 the water depth was 85 ft, which was beyond the 50-ft operational depth for using the vibratory-hammer sampler. Attempts were made to drive a core barrel into the sediment but this method proved unsuccessful because of the fine consistency of the sediment. Finally, a van Veen grab was used to collect approximately 6 gal of sediment; any sediment in contact with the grab sampler was removed before compositing. The grab samples were labeled and stored at 4°C until subsampled for chemistry.

2.2 COMPOSITING OF CORE SAMPLES FOR CHEMICAL ANALYSIS

Upon receipt of samples at MSL, cores were inventoried against chain-of-custody forms and stored at 4°C until needed for compositing. The original compositing scheme required splitting the cores longitudinally, compositing the 4-ft sections, and subsampling for chemistry (grain size and TOC). Aliquots from each section were then combined and subsampled for dioxin analysis. Nine stations were subsampled for dioxins. Any sediment not used for chemical analysis was archived and stored at 0°C in the event that further analysis is required. This original compositing scheme and selection of sampling stations was designed by USACE. Because of the semi-solid nature of the cores, a slightly different compositing scheme developed by USACE and MSL personnel was performed. The cores were uncapped at one end and the sediment was gently slid out of the liner into a clean stainless steel bowl. This procedure consistently provided a sample that was relatively intact. Each sample was geologically described, and all pertinent information about the sample was recorded on core data log sheets. Any core length greater than 4 ft long was subsampled for chemistry according to the original compositing scheme. A total of seven sites had cores greater than 4 ft in length and were subsampled and chemically analyzed. The remaining 26 sites produced cores less than 4 ft long, so the entire core was composited and subsampled for grain size, TOC, and where appropriate, dioxins. Before subsampling for chemistry, all the cores were mixed to a uniform homogenous consistency.

Dioxin, TOC, and archived samples were collected in glass jars certified for EPA Contract Laboratory Programs (CLP) (I-chem Research). Dioxin samples were kept at 4°C until analyzed. The TOC samples were freeze dried before analysis. Archived samples are maintained in freezers in the event that further analysis is required. Grain size samples were collected in 4-oz plastic jars and stored at 4°C until analyzed. Sediment remaining from each individual core was also archived and stored in freezers, in the event that any one core may need to be reexamined following analyses of the initial nine dioxin composites.

2.3 ANALYTICAL METHODS

The following sections briefly describe the methods used for analysis of sediment. Samples from 33 stations plus 7 samples from cores longer than 4 ft (for a total of 40 sediment samples) were submitted for chemical analyses. All sediment samples were analyzed for TOC

at Global Geochem in Canoga Park, California and measured for grain size fractions at Soil Technologies in Bainbridge Island, Washington. Nine samples were analyzed for chlorinated dioxins and furans at Twin City Testing in St. Paul, Minnesota.

2.3.1 Grain Size

Grain size of sediment samples was determined for four fractions: gravel, sand, silt, and clay following the Puget Sound Estuary Program (PSEP) Protocols for Measuring Selected Environmental Variables in Puget Sound (PSEP 1986). These methods are consistent with ASTM D421 (ASTM 1978) and D422 (ASTM 1972).

Approximately 25 g of sediment was removed for analysis of total solids while another 10- to 100-g aliquot was weighed for grain size analysis. To separate the coarser sand and gravel fraction from the silt/clay fraction, sediment was washed with distilled water through a 63.5- μm (4.0 phi) sieve into a 1-L graduated cylinder. The coarse fraction was dried, weighed, and shaken through a nest of sieves to yield the required seven coarse subfractions. Any material still passing the final 63.5- μm sieve was added to the previous fines to determine the silt/clay fraction.

The silt/clay fraction was then subdivided by a pipet technique based on Stoke's Law of differential settling velocities for different sized particles. The silt/clay fraction was disassociated by a dispersant in distilled water in a 1-L graduated cylinder. At specified time intervals and specified depths below the surface, 20-ml aliquots of suspension were withdrawn from the graduated cylinder, delivered to a preweighed container, and dried to constant weight at $90^{\circ} \pm 2^{\circ}\text{C}$.

Quality control measures included duplicate analysis of samples Snake RM 138.07 and RM 138.34. Spikes, standard reference materials (SRMs), or minimum detection limits do not apply to grain size. Results were reported as percent gravel, sand, silt, and clay.

2.3.2 Total Organic Carbon

The TOC analysis was performed by Global Geochem. The TOC measurement included the amount of non-volatile, partially volatile, volatile, and particulate organic compounds in a sample. The TOC in sediment was determined by measuring the carbon dioxide released during combustion of the sample (PSEP 1986; SW846 Method 9060, EPA 1986). The sediment sample was dried and ball milled to a fine powder. Before combustion,

Inorganic carbonate was removed by acidification. Quality control measures included triplicate analysis on 10% of the samples (Snake RM 138.07.1 and RM 138.34.1) and analysis of the SRM MESS-I. Results were reported as percent of dry weight.

2.3.3 Chlorinated Dioxins and Furans

Chlorinated dioxins and furans are abbreviated in this section in the following manner:

| <u>Abbreviation</u> | <u>Chlorinated Compound</u> |
|---------------------|--------------------------------|
| HpCDD | Heptachlorodibenzodioxin |
| HpCDF | Heptachlorodibenzofuran |
| HxCDD | Hexachlorodibenzodioxin |
| HxCDF | Hexachlorodibenzofuran |
| OCDD | Octachlorodibenzodioxin |
| OCDF | Octachlorodibenzofuran |
| PCDD | Polychlorinated dibenzodioxin |
| PCDF | Polychlorinated dibenzofuran |
| PCDPE | Polychlorinated diphenyl ether |
| PeCDD | Pentachlorodibenzodioxin |
| PeCDF | Pentachlorodibenzofuran |
| TCDD | Tetrachlorodibenzodioxin |
| TCDF | Tetrachlorodibenzofuran |

Sediment samples from the Snake and Clearwater rivers were analyzed for 21 congeners of polychlorinated dibenzodioxins (PCDDs) and furans (PCDFs) using a modified EPA Method 8290 (EPA 1986). This method is referred to as an isotope dilution method because isotopes of each compound of interest are spiked into the samples prior to extraction as internal standards for final quantification. A number of modifications of EPA Method 8290 were used in dioxin analyses and were primarily drawn from the more recent EPA Method 1613. One modification involves the calibration and spiking standards described in Method 1613 that were substituted for those described in Method 8290. This modification expands the calibration range and introduces additional isotopically labeled standards that improve the accuracy of the quantifications. The analyte enrichment process also contains modifications from Method 1613. These modifications include changes to column preparation and elution. Other modifications included as standard operating procedures include the use of 1- μ L

injections and elimination of the end of day continuing calibration and analysis. The following provides a summary of the extraction and quantification procedures.

Sediment aliquots were subsampled and spiked with isotopically labeled internal standards and continuously extracted for 18 h with benzene in a Soxhlet extraction apparatus. Extracts were then reduced and exchanged into hexane using a Kuderna-Danish concentrator. Hexane extracts were "cleaned" to remove interfering matrices following an analytic enrichment process involving liquid chromatography of the extract through acidified silica gel and sodium hydroxide. Extracts were spiked with an enrichment efficiency standard (^{37}Cl -2,3,7,8-TCDD) prior to the enrichment process.

After the silica gel cleanup, the extracts were reduced again to 1 ml and fractionated on a variety of other columns, including alumina and activated carbon, and eluted with various solvents to isolate the compounds of interest. The final extracts were transferred back to hexane and spiked with the two recovery standards (1,2,3,4-TCDD- $^{13}\text{C}_{12}$ and 1,2,3,7,8,9-HxCDD- $^{13}\text{C}_{12}$).

The extracts were analyzed for the presence of PCDDs and PCDFs using a combined capillary column gas chromatography/high resolution mass spectrometry (GC/HRMS). This resolution was sufficient to resolve most interferences, and thus assured the detected levels of the PCDD/PCDF were not related to interferences. The PCDD/PCDF isomers were quantified by comparison of their responses to the responses of the labeled internal standards. Relative response factors were calculated from analyses of standard mixtures containing representatives of each of the PCDD/PCDF congener classes at five concentration levels and each of the internal standards at one concentration level. The detection limit was based on producing a signal that was 2.5 times the noise level and was calculated for each 2,3,7,8-substituted isomer of any tetra- through octa-chlorinated congener class. The noise heights used to calculate the detection limits were measured at the retention time of the specific isomer.

Extraction efficiency and enrichment efficiency were determined by comparing the recovery of the enrichment efficiency standard (^{37}Cl -2,3,7,8-TCDD) and the $^{13}\text{C}_{12}$ labeled internal standard relative to one of the recovery standards ($^{13}\text{C}_{12}$ and 1,2,3,7,8,9-HxCDD- $^{13}\text{C}_{12}$).

Matrix spike and matrix spike duplicate analyses were performed on Snake RM 140.22.1 to assess both accuracy and precision of the analyses. A method blank was also analyzed. Results were reported as pptr dry weight.

3.0 QUALITY CONTROL SUMMARY AND RESULTS

Quality control data include matrix spikes to assess accuracy (percent recovery), spikes and spike duplicates and analytical replicates to assess precision [relative percent difference (RPD) and relative standard deviation (RSD)], and method blanks to assess possible contamination of samples. The results of the chemical analyses and quality control samples are described below and presented in Tables 3.1 through 3.5.

3.1 GRAIN SIZE

Forty samples were analyzed for four fractions of grain size (Table 3.1). The accuracy of the analysis was measured by determining the estimated recovery of total material calculated by summing the amount of material measured in each grain size fraction. Estimated recoveries ranged from 95.5% to 104.8%. Two samples were analyzed in duplicate to determine the precision of the measurement. Relative percent differences between replicate analyses were generally less than 25% with the exception of those fractions that contained small (<5%) total mass. The RPDs for these fractions were higher, but the values reflect the differences between very small amounts of material.

The majority of sediments consisted of silty sands. A smaller number of samples consisted of sandy silts. All samples contained less than 15% clay with the exception of one sample from Snake RM 138.34.1, which contained approximately 20% clay.

3.2 TOTAL ORGANIC CARBON

Total organic carbon was measured on a total of 40 sediment samples (Table 3.2). Two samples were analyzed in triplicate (Snake RM 138.07.1 and RM 138.34.1) to assess precision. The RSD for each set of triplicates was low, ranging from 3.62% to 8.09%. One SRM (sample MESS-1) was also analyzed. Although this sample is not certified for TOC concentration, past experience analyzing this sample has established a TOC concentration of approximately 2.2%. This agrees well with the measured value of 2.36% for this set of analyses.

The TOC concentrations for Snake River sediment samples ranged from 0.08% to 2.91%, with the majority of samples above 1.0%.

TABLE 3.1. Sediment Grain Size Analysis and Total Solids Results

| Sampling Station | % Total Solids | Estimated Recovery (%) | % Dry Weight in Each Size Fraction | | | | % Clay <3.9 µm |
|------------------|----------------|------------------------|------------------------------------|----------------------|--------------------|----------------|----------------|
| | | | % Gravel >2.00 mm | % Sand 0.063-2.00 mm | % Silt 3.9-62.5 µm | % Clay <3.9 µm | |
| 138.71.3 | 47.40 | 100.61 | 0.36 | 63.25 | 24.87 | 11.52 | |
| 138.71.2U(a) | 69.76 | 99.78 | 0.06 | 90.08 | 5.75 | 4.11 | |
| 138.71.2L(b) | 80.21 | 102.42 | 0.13 | 91.32 | 5.88 | 2.67 | |
| 138.71.1 | 67.41 | 97.91 | 0.10 | 86.13 | 6.41 | 7.36 | |
| 138.07.2 | 68.27 | 03.21 | 0.01 | 97.43 | 0.20 | 2.36 | |
| 138.07.1 | 59.64 | 95.22 | 1.46 | 79.74 | 15.12 | 3.67 | |
| 138.07.1 | 61.85 | 98.96 | 1.88 | 79.07 | 12.38 | 6.67 | |
| 138.34.1 | 53.72 | 97.73 | 0.13 | 26.77 | 52.34 | 20.76 | |
| 138.34.1 | 53.80 | 100.00 | 0.39 | 27.40 | 52.10 | 20.10 | |
| 138.34.2 | 57.34 | 97.53 | 0.21 | 50.25 | 35.53 | 14.01 | |
| 138.34.3 | 79.34 | 101.74 | 0.39 | 94.91 | 2.15 | 2.55 | |
| 138.34.4 | 76.64 | 101.79 | 0.00 | 99.31 | 0.54 | 0.15 | |
| 0.53.1 | 56.90 | 96.91 | 10.29 | 45.81 | 38.51 | 5.39 | |
| 0.53.2 | 70.03 | 101.12 | 2.55 | 84.70 | 9.96 | 2.79 | |
| 0.41.1 | 55.37 | 102.57 | 0.32 | 36.83 | 54.09 | 8.76 | |
| 0.41.2 | 63.76 | 101.79 | 1.18 | 70.57 | 24.34 | 3.92 | |
| 0.41.3 | 79.95 | 100.91 | 32.49 | 62.20 | 4.51 | 0.80 | |
| 137.94.2 | 70.51 | 101.39 | 8.07 | 86.93 | 1.04 | 3.96 | |
| 139.29.1 | 64.27 | 96.73 | 0.50 | 81.03 | 11.22 | 7.25 | |
| 139.29.2 | 65.00 | 95.68 | 5.22 | 59.34 | 26.65 | 8.80 | |
| 139.29.3U | 62.91 | 100.26 | 0.13 | 49.47 | 38.09 | 12.31 | |
| 139.29.3L | 61.18 | 97.85 | 0.19 | 43.90 | 41.31 | 14.60 | |
| 0.28.3U | 60.82 | 98.14 | 1.09 | 42.21 | 42.90 | 13.80 | |
| 0.28.3L | 79.26 | 100.33 | 20.92 | 62.42 | 11.06 | 5.59 | |
| 0.28.1U | 56.53 | 97.42 | 0.10 | 32.56 | 51.64 | 15.70 | |
| 0.28.1L | 66.44 | 92.23 | 30.17 | 35.76 | 24.57 | 9.51 | |
| 0.28.2U | 74.62 | 99.50 | 14.12 | 57.03 | 19.24 | 9.61 | |
| 0.28.2L | 85.21 | 97.63 | 32.49 | 55.72 | 7.91 | 3.88 | |
| 138.52.3 | 75.25 | 98.21 | 18.75 | 74.71 | 2.22 | 4.31 | |
| 138.52.2 | 67.75 | 96.16 | 4.90 | 81.69 | 6.13 | 7.28 | |

TABLE 3.1. (contd)

| Sampling Station | % Total Solids | Estimated Recovery(%) | % Dry Weight in Each Size Fraction | | | | %Clay $\leq 3.9 \mu\text{m}$ |
|------------------|----------------|-----------------------|------------------------------------|---------------------|------------------------------|------------------------------|------------------------------|
| | | | %Gravel $\geq 2.00\text{mm}$ | %Sand 0.063-2.00 mm | %Silt 3.9-62.5 μm | %Clay $\leq 3.9 \mu\text{m}$ | |
| 138.52.1 | 63.64 | 97.41 | 0.57 | 81.57 | 10.24 | 7.63 | |
| 138.94.2 | 78.26 | 98.42 | 0.07 | 95.99 | 1.20 | 2.74 | |
| 138.94.1U | 58.75 | 97.01 | 0.27 | 82.34 | 11.28 | 6.11 | |
| 139.22.4L | 54.61 | 104.84 | 0.53 | 30.46 | 51.05 | 17.96 | |
| 139.22.4U | 59.41 | 100.11 | 0.61 | 41.35 | 45.99 | 12.05 | |
| 139.22.1 | 62.65 | 96.58 | 0.04 | 81.52 | 10.87 | 7.57 | |
| 139.22.3 | 59.15 | 100.70 | 0.46 | 57.53 | 30.89 | 11.12 | |
| 137.94.1 | 78.01 | 98.29 | 17.12 | 78.62 | 1.78 | 2.47 | |
| 119.56.1V(c) | 48.00 | 103.08 | 0.02 | 19.39 | 63.81 | 16.78 | |
| 119.56.1P(d) | 52.29 | 99.86 | 0.06 | 43.12 | 44.62 | 12.20 | |
| 140.22.1 | 45.36 | 95.50 | 0.10 | 68.94 | 20.10 | 10.86 | |

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Snake River Quality Control Data for Analytical Replicates of Grain Size Measurements

| | | | | | | |
|----------------|-------|--------|------|-------|-------|-------|
| 138.07.1 Rep 1 | 59.64 | 95.22 | 1.46 | 79.74 | 15.12 | 3.67 |
| 138.07.1 Rep 2 | 61.85 | 98.96 | 1.88 | 79.07 | 12.38 | 6.67 |
| RPD: | 4% | - | 25% | 1% | 20% | 58% |
| I-STAT: | 0.02 | - | 0.13 | 0.00 | 0.10 | 0.29 |
| 138.34.1 Rep 1 | 53.72 | 97.73 | 0.13 | 26.77 | 52.34 | 20.76 |
| 138.34.1 Rep 2 | 53.80 | 100.00 | 0.39 | 27.40 | 52.10 | 20.10 |
| RPD: | 0% | - | 100% | 2% | 0% | 3% |
| I-STAT: | 0.00 | - | 0.50 | 0.01 | 0.00 | 0.02 |

- (a) 'J' Indicates sample taken from first 4 ft of core length.
- (b) 'L' Indicates sample taken from any core if greater than 4 ft in length.
- (c) 'V' Indicates sample taken with a van Veen grab.
- (d) 'P' Indicates sample taken with a Ponar grab.

TABLE 3.2. Sediment Total Organic Carbon (TOC) Content in Percent Dry Weight

| <u>Sampling Station</u> | <u>Q/A Triplicates</u> | <u>TOC (% dry weight)</u> | <u>RSD</u> |
|-------------------------|------------------------|---------------------------|------------|
| 0.28.1L(a) | | 1.96 | |
| 0.28.1U(b) | | 1.94 | |
| 0.28.2L | | 0.23 | |
| 0.28.2U | | 0.68 | |
| 0.28.3L | | 0.61 | |
| 0.28.3U | | 1.93 | |
| 0.41.1 | | 2.12 | |
| 0.41.2 | | 0.97 | |
| 0.41.3 | | 0.32 | |
| 0.53.1 | | 1.89 | |
| 0.53.2 | | 0.75 | |
| 119.56.1P(c) | | 1.79 | |
| 119.56.1V(d) | | 2.34 | |
| 137.94.1 | | 0.09 | |
| 137.94.2 | | 0.08 | |
| 138.07.1 | REP1 | 1.05 | |
| 138.07.1 | REP2 | 1.27 | |
| 138.07.1 | REP3 | 1.23 | 8.09% |
| 138.07.2 | | 0.11 | |
| 138.34.1 | REP1 | 2.91 | |
| 138.34.1 | REP2 | 2.68 | |
| 138.34.1 | REP3 | 2.88 | 3.52% |
| 138.34.2 | | 2.09 | |
| 138.34.3 | | 0.22 | |
| 138.34.4 | | 0.08 | |
| 138.52.1 | | 0.95 | |
| 138.52.2 | | 0.58 | |
| 138.52.3 | | 0.36 | |
| 138.71.1 | | 0.73 | |
| 138.71.2L | | 0.31 | |
| 138.71.2U | | 0.47 | |
| 138.71.3 | | 2.16 | |
| 138.94.1U | | 1.50 | |
| 138.94.2 | | 0.14 | |
| 139.22.1 | | 0.66 | |
| 139.22.3 | | 2.20 | |

TABLE 3.2. (contd)

| <u>Sampling Station</u> | <u>Q/A Triplicates</u> | <u>TOC (% dry weight)</u> | <u>RSD</u> |
|-------------------------|------------------------|---------------------------|------------|
| 139.22.4 | | NA ^(e) | |
| 139.22.4L | | 2.02 | |
| 139.22.4U | | 1.96 | |
| 139.29.1 | | 0.79 | |
| 139.29.2 | | 1.33 | |
| 139.29.3L | | 2.21 | |
| 139.29.3U | | 1.60 | |
| 140.22.1 | | 2.12 | |

SRM: MESS-1

Observed Value: 2.36

Expected Value: ~2.20

-
- (a) L Indicates sample taken from any core longer than 4 ft.
 - (b) U Indicates sample taken from first 4 ft of core length.
 - (c) P Indicates sample taken with a Ponar grab.
 - (d) V Indicates sample taken with a van Veen grab.
 - (e) NA Indicates not analyzed.

TABLE 3.3. Sediment Polychlorinated Dibenzodioxin (PCDD) and Dibenzofurans (PCDF)

| Analyte | Concentrations measured at sampling stations (ppt, dry weight) | | | | | | | | | | | Method | TEF ^(c) | |
|----------------------------|----------------------------------------------------------------|-------------------|------------------------|----------|-----------|----------|----------|--------------------------|----------|-------|--------------------|--------|--------------------|--|
| | 0.53.1 | 0.41.1 | 0.28.3U ^(a) | 138.94.2 | 138.94.1U | 139.22.4 | 139.22.1 | 119.56.1V ^(b) | 140.22.1 | Blank | TEF ^(c) | | | |
| Chlorinated Dioxins | | | | | | | | | | | | | | |
| 2378-TCDD | 0.45U | 0.46U | 0.34U | 0.80U | 0.58U | 0.32U | 0.74U | 1.50U | 1.00U | 0.45U | 1.000 | | | |
| Total TCDD | 2.40 | 1.40 | 1.80 | 2.20 | 2.60 | 3.10 | 2.60 | 3.30 | 3.50 | 1.90 | 0.000 | | | |
| 12378-PeCDD | 0.85U | 0.19 | 0.21U | 0.08U | 0.60U | 0.49U | 0.44U | 0.67U | 0.65U | 0.55U | 0.000 | | | |
| Total PeCDD | 0.35 | ND ^(d) | ND | 0.61 | ND | 1.20 | 1.70 | ND | 0.52 | 0.82 | 0.000 | | | |
| 123478-HxCDD | 0.60U | 0.63U | 1.30U | 0.25U | 0.53U | 0.37U | 0.38U | 1.30U | 0.84U | 0.20U | 0.000 | | | |
| 123678-HxCDD | 1.00 | 0.77 | 1.70U | 0.30U | 0.58U | 0.75U | 0.33U | 2.00U | 2.50U | 0.37U | 0.000 | | | |
| 123789-HxCDD | 0.37 | 0.52U | 1.20 | 0.12U | 0.20U | 0.47U | 0.45U | 1.40U | 1.10U | 0.34U | 0.000 | | | |
| Total HxCDD | 6.50 | 7.20 | 10.00 | ND | 3.00 | 6.00 | 0.92 | 15.00 | 3.80 | ND | 0.000 | | | |
| 1234678-HpCDD | 13.00 | 13.00 | 21.00 | 2.00 | 7.10 | 15.00 | 7.20 | 14.00 | 7.80 | 1.20 | 0.000 | | | |
| Total HpCDD | 25.00 | 24.00 | 38.00 | 3.70 | 13.00 | 29.00 | 12.00 | 28.00 | 14.00 | 1.90 | 0.000 | | | |
| OCDD | 95.00 | 79.00 | 150.00 | 18.00 | 63.00 | 110.00 | 63.00 | 98.00 | 57.00 | 8.70 | 0.001 | | | |
| Chlorinated Furans | | | | | | | | | | | | | | |
| 2378-TCDF | 0.66 | 0.30U | 0.38 | 0.39 | 0.64 | 0.98 | 0.55 | 5.60 | 0.82U | 0.27U | 0.100 | | | |
| Total TCDF | 5.10 | 1.40 | 1.80 | 0.39 | 1.90 | 3.30 | 0.55 | 14.00 | ND | ND | 0.000 | | | |
| 12378-PeCDF | 0.20U | 0.25U | 0.37U | 0.09U | 0.42U | 0.26U | 0.37U | 0.76U | 0.29U | 0.43U | 0.050 | | | |
| 23478-PeCDF | 0.60 | 0.16 | 0.35U | 0.08U | 0.36U | 0.29 | 0.35U | 0.42 | 0.35U | 0.40U | 0.500 | | | |
| Total PCDF | 5.50 | 0.16 | 0.72 | ND | ND | 0.92 | ND | 1.70 | ND | ND | 0.000 | | | |
| 123478-HxCDF | 0.36 | 0.16 | 0.25 | 0.12U | 0.07U | 0.14U | 0.29U | 0.30U | 0.69U | 0.28U | 0.000 | | | |
| 123678-HxCDF | 0.18 | 0.12 | 0.22U | 0.83U | 0.13U | 0.14U | 0.34U | 0.13 | 0.73U | 0.18U | 0.000 | | | |
| 123789-HxCDF | 1.10 | 0.60 | 0.88 | 0.61 | 0.79 | 0.95 | 0.78 | 0.93 | 0.99 | 0.47 | 0.000 | | | |
| 234678-HxCDF | 0.32U | 0.04U | 0.27U | 0.09U | 0.14U | 0.25U | 0.15U | 0.23U | 0.39U | 0.64U | 0.000 | | | |
| Total HxCDF | 7.10 | 3.60 | 5.80 | 0.61 | 2.20 | 3.90 | 1.90 | 3.90 | 1.70 | 0.82 | 0.000 | | | |
| 1234678-HpCDF | 5.30U | 3.20U | 4.20 | 0.47 | 1.50 | 3.30 | 1.40 | 2.50 | 2.50 | 0.36 | 0.000 | | | |
| 1234789-HpCDF | 0.61U | 0.20U | 0.29U | 0.14U | 0.21U | 0.27U | 0.28U | 0.52U | 0.32U | 0.18U | 0.000 | | | |
| Total HpCDF | ND | ND | 4.20 | 0.47 | 1.50 | 3.30 | 1.40 | 2.80 | 2.50 | 0.36 | 0.000 | | | |
| OCDF | 8.40 | 3.60 | 9.90 | 1.20U | 3.00 | 6.50 | 4.00 | 5.70 | 4.50 | 0.48 | 0.001 | | | |

(a) U Indicates not detected at detection limits shown.

(b) V Indicates sampled with a van Veen grab.

(c) TEF Indicates toxicity equivalency factor (Reference CCMS 1988).

(d) ND Indicates not detected.

TABLE 3.4. Standards for Internal Polychlorinated Dibenzodioxins (PCDD) and Dibenzofurans (PCDF)

| Analyte | Concentrations measured at percent dry weight | | | | | | | | | | Method | |
|---------------------------------------|-----------------------------------------------|--------|------------|----------|-----------|----------|----------|--------------|----------|----------|--------|-------|
| | 53.1 | 0.41.1 | 0.28.3U(a) | 138.94.2 | 138.94.1U | 139.22.4 | 139.22.1 | 119.56.1V(b) | 140.22.1 | 140.22.1 | | |
| Chlorinated Dioxins | | | | | | | | | | | | |
| 2378-TCDD | | | | | | | | | | | | Blank |
| 2378-TCDD-C13 | 97 | 99 | 88 | 87 | 86 | 92 | 109 | 88 | 85 | 68 | | |
| 12378-PeCDD-C13 | 129 | 137 | 120 | 192 | 129 | 108 | 178 | 133 | 48 | 60 | | |
| 123478-HxCDD-C13 | 94 | 47 | 49 | 73 | 58 | 80 | 102 | 42 | 64 | 61 | | |
| 123678-HxCDD-C13 | 91 | 58 | 45 | 84 | 52 | 80 | 91 | 27 | 36 | 61 | | |
| 1234678-HpCDD-C13 | 80 | 84 | 87 | 67 | 78 | 85 | 92 | 81 | 89 | 47 | | |
| OCDD-C13 | 76 | 24 | 78 | 38 | 68 | 76 | 87 | 79 | 63 | 49 | | |
| 2378-TCDF-C13 | 81 | 82 | 78 | 77 | 82 | 78 | 89 | 79 | 78 | 62 | | |
| 12378-PeCDF-C13 | 104 | 105 | 92 | 120 | 104 | 91 | 127 | 100 | 94 | 55 | | |
| 23478-PeCDF-C13 | 120 | 136 | 130 | 242 | 140 | 112 | 186 | 130 | 148 | 59 | | |
| 123478-HxCDF-C13 | 103 | 97 | 98 | 86 | 75 | 94 | 87 | 99 | 71 | 74 | | |
| 123678-HxCDF-C13 | 97 | 93 | 94 | 80 | 72 | 87 | 78 | 93 | 66 | 75 | | |
| 123789-HxCDF-C13 | 86 | 80 | 82 | 85 | 72 | 77 | 93 | 81 | 81 | 72 | | |
| 234678-HxCDF-C13 | 74 | 73 | 82 | 77 | 74 | 75 | 80 | 81 | 78 | 71 | | |
| 1234678-HpCDF-C13 | 77 | 73 | 72 | 65 | 67 | 72 | 75 | 73 | 76 | 62 | | |
| 1234789-HpCDF-C13 | 74 | 75 | 76 | 66 | 73 | 73 | 84 | 74 | 77 | 67 | | |
| Enrichment Efficiency Standard | | | | | | | | | | | | |
| 2378-TCDD-C13 | 94 | 94 | 85 | 86 | 85 | 89 | 102 | 87 | 88 | 63 | | |

(a) U Indicates not detected at detection limits shown.

(b) V Indicates sampled with a van Veen grab.

(c) TEF Indicates toxicity equivalency factor (Reference CCMS 1988).

(d) ND Indicates not detected.

TABLE 3.5. Quality Assurance Data for Polychlorinated Dibenzodioxin (PCDD) and Dibenzofurans (PCDF) (concentrations in ppb dry weight)

| | Method Blank Recovery | | Matrix Spike Duplicate (140.222.1) | | Matrix Spike (140.22.1) | | RPD(a) |
|----------------------------|-----------------------|---------------------|------------------------------------|---------------------|-------------------------|---------------------|--------|
| | Spiked | Recovered %Recovery | Spiked | Recovered %Recovery | Spiked | Recovered %Recovery | |
| Chlorinated Dioxins | | | | | | | |
| 2378-TCDD | 17.70 | 18.58 | 44.44 | 48.89 | 41.67 | 45.83 | 0 |
| Total TCDD | 17.70 | 18.58 | 44.44 | 48.89 | 41.67 | 45.83 | 0 |
| 12378-PeCDD | 88.50 | 97.35 | 222.22 | 206.67 | 208.33 | 208.33 | 7 |
| Total PeCDD | 88.50 | 97.35 | 222.22 | 206.67 | 208.33 | 208.33 | 7 |
| 123478-HxCDD | 88.50 | 106.20 | 222.22 | 244.44 | 208.33 | 229.17 | 0 |
| 123678-HxCDD | 88.50 | 97.35 | 222.22 | 222.22 | 208.33 | 208.33 | 0 |
| 123789-HxCDD | 88.50 | 97.35 | 222.22 | 266.67 | 208.33 | 250.00 | 0 |
| Total HxCDD | 265.49 | 300.88 | 666.67 | 733.33 | 625.00 | 687.50 | 0 |
| 1234678-HpCDD | 88.50 | 97.35 | 222.22 | 244.44 | 208.33 | 208.33 | 10 |
| Total HpCDD | 88.50 | 97.35 | 222.22 | 244.44 | 208.33 | 208.33 | 10 |
| OCDD | 176.99 | 185.84 | 444.44 | 511.11 | 416.67 | 458.33 | 4 |
| Chlorinated Furans | | | | | | | |
| 2378-TCDF | 17.70 | 20.35 | 44.44 | 48.89 | 41.67 | 45.83 | 0 |
| Total TCDF | 17.70 | 20.35 | 44.44 | 48.89 | 41.67 | 45.83 | 0 |
| 12378-PeCDF | 88.50 | 97.35 | 222.22 | 222.22 | 208.33 | 229.17 | 10 |
| 234678-PeCDF | 88.50 | 97.35 | 222.22 | 244.44 | 208.33 | 229.17 | 0 |
| Total PeCDF | 176.99 | 194.69 | 444.44 | 463.67 | 416.67 | 458.33 | 5 |

TABLE 3.5. (contd)

| | Method Blank Recovery | | Matrix Spike Duplicate (140,222.1) | | Matrix Spike (140,22.1) | | RPD(a) |
|---------------|-----------------------|---------------------|------------------------------------|---------------------|-------------------------|---------------------|--------|
| | Spiked | Recovered %Recovery | Spiked | Recovered %Recovery | Spiked | Recovered %Recovery | |
| 123478-HxCDF | 88.50 | 97.35 | 222.22 | 244.44 | 208.33 | 229.17 | 0 |
| 123678-HxCDF | 88.50 | 97.35 | 222.22 | 244.44 | 208.33 | 229.17 | 0 |
| 123789-HxCDF | 88.50 | 88.50 | 222.22 | 222.22 | 208.33 | 208.33 | 0 |
| 234678-HxCDF | 88.50 | 97.35 | 222.22 | 244.44 | 208.33 | 229.17 | 0 |
| Total HxCDF | 353.98 | 380.53 | 888.89 | 955.56 | 833.33 | 895.83 | 0 |
| 1234678-HpCDF | 88.50 | 88.50 | 222.22 | 244.44 | 208.33 | 208.33 | 10 |
| 1234789-HpCDF | 88.50 | 88.50 | 222.22 | 244.44 | 208.33 | 208.33 | 0 |
| Total HpCDF | 176.99 | 176.99 | 444.44 | 488.89 | 416.67 | 416.67 | 10 |
| OCDF | 176.99 | 203.54 | 444.44 | 533.33 | 416.67 | 500.00 | 0 |

(a) RPD is calculated between matrix spike and matrix spike duplicate.

3.3 CHLORINATED DIOXINS AND FURANS

Chlorinated dibenzodioxins and dibenzofurans were measured in nine sediment samples from the Snake River (Table 3.3). A matrix spike, matrix spike duplicate (Snake RM 140.22.1), and a method blank were also analyzed. Various surrogates and internal standards (Table 3.4) were also added to the samples both before and during extraction and chromatography to assess the efficiency of different portions of the analysis as described in Section 2.3.3.

Low levels of total TCDD, total PeCDD, total HpCDD, and OCDD were detected in the method blank at concentrations ranging from 0.82 to 8.7 pptr. Total HxCDF, total HeCDF, and OCDF were also measured in the method blank at concentrations less than 1 pptr.

The recoveries of the enrichment efficiency standards ranged from 63% to 102% for the samples analyzed. Percent recoveries of the internal standard used to quantify the analytes varied widely, generally ranging from 50% to 150%. Analyte concentrations were quantified based on these recoveries; therefore, this range in internal standard recoveries does not affect the measurement of analyte concentrations.

Two of the samples, Clearwater RMs 0.53.1 and 0.41.1, were found to contain PCDPEs, substances that can give false positive responses for PCDFs. Those PCDFs with a simultaneous response in the PCDPE ion trade were not included in the calculations because of the possibility that the PCDF was an artifact produced from the PCDPE. The reported detection limits for any affected 2,3,7,8-substituted isomers are, therefore, elevated.

Matrix spike and matrix spike duplicate recoveries (Table 3.5) ranged from 93% to 120%, and RPD values between spike and spike duplicate recoveries ranged from 0% to 10%. Spiking levels ranged from 17.70 to 888.89 pptr. Although somewhat higher than measured sample concentrations, these are standard spiking levels used by the laboratory on a routine basis.

Some chlorinated dioxin congeners were detected in all nine sediment samples analyzed for dioxins/furans. Concentrations in samples ranged from approximately 2.2 pptr for total TCDD (similar to concentrations found in the method blank) to 110 pptr for OCDD. Each of the 11 transects and the 2 reference sites showed no concentrations of 2,3,7,8 TCDD at detection limits ranging from 0.34 pptr to 1.5 pptr (Figure 3.1). These ranges are within the target detection limit of 1 pptr. Chlorinated furans were also detected in all samples ranging

from 0.12 pptr (1,2,3,4,6,7,8-HxCDF) to 9.9 pptr (OCDF). Chlorinated furan concentrations of 2,3,7,8-TCDF were 0.38 pptr for Clearwater RM 0.28.3 to 5.6 pptr for Snake RM 119.56.1. The higher concentration of TCDF for the downstream reference site Snake RM 119.56 may be related to sediment grain size and its relatively high organic carbon concentration, a phase with which dioxin/furan materials are closely associated. Again the reference areas were carefully chosen to ensure a lack of contamination by previously disposed dredged material.

Ranges for OCDD and OCDF were from 8.7 to 150 and 0.48 to 9.9 pptr, respectively. According to EPA Method 8290, the presence of OCDD and OCDF in the method blank and the test sites is not considered a problem because of their ubiquitous nature.

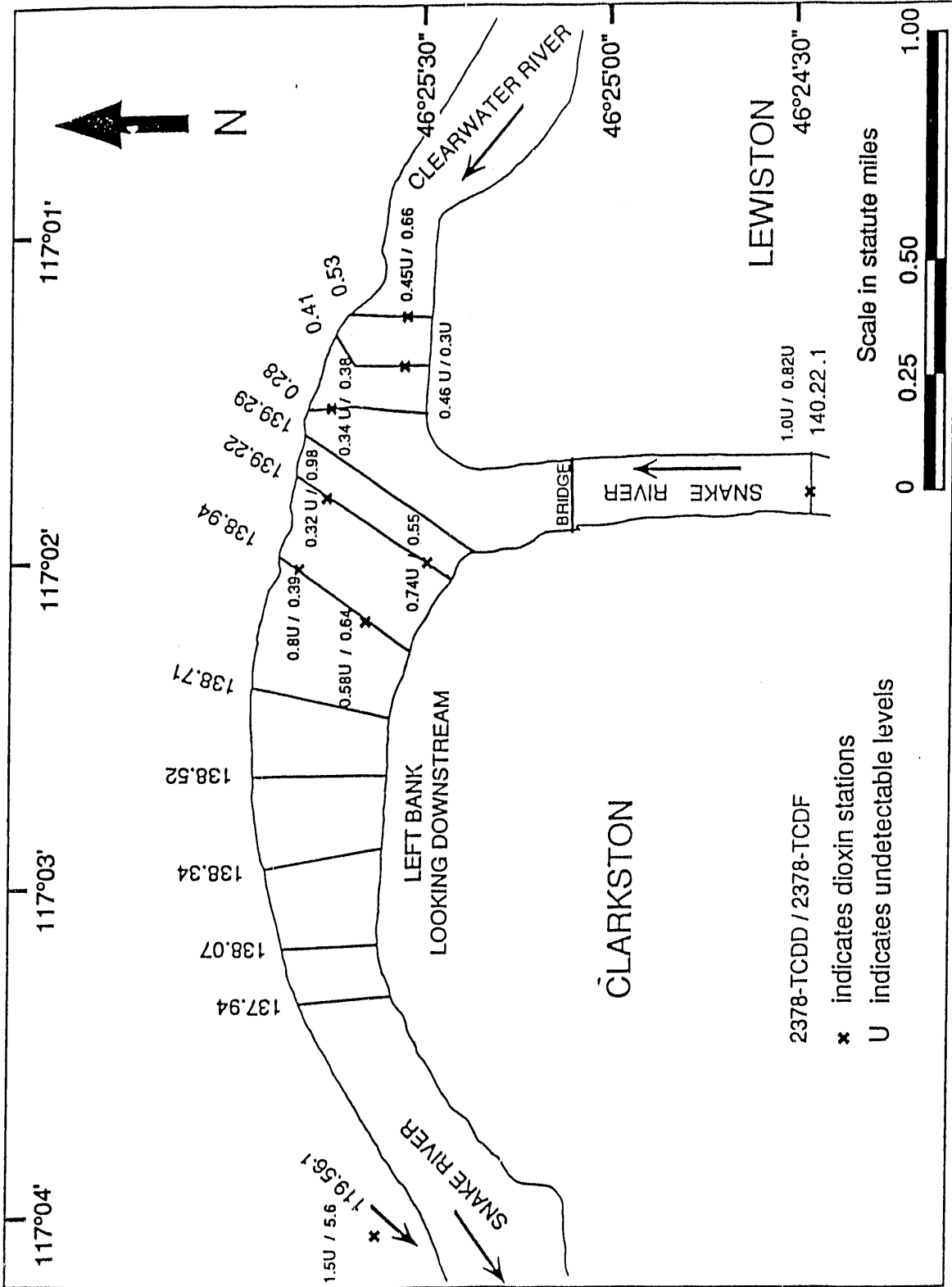


FIGURE 3.1. Concentrations of 2378-TCDD and 2378-TCDF (ppt dry weight) found in Snake River Dioxin

4.0 REFERENCES

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