

## Polychlorinated Dibenzo-*P*-Dioxins (PCDDs) and Dibenzofurans (PCDFs) in Snake River Suspended Particulate Matter

### Abstract

We measured concentrations of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD) and other polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDDs/PCDFs) in suspended particulate matter (SPM) collected near the mouth of the Snake River during October 1996. The objective of this survey was to estimate the daily 2,3,7,8-TCDD load at the Snake River mouth under low-flow conditions and compare it to the target load for the Snake River watershed as described in EPA's total maximum daily load (TMDL) for the Columbia River basin. Two PCDDs and three PCDFs were detected in SPM; 2,3,7,8-TCDD was not found at a detection limit of 0.24 pg/g. The total *maximum possible* load of 2,3,7,8-TCDD at the Snake River mouth was 0.25 mg/day, about one-fifth of the target load for the Snake River watershed. The total *maximum possible* toxicity equivalent (TEQ) load was estimated to be 0.76 mg/day. We recommend additional monitoring to determine upstream loading of PCDDs/PCDFs and to assess the effects of high flows on the downstream transport of these compounds.

### Introduction

#### Background

Since the late 1980s there have been concerns about dioxin/furan contamination of the Washington reach of the Snake River. These concerns arose when 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD; frequently referred to as dioxin) was found in effluent from the Potlatch Corporation bleached kraft pulp mill in Lewiston, Idaho during a joint U.S. Environmental Protection Agency (EPA)/industry survey of 104 pulp mills nationwide (EPA, 1988). This survey, commonly known as the 104 Mill Study, examined mills bleaching pulp with chlorine after it was discovered that this process leads to the formation of 2,3,7,8-TCDD and other polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDDs/PCDFs).

The mean concentration of 2,3,7,8-TCDD in Potlatch's final effluent during the 104 Mill Study was 75 pg/L (EPA, 1988). Based on an average discharge from the Potlatch facility of  $1.46 \times 10^8$  L/day, this concentration loaded 11.0 mg 2,3,7,8-TCDD/day to the Snake River (EPA, 1990). The resulting concentration of 2,3,7,8-TCDD in the water column, calculated using the harmonic mean flow of the Snake River near Clarkston, Washington ( $8.74 \times 10^{10}$  L/day) averaged 0.13 pg/L, ten times above the EPA criterion to protect human health (0.013 pg/L; EPA, 1986a). Aside from 2,3,7,8-TCDD, a substantial concentration (340 pg/L) of 2,3,7,8-tetrachlorodibenzofuran (2,3,7,8-TCDF) was found in Potlatch effluent. 2,3,7,8-TCDF has one-tenth the toxicity of 2,3,7,8-TCDD but is generally more prevalent in pulp mill effluent (Barnes *et al.*, 1989; Mah *et al.*, 1989).

During 1991, EPA established a total maximum daily load (TMDL) for 2,3,7,8-TCDD to limit its discharge to the Columbia River basin (EPA, 1991). The TMDL is restricted to 2,3,7,8-TCDD because it is the only PCDD/PCDF with an established EPA criterion for water quality. It contains a watershed target of 1.18 mg 2,3,7,8-TCDD/day at the mouth of the Snake River in which is nested a waste load allocation (WLA) of 0.39 mg 2,3,7,8-TCDD/day for the Potlatch mill. Other potential point sources of 2,3,7,8-TCDD in the Snake River basin include municipal treatment works and wood preservers, but none of these sources was deemed large enough to warrant separate WLAs.

Since release of the 104 Mill Study, Potlatch has made a number of modifications designed to reduce their discharge of PCDDs/PCDFs (EPA, 1990; Michael Letourneau, EPA Environmental Scientist, written communication). However, there are limited data available to evaluate the effectiveness of these changes. There have also been no data collected to determine if the Snake River is within its loading capacity for 2,3,7,8-TCDD as detailed in the TMDL for the Columbia River basin.

## **Objectives**

The objective of this survey was to estimate the daily 2,3,7,8-TCDD load at the Snake River mouth under low-flow conditions and compare it to the target load for the Snake River watershed as described in EPA's TMDL for the Columbia River basin.

## **Methods**

### **Sampling Procedures**

The 2,3,7,8-TCDD load was estimated from samples of suspended particulate matter (SPM) collected near the mouth of the Snake River. SPM was collected over the course of several days using a continuous-flow, high-speed centrifuge, and analyzed for 2,3,7,8-substituted PCDDs/PCDFs. Our experience has shown that SPM collected downstream of bleached kraft pulp mills contain a mixture of 2,3,7,8-PCDDs/PCDFs (Johnson *et al.*, 1991; Serdar *et al.* 1993 & 1994).

The SPM sample was collected off the right bank of the Snake River, approximately 2.2 miles downstream of Ice Harbor Dam (Figure 1). This site was selected because it is below the last of the Snake River dams but above the influence of the Columbia River and should therefore yield a representative estimate of 2,3,7,8-TCDD loads to the Columbia River. Sample collection coincided with normal operations at the Potlatch mill and Ice Harbor Dam (Alan Prouty, Potlatch Corp. and David Woodland, Army Corps of Engineers, personal communications).

Two Sedisamp II continuous-flow centrifuges (model 101IL) were used to collect the SPM in a manner described by Johnson *et al.* (1991) and Serdar *et al.* (1993 & 1994). Water was pumped from an intake situated in 14-ft deep water and approximately 30 feet offshore in the main current of the river. The intake was periodically adjusted to 2-, 7-, and 12-ft depths to approximate a depth-integrated sample.

To avoid sample contamination, all surfaces coming in contact with the samples were pre-cleaned by scrubbing with Liquinox® detergent, followed by sequential rinses with hot tap water, de-ionized water, acetone, and hexane. Tubing and fittings were Teflon® or Teflon-lined except for Silastic® tubing on the peristaltic pump and Nalgene® tubing used for the intake line. Centrifuge bowl parts are constructed of high quality stainless steel.

Sampling was conducted during October 22-24, 1996. Approximately 13,700 L of Snake River water was centrifuged over the course of 38.2 hours, yielding 191 g of SPM (wet). The centrifuge demonstrated nearly 100% SPM removal efficiency based on data from laboratory analysis of water samples and from pump-flow measurements. SPM accumulated by the centrifuge was scraped from the centrifuge bowl and placed in an amber glass jar specially cleaned for trace organics analysis.

Seven water samples were also collected at approximately six-hour intervals for analysis of total organic carbon (TOC), dissolved organic carbon (DOC), total suspended solids (TSS), pH, and temperature. Water samples for TOC and DOC analysis were preserved with sulfuric acid to pH < 2. DOC samples were filtered in the field prior to acidification. Measurements of pH and temperature were done in the field. All samples for laboratory analysis were kept on ice while in the field.

### **Analytical Procedures**

Analysis of 2,3,7,8-PCDDs/PCDFs was performed at the Quanterra, Inc. laboratory in West Sacramento, California using EPA Method 1613A high resolution GC/MS. All additional analyses were conducted at the Ecology/EPA Manchester Environmental Laboratory. Table 1 summarizes the analytical methods used.

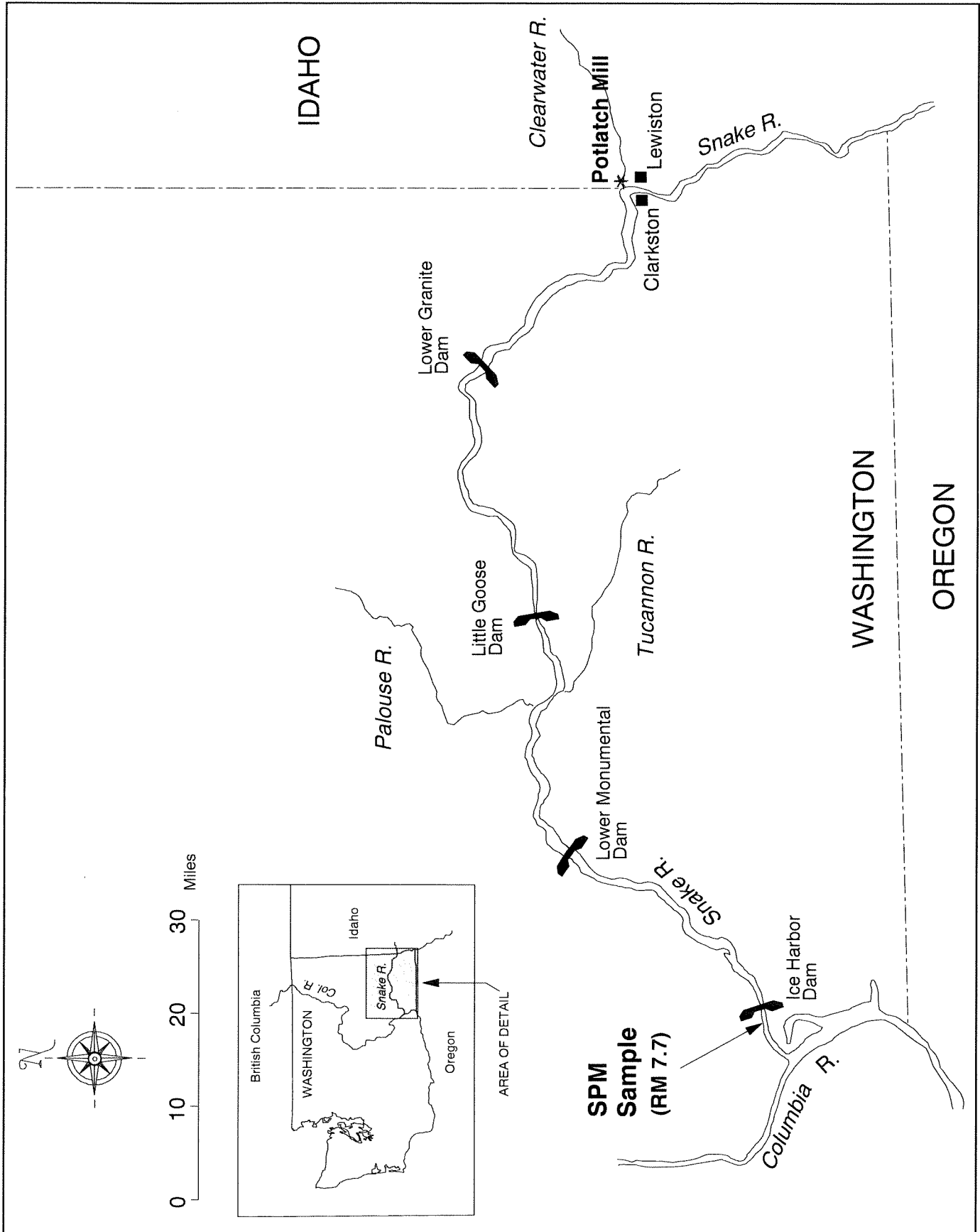


Figure 1. Sampling Site for Snake River Suspended Particulate Matter.

Table 1. Methods Used for Analysis of Snake River SPM and Water.

Parameter	Detection Limit	Method	Method No.
<u>SPM</u>			
2,3,7,8-PCDDs/PCDFs	0.12-2.5 pg/g	HRGC/MS	EPA 1613A
TOC	1 mg/g	convert to CO <sub>2</sub> /NDIR	PSEP*-TOC
% Moisture	0.1 % resolution	dry at 103-105° C	EPA 160.3
<u>Water</u>			
TOC	1 mg/L	convert to CO <sub>2</sub> /NDIR	EPA 415.1
DOC	1 mg/L	filter/convert to CO <sub>2</sub> /NDIR	EPA 415.1
TSS	1 mg/L	filter/dry at 103-105° C	EPA 160.2

\*Puget Sound Estuary Program (EPA, 1986b)

## Quality of the Data

Quality of the PCDD/PCDF data was assessed by Quanterra staff and Stuart Magoon of the Manchester Laboratory. QA/QC data are in the Appendix.

All aspects of QA/QC indicate that PCDD/PCDF data were of high quality. Isotope and matrix spike recoveries were within limits established for Method 1613A. Holding times were met and no target analytes were detected in the method blank. Precision, determined from triplicate analysis of the sample, ranged from 0 to 10% relative standard deviation (standard deviation divided by the mean).

Results for 1,2,3,4,6,7,8-HpCDF were qualified as estimates (“J”) because this analyte was detected at concentrations between the theoretical method detection limit and the practical quantitation limit.

Quality of the TOC, DOC, and TSS data was also very good based on results of matrix spikes, laboratory duplicates, and replicate field sample analyses (Appendix). All other QA/QC data were within limits specified by the methods.

## Results

### Concentrations of 2,3,7,8-PCDDs/PCDFs in SPM

Two PCDDs and three PCDFs were detected in the SPM sample (Table 2). 2,3,7,8-TCDD was not found at a detection limit of 0.24 pg/g. 2,3,7,8-TCDF was present at 2.0 pg/g. Of the five PCDD/PCDF compounds detected, all but 2,3,7,8-TCDF were hepta- or octa-chlorinated. Octachlorodibenzo-*p*-dioxin (OCDD) was the predominant compound, with a concentration one-to-two orders of magnitude higher than other congeners. Other water quality parameters measured in Snake River water (Table 3) were similar to values normally observed during autumn (USGS, 1986-1995).

Table 2. Concentrations of 2,3,7,8-PCDDs/PCDFs in Snake River SPM (pg/g, dry weight basis).

	Analysis 1	Analysis 2	Analysis 3	mean
2,3,7,8-TCDD	U (0.32)	U (0.29)	U (0.24)	nd
1,2,3,7,8-PeCDD	U (0.26)	U (0.29)	U (0.23)	nd
1,2,3,4,7,8-HxCDD	U (0.34)	U (0.40)	U (0.40)	nd
1,2,3,6,7,8-HxCDD	U (1.3)	U (1.3)	U (1.1)	nd
1,2,3,7,8,9-HxCDD	U (1.2)	U (1.2)	U (1.1)	nd
<b>1,2,3,4,6,7,8-HpCDD</b>	<b>27</b>	<b>25</b>	<b>22</b>	<b>25</b>
<b>OCDD</b>	<b>230</b>	<b>200</b>	<b>190</b>	<b>207</b>
<b>2,3,7,8-TCDF</b>	<b>2.0</b>	<b>2.0</b>	<b>2.0</b>	<b>2.0</b>
1,2,3,7,8-PeCDF	U (0.23)	U (0.19)	U (0.23)	nd
2,3,4,7,8-PeCDF	U (0.32)	U (0.29)	U (0.26)	nd
1,2,3,4,7,8-HxCDF	U (0.48)	U (0.45)	U (0.42)	nd
1,2,3,6,7,8-HxCDF	U (0.26)	U (0.20)	U (0.29)	nd
2,3,4,6,7,8-HxCDF	U (0.58)	U (0.58)	U (0.53)	nd
1,2,3,7,8,9-HxCDF	U (0.12)	U (0.064)	U (0.061)	nd
<b>1,2,3,4,6,7,8-HpCDF</b>	<b>5.2 J</b>	<b>4.8 J</b>	<b>4.4 J</b>	<b>4.8 J</b>
1,2,3,4,7,8,9-HpCDF	U (0.29)	U (0.32)	U (0.29)	nd
<b>OCDF</b>	<b>18</b>	<b>16</b>	<b>15</b>	<b>16</b>
% Moisture in SPM	62.2	62.2	62.2	62.2
% TOC in SPM	4.0	3.7	3.7	3.8

U=Undetected at concentration in parentheses

nd=not detected

J=estimated concentration

detected PCDDs/PCDFs in **bold** print

Table 3. Water Quality During SPM Collection.

	n	mean	std. dev.
TOC (mg/L)	7	2.8	0.2
DOC (mg/L)	7	1.4	0.4
TSS (mg/L)	7	4.3	0.5
pH (s.u.)	7	7.6	0.2
Temp. (° C)	7	14.5	0.7
Snake River discharge (L/s)*		577,940	

\*@ Ice Harbor Dam during sample collection. Data provided by Dave Reese, U.S. Army Corps of Engineers.

## Estimated Maximum Possible 2,3,7,8-TCDD Load

### Solid Phase

The daily particulate or solid phase load for 2,3,7,8-TCDD was calculated as the product of its concentration in SPM, the total suspended solids (TSS) concentration in water, and the daily Snake River discharge. Since 2,3,7,8-TCDD was not detected in the SPM sample, its *maximum possible* solid phase load was estimated by substituting the detection limit for an actual concentration. By using a mean detection limit of 0.28 pg/g, mean TSS in water of 4.3 mg/L (0.0043 g/L), and a mean Snake River discharge of  $5.0 \times 10^{10}$  L/day, the *maximum possible* solid phase load was calculated to be  $6.0 \times 10^7$  pg/day or 0.06 mg/day.

### Dissolved Phase

Due to the low concentration of suspended solids, some fraction of the 2,3,7,8-TCDD in the Snake River was likely to be contained in the dissolved phase. Although dissolved 2,3,7,8-TCDD was not measured, its distribution between solid and dissolved phases may be calculated based on its sorption partition coefficient ( $K_{oc}$ ), a value derived from a hydrophobic compound's equilibrium distribution between sediment and water and normalized to organic carbon. The fraction of 2,3,7,8-TCDD in the dissolved phase can be calculated from the equation:

$$\text{Fraction of dissolved 2,3,7,8-TCDD} = \{1 + (K_{oc} \times \text{Fraction OC in SPM} \times \text{Fraction SPM in water})\}^{-1}$$

$K_{oc}$  values are obtained experimentally, that is by observations of partitioning between water and solid phases with known organic carbon content, or they may be calculated using other properties of a compound, such as its relative solubility in octanol and water. Mackay *et al.* (1992) have compiled thirty-three 2,3,7,8-TCDD  $K_{oc}$  values from the literature, derived both empirically and theoretically, and ranging from  $1.15 \times 10^3$  to  $3.89 \times 10^7$  with a median value of  $2.00 \times 10^6$ .

Using a  $K_{oc}$  of  $2.00 \times 10^6$ , an OC fraction of 0.038, and a fraction of SPM in water (TSS) of  $4.3 \times 10^{-6}$ , approximately 75% of 2,3,7,8-TCDD was theoretically in the dissolved phase. Therefore, the *maximum possible* dissolved phase load was approximately 0.19 mg/day and the total (solid + dissolved) *maximum possible* 2,3,7,8-TCDD load in the Snake River was approximately 0.25 mg/day.

### **2,3,7,8-PCDD/PCDF and Toxicity Equivalent Loads**

All seventeen PCDDs/PCDFs with chlorine atoms in the 2, 3, 7, and 8 positions (*e.g.* 1,2,3,4,6,7,8-HpCDD) are considered to have a high level of toxicity, with 2,3,7,8-TCDD being the most toxic. Because these compounds are often found in mixtures, the sum of their toxicity may be converted to an equivalent concentration of 2,3,7,8-TCDD,

commonly referred to as a toxicity equivalent, or TEQ. TEQs have no regulatory basis, but instead were derived to estimate risks associated with exposure to 2,3,7,8-PCDD/PCDF mixtures (Barnes *et al.*, 1989). The TEQ of a 2,3,7,8-PCDD/PCDF mixture is the sum of the individual congener concentrations multiplied by their toxicity relative to 2,3,7,8-TCDD. A compound's toxicity relative to 2,3,7,8-TCDD is called the toxicity equivalency factor.

Table 4 shows the loads of all 2,3,7,8-PCDDs/PCDFs calculated using the same method as for 2,3,7,8-TCDD. Detection limits were used where actual concentrations are not available, and median  $K_{oc}$  values were used where reported by Mackay *et al.* (1992).

Table 4 also shows the toxicity equivalency factors for all 2,3,7,8-PCDDs/PCDFs and the corresponding Snake River toxicity equivalency load for each compound. The total *maximum possible* toxicity equivalent load, that is the sum of the toxicity equivalency loads for each compound, was estimated to be 0.76 mg/day.



Table 4. 2,3,7,8-PCDD/PCDF and Toxicity Equivalent Loads in the Snake River.

	Load in Solid Phase (mg/day)		K <sub>oc</sub> <sup>a</sup>	Percent in Dissolved Phase		Load in Dissolved Phase (mg/day)		Total Load (mg/day)	Toxicity Equivalency Factor	Toxicity Equivalent Load (mg/day)
	Phase (mg/day)			Dissolved Phase		Dissolved Phase				
2,3,7,8-TCDD	0.06 <sup>b</sup>		2.00 x 10 <sup>6</sup>	75%	0.19 <sup>b</sup>		0.25 <sup>b</sup>	1	0.25	
1,2,3,7,8-PeCDD	0.06 <sup>b</sup>		nr				0.06 <sup>b,c</sup>	0.5	0.03	
1,2,3,4,7,8-HxCDD	0.08 <sup>b</sup>		1.05 x 10 <sup>6</sup>	85%	0.48 <sup>b</sup>		0.56 <sup>b</sup>	0.1	0.056	
1,2,3,6,7,8-HxCDD	0.26 <sup>b</sup>		nr				0.26 <sup>b,c</sup>	0.1	0.026	
1,2,3,7,8,9-HxCDD	0.25 <sup>b</sup>		nr				0.25 <sup>b,c</sup>	0.1	0.025	
1,2,3,4,6,7,8-HpCDD	5.28		4.90 x 10 <sup>6</sup>	56%	6.62		11.90	0.01	0.119	
OCDD	44.23		1.20 x 10 <sup>7</sup>	34%	22.59		66.82	0.001	0.0668	
2,3,7,8-TCDF	0.43		1.59 x 10 <sup>7</sup>	28%	0.16		0.59	0.1	0.059	
1,2,3,7,8-PeCDF	0.05 <sup>b</sup>		nr				0.05 <sup>b,c</sup>	0.05	0.0025	
2,3,4,7,8-PeCDF	0.06 <sup>b</sup>		1.28 x 10 <sup>7</sup>	32%	0.03 <sup>b</sup>		0.09 <sup>b</sup>	0.5	0.045	
1,2,3,4,7,8-HxCDF	0.10 <sup>b</sup>		2.51 x 10 <sup>7</sup>	20%	0.02 <sup>b</sup>		0.12 <sup>b</sup>	0.1	0.012	
1,2,3,6,7,8-HxCDF	0.05 <sup>b</sup>		nr				0.05 <sup>b,c</sup>	0.1	0.005	
2,3,4,6,7,8-HxCDF	0.12 <sup>b</sup>		nr				0.12 <sup>b,c</sup>	0.1	0.012	
1,2,3,7,8,9-HxCDF	0.02 <sup>b</sup>		nr				0.02 <sup>b,c</sup>	0.1	0.002	
1,2,3,4,6,7,8-HpCDF	1.03		2.34 x 10 <sup>6</sup>	72%	2.69		3.72	0.01	0.0372	
1,2,3,4,7,8,9-HpCDF	0.06 <sup>b</sup>		2.56 x 10 <sup>6</sup>	71%	0.16 <sup>b</sup>		0.22 <sup>b</sup>	0.01	0.0022	
OCDF	3.50		5.62 x 10 <sup>6</sup>	52%	3.81		7.31	0.001	0.0073	
Total Toxicity Equivalent Load (mg/day)										0.7570

<sup>a</sup>from Mackay *et al.*, 1992

<sup>b</sup>Estimated *maximum possible* load based on detection limits

<sup>c</sup>Does not include dissolved fraction

nr = not reported

## Discussion

We were able to meet the stated objective in terms of estimating the *maximum possible* load of 2,3,7,8-TCDD at the Snake River mouth; 0.25 mg/day or about one-fifth of the EPA TMDL of 1.18 mg/day. As some reviewers have pointed out, the TMDL is based on the Snake River's harmonic mean flow at the mouth of  $9.06 \times 10^{10}$  L/day whereas the load calculated here was based on a flow of  $4.99 \times 10^{10}$  L/day. If, however, comparisons are made of water column concentrations, which are flow-neutral expressions, the *maximum possible* concentration of 2,3,7,8-TCDD in the Snake River during this survey was only 40% of the EPA water quality criterion (0.005 vs. 0.013 pg/L). However, the total *maximum possible* TEQ concentration in water, 0.015 pg/L, does exceed this criterion.

As mentioned previously, the calculated TEQ load is probably an overestimate because it takes into account compounds which were not detected. For instance, one-third of this estimate is contributed by 2,3,7,8-TCDD, which was not detected. If only the five detected PCDDs/PCDFs were considered, the TEQ load would be estimated at 0.29 mg/day, with 1,2,3,4,6,7,8-HpCDD as the major contributor to the overall toxicity.

This is the second of two Columbia River sub-basins where we have acquired data on daily loads of 2,3,7,8-TCDD and other PCDDs/PCDFs -- the other being the Columbia River watershed north of the Washington/Canada border. These two sub-basins are very similar in that both contain a single bleached kraft pulp mill which has, in the past, been responsible for the vast majority of PCDD/PCDD loading in each basin. The Columbia River north of the international boundary is also one of the three sub-basins selected for watershed loading targets in EPA's TMDL for 2,3,7,8-TCDD, due to PCDD/PCDF contamination from the Celgar pulp mill in Castlegar, British Columbia. The Willamette River watershed in Oregon is the third sub-basin with a loading target for 2,3,7,8-TCDD.

Like Potlatch, the Celgar pulp mill in B.C. initiated a number of changes, beginning around 1989, to reduce its production and discharge of PCDDs/PCDFs. From 1990 until 1994, we analyzed PCDDs/PCDFs in SPM collected from the Columbia River 40 miles downstream of Celgar to gauge the effectiveness of these changes. Data from this monitoring indicated that improvements made at Celgar resulted in reductions of SPM-bound PCDDs/PCDFs, especially 2,3,7,8-TCDF (Johnson *et al.*, 1991; Serdar *et al.*, 1993, 1994, & 1997-Draft).

Results of the present survey suggest that modifications instituted by Potlatch since 1988 have decreased their discharge of 2,3,7,8-TCDD, 2,3,7,8-TCDF, and possibly other PCDDs/PCDFs to the Snake River. Loads of 2,3,7,8-TCDD and 2,3,7,8-TCDF measured during this survey represent reductions of 98% and 99%, respectively, when

compared to loads measured during the 104 Mill Study. Of course, analysis of SPM at the mouth of the Snake River cannot be considered an accurate appraisal of concurrent discharges by Potlatch; four dams and 130 river miles stand between Potlatch and the Snake River mouth. Settling of particulate matter and resuspension of sediments are some of the processes which affect the transport of sediment-bound chemicals and therefore preclude giving these comparisons too much weight. Nonetheless, limited data on 2,3,7,8-TCDD and 2,3,7,8-TCDF in Potlatch's effluent from 1989-1990 indicate that significant reductions were being observed by late 1989 (Michael Letourneau, EPA Environmental Scientist, written communication). These data, coupled with the results of monitoring downstream of the Celgar mill, provide indirect evidence that PCDD/PCDF loading to the Snake River may be declining. An analysis of effluent from the potlatch mill, or nearby downstream monitoring, is probably the best way to determine if this is the case.

## Conclusion

The total *maximum possible* load of 2,3,7,8-TCDD at the Snake River mouth was 0.25 mg/day, about one-fifth of the target load for the Snake River watershed as described in EPA's TMDL for the Columbia River basin.

## Recommendations

- Measure 2,3,7,8-TCDD and other PCDDs/PCDFs in final effluent from the Potlatch pulp mill to determine if it meets their waste load allocation as described in the TMDL. Alternatively, measure these compounds in the Snake River just below the dilution zone for Potlatch's effluent to gauge their compliance with the TMDL.
- Monitor PCDDs/PCDFs in SPM at the Snake River mouth during high flow periods to assess the possible effects of increased sediment transport and sediment resuspension.

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## Acknowledgments

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- Kitty Bickle, Pam Covey, Debbie Lacroix, Stuart Magoon, Will White, and other staff of the Manchester Laboratory for sample handling and analysis, contract preparation, and data review.
- Mike Letourneau of EPA Region 10 provided information about the Potlatch mill, and Dave Reese of the ACOE Walla Walla District provided flow data.
- The report benefited from reviews by Bob Cusimano, Larry Goldstein, Art Johnson, Dale Norton, and Bill Yake of Ecology, as well as Rob Pedersen of EPA Region 10.
- Joan LeTourneau proofread and formatted the final report.

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## Contacts

Dave Serdar                      Washington State Department of Ecology  
   Environmental Investigations and Laboratory Services  
   Toxics Investigations Section  
   (360) 407-6772

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If you have special accommodation needs or require this document in alternative format, please contact Joan LeTourneau at (360) 407-6764 (voice) or (360) 407-6006 (TDD).

## **Appendix**


State of Washington Department of Ecology  
Manchester Environmental Laboratory  
7411 Beach Dr. East Port Orchard WA. 98366

Data Review  
January 30, 1997

Project: Dioxin in Snake River SPM

Samples: 438140

Laboratory: Quanterra

By: Stuart Magoon 

**Data Review for Polychlorodibenzo-p-dioxin and furan**  
( Tetra - octa PCDD/PCDF)  
on the Snake River suspended particulate matter sample.

Data from these analyses were reviewed for qualitative and quantitative accuracy, validity, and usefulness, following the National Functional Guidelines for Organic Data Review adapted for high resolution dioxin analysis.

These samples were prepared and analyzed according to EPA method 1613A.

The results are reported in Pico grams per gram (pg/g); parts per trillion dry weight.

Quanterra Laboratories has developed their own data "flags". The definitions of these "flags" are described as notes on the second page of each sample report sheet.

Flags are added by the laboratory performing the analysis, usually the analyst. Qualifiers are added by the data reviewer as part of addressing the usability of the data. Generally the flags signal the reviewer to access the results and determine what to do about the fact that flags were added. For your reporting purposes the "flags" should not be considered part of the final result. The qualifiers, however, are to be considered part of the final result.

## PCDD/PCDF Analysis

### **Holding times:**

EPA method 1613A does not specify a holding time from collection to extraction. However, EPA method 8290 recommends a holding time of thirty days (30) from the date of collection to the date of extraction. This sample was extracted ten (10) days after collection.

The sample extracts were analyzed forty (40) days after extraction, within the 40 day holding time required for EPA method 1613A.

### **Method Blank:**

No target analytes were detected in the method blank.

### **Calibration:**

The calibration standards were within 20 % relative standard deviations (RSD). All the ion abundance ratios were within +/- 15% of the theoretical value.

### **Internal Standard Recoveries:**

Internal standard recoveries for the all of the internal standards were well within the limits of 25 - 150%.

### **Isotopic abundance ratios:**

Every dioxin and furan isomer reported as detected met the isotopic abundance ratios criteria for positive identification.

### **Precision:**

This sample was analyzed in triplicate as specified in the QAPP. The relative differences between the sample, duplicate, and triplicate have been provided in table 1. The RPDs ranged from 0% to 22.2%, with a mean of 9.84%.



**Table 1**

Analyte	Sample original	Sample Duplicate	Sample Triplicate	RPD org&dup	RPD org&trp	RPD dup&trp	Sample Average
TCDF (total)	8.4	8.2	8	2.41%	4.88%	2.47%	8.2
2,3,7,8-TCDF	2	2	2	0.00%	0.00%	0.00%	2
HpCDFs (total)	15	14	12	6.90%	22.2%	15.4%	14
1,2,3,4,6,7,8-HpCDF	5.2	4.8	4.4	8.00%	16.7%	8.70%	4.8
OCDF	18	16	15	11.8%	18.2%	6.45%	16
TCDDs (total)	0.77	0.69	0.69	11.0%	11.0%	0.00%	0.72
HxCDDs (total)	4	3.5	3.4	13.3%	16.2%	2.9%	3.6
HpCDDs (Total)	58	54	48	7.14%	18.9%	11.8%	53
1,2,3,4,6,7,8-HpCDD	27	25	22	7.69%	20.4%	12.8%	25
OCDD	230	200	190	13.9%	19.0%	5.13%	207

**Matrix Spike:**

Matrix spike recoveries ranged from 66-95%. Although there are no established QC limits for this particular matrix, there are established limits for the laboratory control spike sample (Ottawa sand). These limits have been provided with the LCS analysis and can serve as guidance limits for the sample from the Snake River. Each analyte spike into the native sample (438140) demonstrated acceptable recoveries based on this comparison.

**Summary:**

This data is acceptable for use as amended. All analytes detected between the theoretical method detection limit ("DL") and the practical quantitation limit have been qualified with a "J".

*Quanterra Incorporated*  
880 Riverside Parkway  
West Sacramento, California 95605

916 373-5600 Telephone  
916 372-1059 Fax

December 19, 1996

QUANTERRA INCORPORATED PROJECT NUMBER: **090343**

Stuart Magoon  
Washington State Department of ecology  
Manchester Laboratory  
7411 Beach Drive East  
Port Orchard, WA 98366

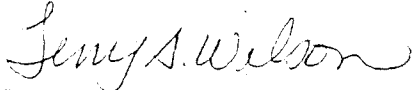
Dear Mr. Magoon:

This report contains the analytical results for the one soil sample which was received under chain of custody by Quanterra Incorporated on 01 November 1996 for your Snake River Project.

The case narrative is an integral part of this report.

If you have any questions, please feel free to call.

Sincerely,



Terry A. Wilson  
Project Manager  
Advanced Technology

TW/ct

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Includes Sample: 1SA, 1DU, 1 TR, 1MS

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Laboratory Control Sample

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**CASE NARRATIVE**

**QUANTERRA INCORPORATED PROJECT NUMBER 090343**

Detection limits for dioxins and furans are reported on a sample specific basis and all results are recovery corrected per the isotope dilution technique.

There were no anomalies associated with this report.

## QUANTERRA INCORPORATED QUALITY CONTROL PROGRAM

Quanterra has implemented an extensive Quality Control (QC) program to ensure the production of scientifically sound, legally defensible data of known documentable quality. This QC program is based upon requirements in "Test Methods for Evaluating Solid Waste", USEPA SW-846, Third Edition. It applies whenever SW-846 analytical methods are used. It also applies in whole or in part whenever project requirements fail to specify some aspect of QC practices described here. It does not apply when other well defined QC programs (e.g. CLP or CLP-like) are specified. This is Quanterra's base QC program for environmental analysis.

### **Definitions:**

Quality Control Batch. The quality control (QC) batch is a set of up to 20 field samples plus associated laboratory QC samples that are similar in composition (matrix) and that are processed within the same time period with the same reagent and standard lots.

Surrogate. A surrogate (or internal standard) is an organic compound similar in chemical behavior to the target analyte, but not normally found in environmental samples. Surrogates (or IS) are added to all samples in a batch to monitor the effects of both the matrix and the analytical process on accuracy.

Method Blank. A method blank (MB) is a control sample prepared using the same reagents used for the samples. As part of the QC batch, it accompanies the samples through all steps of the sample extraction and cleanup procedure. The method blank is used to monitor the level of contamination introduced to a batch of samples as a result of processing in the laboratory.

Laboratory Control Sample. A laboratory control sample (LCS) is prepared using a well characterized matrix (e.g., reagent water or Ottawa sand) that is spiked with known amounts of representative analytes. Alternate matrices (e.g., glass beads) may be used for soil analyses when Ottawa sand is not appropriate. As part of a QC batch, it accompanies the samples through all steps of the sample extraction and cleanup process. The LCS is used to monitor the accuracy of the analytical process independent of possible interference effects due to sample matrix.

Duplicate Control Sample. Duplicate laboratory control samples (DCS) consists of a pair of LCSs analyzed within the same QC batch to monitor precision and accuracy independent of sample matrix effects.

SAMPLE DESCRIPTION INFORMATION  
for  
Washington State Dept. of Ecology

Lab ID	Client ID	Matrix	Sampled		Received Date
			Date	Time	
090343-0001-MB	Method Blank	SOIL			01 NOV 96
090343-0001-SA	438140 (Sample)	SOIL			01 NOV 96
090343-0001-DU	438140 (Duplicate lab analysis)	SOIL			01 NOV 96
090343-0001-TR	438140 (TriPLICATE lab analysis)	SOIL			01 NOV 96
090343-0001-MS	438140 (Matrix spike)	SOIL			01 NOV 96



Environmental Services

POLYCHLORINATED DIOXINS/FURANS ISOMER SPECIFIC ANALYSIS Method 1613A

Client Name: Washington State Dept. of Ecology
Client ID: 438140
Lab ID: 090343-0001-SA
Matrix: SOIL
Authorized: 01 NOV 96

Sampled: Unknown
Prepared: 22 NOV 96

Received: 01 NOV 96
Analyzed: 13 DEC 96

Sample Amount: 20.0 G wet wt
Column Type: DB-5

Table with 5 columns: Parameter, Result, Dry Weight Units, Detection Limit, Data Qualifiers. Rows include Furans (TCDFs, PeCDFs, HxCDFs, HpCDFs, OCDF) and Dioxins (TCDDs, PeCDDs, HxCDDs, HpCDDs, OCDD).

(continued on following page)

ND = Not detected
NA = Not applicable

Reported By: Jill Kellmann

Approved By: Mark Bechthold

The cover letter is an integral part of this report.
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POLYCHLORINATED DIOXINS/FURANS  
ISOMER SPECIFIC ANALYSIS (CONT.)  
Method 1613A

Client Name: Washington State Dept. of Ecology

Client ID: 438140

Lab ID: 090343-0001-SA

Matrix: SOIL

Authorized: 01 NOV 96

Sampled: Unknown

Prepared: 22 NOV 96

Received: 01 NOV 96

Analyzed: 13 DEC 96

Sample Amount 20.0 G ~~wet wt~~  
Column Type DB-5

	% Recovery
13C-2,3,7,8-TCDF	95
13C-1,2,3,7,8-PeCDF	84
13C-2,3,4,7,8-PeCDF	85
13C-1,2,3,4,7,8-HxCDF	98
13C-1,2,3,6,7,8-HxCDF	94
13C-2,3,4,6,7,8-HxCDF	101
13C-1,2,3,7,8,9-HxCDF	94
13C-1,2,3,4,6,7,8-HpCDF	79
13C-1,2,3,4,7,8,9-HpCDF	89
13C-2,3,7,8-TCDD	91
37C1-2,3,7,8-TCDD	86
13C-1,2,3,7,8-PeCDD	98
13C-1,2,3,4,7,8-HxCDD	99
13C-1,2,3,6,7,8-HxCDD	97
13C-1,2,3,4,6,7,8-HpCDD	97
13C-OCDD	102

Percent Moisture is 62.2%. All results and limits are reported on a dry weight basis.

Note g : 2,3,7,8-TCDF results have been confirmed on a DB-225 column.

Note @ : Result is an estimated value that is below the lower calibration limit but above the target detection limit.

ND = Not detected  
NA = Not applicable

Reported By: Jill Kellmann

Approved By: Mark Bechthold

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POLYCHLORINATED DIOXINS/FURANS  
ISOMER SPECIFIC ANALYSIS  
Method 1613A

Client Name: Washington State Dept. of Ecology  
 Client ID: 438140  
 Lab ID: 090343-0001-DU  
 Matrix: SOIL  
 Authorized: 01 NOV 96  
 Sampled: Unknown  
 Prepared: 22 NOV 96  
 Received: 01 NOV 96  
 Analyzed: 13 DEC 96

Sample Amount: 20.0 G *wet wt*  
 Column Type: DB-5

Parameter	Result	Dry Weight Units	Detection Limit	Data Qualifiers
<b>Furans</b>				
TCDFs (total)	8.2	pg/g	--	
2,3,7,8-TCDF	2.0	pg/g	--	g
PeCDFs (total)	ND	pg/g	2.1	
1,2,3,7,8-PeCDF	ND	pg/g	0.19	
2,3,4,7,8-PeCDF	ND	pg/g	0.29	
HxCDFs (total)	ND	pg/g	2.1	
1,2,3,4,7,8-HxCDF	ND	pg/g	0.45	
1,2,3,6,7,8-HxCDF	ND	pg/g	0.20	
2,3,4,6,7,8-HxCDF	ND	pg/g	0.58	
1,2,3,7,8,9-HxCDF	ND	pg/g	0.064	
HpCDFs (total)	14	pg/g	--	
1,2,3,4,6,7,8-HpCDF	4.8 <i>J</i>	pg/g	--	@
1,2,3,4,7,8,9-HpCDF	ND	pg/g	0.32	
OCDF	16	pg/g	--	
<b>Dioxins</b>				
TCDDs (total)	0.69	pg/g	--	
2,3,7,8-TCDD	ND	pg/g	0.29	
PeCDDs (total)	ND	pg/g	0.85	
1,2,3,7,8-PeCDD	ND	pg/g	0.29	
HxCDDs (total)	3.5	pg/g	--	
1,2,3,4,7,8-HxCDD	ND	pg/g	0.40	
1,2,3,6,7,8-HxCDD	ND	pg/g	1.3	
1,2,3,7,8,9-HxCDD	ND	pg/g	1.2	
HpCDDs (total)	54	pg/g	--	
1,2,3,4,6,7,8-HpCDD	25	pg/g	--	
OCDD	200	pg/g	--	

(continued on following page)

ND = Not detected  
 NA = Not applicable

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POLYCHLORINATED DIOXINS/FURANS  
ISOMER SPECIFIC ANALYSIS (CONT.)  
Method 1613A

Client Name: Washington State Dept. of Ecology

Client ID: 438140

Lab ID: 090343-0001-DU

Matrix: SOIL

Authorized: 01 NOV 96

Sampled: Unknown

Prepared: 22 NOV 96

Received: 01 NOV 96

Analyzed: 13 DEC 96

Sample Amount 20.0 G *wet*  
Column Type DB-5

	% Recovery
13C-2,3,7,8-TCDF	95
13C-1,2,3,7,8-PeCDF	79
13C-2,3,4,7,8-PeCDF	85
13C-1,2,3,4,7,8-HxCDF	90
13C-1,2,3,6,7,8-HxCDF	89
13C-2,3,4,6,7,8-HxCDF	99
13C-1,2,3,7,8,9-HxCDF	92
13C-1,2,3,4,6,7,8-HpCDF	64
13C-1,2,3,4,7,8,9-HpCDF	82
13C-2,3,7,8-TCDD	91
37Cl-2,3,7,8-TCDD	88
13C-1,2,3,7,8-PeCDD	92
13C-1,2,3,4,7,8-HxCDD	93
13C-1,2,3,6,7,8-HxCDD	96
13C-1,2,3,4,6,7,8-HpCDD	92
13C-OCDD	98

Percent Moisture is 62.2%. All results and limits are reported on a dry weight basis.

Note g : 2,3,7,8-TCDF results have been confirmed on a DB-225 column.

Note @ : Result is an estimated value that is below the lower calibration limit but above the target detection limit.

ND = Not detected

NA = Not applicable

Reported By: Jill Kellmann

Approved By: Mark Bechthold

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Environmental Services

POLYCHLORINATED DIOXINS/FURANS ISOMER SPECIFIC ANALYSIS Method 1613A

Client Name: Washington State Dept. of Ecology
Client ID: 438140
Lab ID: 090343-0001-TR
Matrix: SOIL
Authorized: 01 NOV 96
Sampled: Unknown
Prepared: 22 NOV 96
Received: 01 NOV 96
Analyzed: 13 DEC 96

Sample Amount 20.0 G wet in
Column Type DB-5

Table with columns: Parameter, Result, Dry Weight Units, Detection Limit, Data Qualifiers. Rows include Furans (TCDFs, PeCDFs, HxCDFs, HpCDFs, OCDF) and Dioxins (TCDDs, PeCDDs, HxCDDs, HpCDDs, OCDD).

(continued on following page)

ND = Not detected
NA = Not applicable

Reported By: Jill Kellmann
Approved By: Mark Bechthold

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POLYCHLORINATED DIOXINS/FURANS  
ISOMER SPECIFIC ANALYSIS (CONT.)  
Method 1613A

Client Name: Washington State Dept. of Ecology  
 Client ID: 438140  
 Lab ID: 090343-0001-TR  
 Matrix: SOIL  
 Authorized: 01 NOV 96  
 Sampled: Unknown  
 Prepared: 22 NOV 96  
 Received: 01 NOV 96  
 Analyzed: 13 DEC 96

Sample Amount 20.0 G *wet wt*  
 Column Type DB-5

	% Recovery
13C-2,3,7,8-TCDF	98
13C-1,2,3,7,8-PeCDF	79
13C-2,3,4,7,8-PeCDF	83
13C-1,2,3,4,7,8-HxCDF	93
13C-1,2,3,6,7,8-HxCDF	92
13C-2,3,4,6,7,8-HxCDF	96
13C-1,2,3,7,8,9-HxCDF	94
13C-1,2,3,4,6,7,8-HpCDF	82
13C-1,2,3,4,7,8,9-HpCDF	92
13C-2,3,7,8-TCDD	92
37Cl-2,3,7,8-TCDD	90
13C-1,2,3,7,8-PeCDD	102
13C-1,2,3,4,7,8-HxCDD	94
13C-1,2,3,6,7,8-HxCDD	95
13C-1,2,3,4,6,7,8-HpCDD	97
13C-OCDD	103

Percent Moisture is 62.2%. All results and limits are reported on a dry weight basis.

Note g : 2,3,7,8-TCDF results have been confirmed on a DB-225 column.

Note @ : Result is an estimated value that is below the lower calibration limit but above the target detection limit.

ND = Not detected  
 NA = Not applicable

Reported By: Jill Kellmann

Approved By: Mark Bechthold

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MATRIX SPIKE / MATRIX SPIKE DUPLICATE REPORT  
 Advanced Technology Group - High Resolution  
 Project: 090343

Test: 1613-EPA-S  
 Matrix: SOIL  
 Sample: 090343-0001  
 Units: pg/g

Method: 1613A

Collection Date:

Analyte	----- Concentration -----							
	Sample Result	MS Result	MSD Result	Amount Spiked MS	MSD	%Recovery MS	MSD	% RPD
2,3,7,8-TCDF	2.0 g	24 g	NA	26		84		NC
1,2,3,7,8-PeCDF	ND	110	NA	130		79		NC
2,3,4,7,8-PeCDF	ND	110	NA	130		81		NC
1,2,3,4,7,8-HxCDF	ND	110	NA	130		86		NC
1,2,3,6,7,8-HxCDF	ND	110	NA	130		85		NC
2,3,4,6,7,8-HxCDF	ND	110	NA	130		85		NC
1,2,3,4,6,7,8-HpCDF	5.2 @	120	NA	130		83		NC
1,2,3,4,7,8,9-HpCDF	ND	110	NA	130		82		NC
OCDF	18	230	NA	260		78		NC
2,3,7,8-TCDD	ND	25	NA	26		95		NC
1,2,3,7,8-PeCDD	ND	110	NA	130		83		NC
1,2,3,4,7,8-HxCDD	ND	120	NA	130		88		NC
1,2,3,6,7,8-HxCDD	ND	120	NA	130		90		NC
1,2,3,7,8,9-HxCDD	ND	120	NA	130		88		NC
1,2,3,4,6,7,8-HpCDD	27	140	NA	130		83		NC
OCDD	230	400	NA	260		66		NC

Internal Standards	----- %Recovery -----		
	Sample	MS	MSD
13C-2,3,7,8-TCDF	95	102	NA
13C-1,2,3,7,8-PeCDF	84	82	NA
13C-2,3,4,7,8-PeCDF	85	89	NA
13C-1,2,3,4,7,8-HxCDF	98	89	NA
13C-1,2,3,6,7,8-HxCDF	94	88	NA
13C-2,3,4,6,7,8-HxCDF	101	91	NA
13C-1,2,3,7,8,9-HxCDF	94	92	NA
13C-1,2,3,4,6,7,8-HpCDF	79	65	NA
13C-1,2,3,4,7,8,9-HpCDF	89	77	NA
13C-2,3,7,8-TCDD	91	96	NA
13C-1,2,3,7,8-PeCDD	98	100	NA
13C-1,2,3,4,7,8-HxCDD	99	94	NA
13C-1,2,3,6,7,8-HxCDD	97	91	NA
13C-1,2,3,4,6,7,8-HpCDD	97	87	NA
13C-OCDD	102	81	NA

@ = Result is an estimated value that is below the lower calibration limit but above the target detection limit.

g = 2,3,7,8-TCDF results have been confirmed on a DB-225 column.

NA = Not Applicable

NC = Not Calculated, calculation not applicable.

ND = Not Detected

All calculations are performed before rounding to avoid round-off errors in calculated results.



POLYCHLORINATED DIOXINS/FURANS  
ISOMER SPECIFIC ANALYSIS  
Method 1613A

Client Name: Washington State Dept. of Ecology  
 Client ID: Method Blank  
 Lab ID: 090343-0001-MB  
 Matrix: SOIL  
 Authorized: 01 NOV 96  
 Sampled: NA  
 Prepared: 22 NOV 96  
 Received: NA  
 Analyzed: 11 DEC 96

Sample Amount 20.0 G  
 Column Type DB-5

Parameter	Result	Units	Detection Limit	Data Qualifiers <i>Flag</i>
<b>Furans</b>				
TCDFs (total)	ND	pg/g	0.032	
2,3,7,8-TCDF	ND	pg/g	0.032	
PeCDFs (total)	ND	pg/g	0.045	
1,2,3,7,8-PeCDF	ND	pg/g	0.040	
2,3,4,7,8-PeCDF	ND	pg/g	0.045	
HxCDFs (total)	ND	pg/g	0.16	
1,2,3,4,7,8-HxCDF	ND	pg/g	0.043	
1,2,3,6,7,8-HxCDF	ND	pg/g	0.041	
2,3,4,6,7,8-HxCDF	ND	pg/g	0.16	
1,2,3,7,8,9-HxCDF	ND	pg/g	0.027	
HpCDFs (total)	ND	pg/g	0.084	
1,2,3,4,6,7,8-HpCDF	ND	pg/g	0.058	
1,2,3,4,7,8,9-HpCDF	ND	pg/g	0.084	
OCDF	ND	pg/g	0.11	
<b>Dioxins</b>				
TCDDs (total)	ND	pg/g	0.10	
2,3,7,8-TCDD	ND	pg/g	0.035	
PeCDDs (total)	ND	pg/g	0.31	
1,2,3,7,8-PeCDD	ND	pg/g	0.071	
HxCDDs (total)	ND	pg/g	0.053	
1,2,3,4,7,8-HxCDD	ND	pg/g	0.053	
1,2,3,6,7,8-HxCDD	ND	pg/g	0.048	
1,2,3,7,8,9-HxCDD	ND	pg/g	0.047	
HpCDDs (total)	ND	pg/g	0.082	
1,2,3,4,6,7,8-HpCDD	ND	pg/g	0.082	
OCDD	ND	pg/g	0.72	

(continued on following page)

ND = Not detected  
 NA = Not applicable

Reported By: Andre Algazi

Approved By: Mark Bechthold

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Environmental  
Services

POLYCHLORINATED DIOXINS/FURANS  
ISOMER SPECIFIC ANALYSIS (CONT.)  
Method 1613A

Client Name: Washington State Dept. of Ecology

Client ID: Method Blank

Lab ID: 090343-0001-MB

Matrix: SOIL

Authorized: 01 NOV 96

Sampled: NA

Prepared: 22 NOV 96

Received: NA

Analyzed: 11 DEC 96

Sample Amount 20.0 G  
Column Type DB-5

% Recovery

13C-2,3,7,8-TCDF	97
13C-1,2,3,7,8-PeCDF	93
13C-2,3,4,7,8-PeCDF	94
13C-1,2,3,4,7,8-HxCDF	94
13C-1,2,3,6,7,8-HxCDF	94
13C-2,3,4,6,7,8-HxCDF	95
13C-1,2,3,7,8,9-HxCDF	95
13C-1,2,3,4,6,7,8-HpCDF	72
13C-1,2,3,4,7,8,9-HpCDF	79
13C-2,3,7,8-TCDD	92
37Cl-2,3,7,8-TCDD	85
13C-1,2,3,7,8-PeCDD	99
13C-1,2,3,4,7,8-HxCDD	95
13C-1,2,3,6,7,8-HxCDD	97
13C-1,2,3,4,6,7,8-HpCDD	98
13C-OCDD	98

ND = Not detected  
NA = Not applicable

Reported By: Andre Algazi

Approved By: Mark Bechthold

The cover letter is an integral part of this report.  
Rev 230787

LABORATORY CONTROL SAMPLE REPORT  
Advanced Technology Group - High Resolution  
Project: 090343

Category: 1613-HR-S C14-C18 D/F plus 2378-substituted isomers by Method 1613  
Test: 1613-EPA-S  
Matrix: SOLID  
QC Lot: 22 NOV 96-A  
Concentration Units: pg/uL

QC Run: 13 DEC 96-B

Analyte	Concentration		Accuracy(%)	
	Spiked	Measured	LCS	Limits
2,3,7,8-TCDF	10.0	8.90	89	69-152
1,2,3,7,8-PeCDF	50.0	43.1	86	71-139
2,3,4,7,8-PeCDF	50.0	36.8	74	69-144
1,2,3,4,7,8-HxCDF	50.0	44.3	89	70-123
1,2,3,6,7,8-HxCDF	50.0	44.0	88	76-133
2,3,4,6,7,8-HxCDF	50.0	44.5	89	65-139
1,2,3,7,8,9-HxCDF	50.0	44.6	89	75-125
1,2,3,4,6,7,8-HpCDF	50.0	44.4	89	59-144
1,2,3,4,7,8,9-HpCDF	50.0	43.8	88	63-148
OCDF	100	84.4	84	32-190
2,3,7,8-TCDD	10.0	8.97	90	69-138
1,2,3,7,8-PeCDD	50.0	42.7	85	71-136
1,2,3,4,7,8-HxCDD	50.0	42.8	86	73-141
1,2,3,6,7,8-HxCDD	50.0	44.7	89	84-125
1,2,3,7,8,9-HxCDD	50.0	46.8	94	43-171
1,2,3,4,6,7,8-HpCDD	50.0	43.5	87	72-133
OCDD	100	86.9	87	79-141
13C-2,3,7,8-TCDF	100	97.8	98	25-150
13C-1,2,3,7,8-PeCDF	100	90.9	91	25-150
13C-2,3,4,7,8-PeCDF	100	64.8	65	25-150
13C-1,2,3,4,7,8-HxCDF	100	99.4	99	25-150
13C-1,2,3,6,7,8-HxCDF	100	94.6	95	25-150
13C-2,3,4,6,7,8-HxCDF	100	91.5	92	25-150
13C-1,2,3,7,8,9-HxCDF	100	98.0	98	25-150
13C-1,2,3,4,6,7,8-HpCDF	100	86.8	87	25-150
13C-1,2,3,4,7,8,9-HpCDF	100	90.7	91	25-150
13C-2,3,7,8-TCDD	100	89.2	89	25-150
37Cl-2,3,7,8-TCDD	40.0	33.7	84	25-150
13C-1,2,3,7,8-PeCDD	100	95.4	95	25-150
13C-1,2,3,4,7,8-HxCDD	100	95.7	96	25-150
13C-1,2,3,6,7,8-HxCDD	100	96.2	96	25-150
13C-1,2,3,4,6,7,8-HpCDD	100	95.7	96	25-150
13C-OCDD	200	185	92	25-150

Calculations are performed before rounding to avoid round-off errors in calculated results.



Washington State Department of Ecology  
Manchester Laboratory

November 26, 1996

TO: Dave Serdar

FROM: Debbie Lacroix, Chemist *DL*

SUBJECT: General Chemistry Quality Assurance memo for the Dioxin in Snake River SPM Project

### **SUMMARY**

The data generated by the analysis of these samples can be used noting the qualifications discussed in this memo. All DOC data except for samples 96438133 and 438134 and all TOC data have been qualified as estimates. The data for the soil TOC is not included in this memo since analysis has not yet been performed.

### **SAMPLE INFORMATION**

Samples 96438130-40 from the Dioxin in Snake River SPM Project were received by the Manchester Laboratory on 10-25-96 in good condition.

### **HOLDING TIMES**

All analyses were performed within applicable EPA holding times.

### **ANALYSIS PERFORMANCE**

#### Instrument Calibration

Where applicable, instrument calibration was performed before each analysis and verified by initial and verification standards and blanks. Two of the four continuing calibration verification standards for DOC and TOC analysis were not within the relevant EPA control limits. Therefore, the data has been qualified as estimates. A correlation of 0.995 or greater was met as stated in CLP calibration requirements. All balances are calibrated yearly with calibration verification occurring monthly.

#### Procedural Blanks

All procedural blanks were within acceptable limits.

### Spiked Sample Analysis

All spike recoveries were within the acceptance window of +/- 25 %.

### Precision Data

The results of the duplicate analyses of samples were used to evaluate the precision on this sample set. The Relative Percent Differences (RPD) were within their acceptance windows of +/- 20 %.

### Laboratory Control Sample (LCS) Analyses

LCS analyses were within their acceptance windows of +/- 20 %.

Please call Debbie Lacroix at 871-8812 with any questions or concerns about this project.

cc: Bill Kammin  
Project File

Washington State Department of Ecology  
Manchester Laboratory

February 14, 1997

TO: Dave Serdar

FROM: Debbie Lacroix, Chemist *DL*

SUBJECT: General Chemistry Quality Assurance memo for the Dioxin in Snake River  
Sediment TOC

**SUMMARY**

The data generated by the analysis of this sample can be used without qualification. All results are calculated on a dry weight basis at 103°C.

**SAMPLE INFORMATION**

Sample 96438140 from the Dioxin in Snake River project was received by the Manchester Laboratory on 10-25-96 in good condition.

**HOLDING TIMES**

The analysis was performed within applicable EPA holding times.

**ANALYSIS PERFORMANCE**

Instrument Calibration

Where applicable, instrument calibration was performed before each analysis and verified by initial and verification standards and blanks. All initial and continuing calibration verification standards were within the relevant EPA control limits. A correlation of 0.995 or greater was met as stated in CLP calibration requirements. All balances are calibrated yearly with calibration verification occurring monthly. All oven temperatures are checked before and after sample drying to insure control.

Procedural Blanks

All procedural blanks were within acceptable limits.

Spiked Sample Analysis

No spikes were performed on this parameter.

### Precision Data

The results of the triplicate analysis of the sample were used to evaluate the precision on this sample set. The Relative Standard Deviation (RSD) was within its acceptance window of +/- 10 %.

### Laboratory Control Sample (LCS) Analyses

LCS analyses were within their acceptance windows of +/- 20 %.

### Other Quality Assurance Issues

Analysis for this sample was performed on 1-15-97 and a confirmation re-analysis on the sample was performed on 1-29-97. The sample analyzed on 1-29-97 was sent back from the contract lab. The analysis on 1-15-97 produced results of 4.02 % carbon and 4.08 % carbon. Analysis on 1-29-97 produced results of 3.99 %, 3.69 %, and 3.69 % carbon. The results from 1-29-97 were used for data reporting.

Please call Debbie Lacroix at SCAN 871-8812 with any questions or concerns about this project.

cc: Project File

Table A-1. Precision of PCDD/PCDF Analysis.

	Analysis 1	Analysis 2	Analysis 3	RSD
2,3,7,8-TCDD	U (0.32)	U (0.29)	U (0.24)	nc
1,2,3,7,8-PeCDD	U (0.26)	U (0.29)	U (0.23)	nc
1,2,3,4,7,8-HxCDD	U (0.34)	U (0.40)	U (0.40)	nc
1,2,3,6,7,8-HxCDD	U (1.3)	U (1.3)	U (1.1)	nc
1,2,3,7,8,9-HxCDD	U (1.2)	U (1.2)	U (1.1)	nc
1,2,3,4,6,7,8-HpCDD	27	25	22	10%
OCDD	230	200	190	10%
2,3,7,8-TCDF	2	2	2	0%
1,2,3,7,8-PeCDF	U (0.23)	U (0.19)	U (0.23)	nc
2,3,4,7,8-PeCDF	U (0.32)	U (0.29)	U (0.26)	nc
1,2,3,4,7,8-HxCDF	U (0.48)	U (0.45)	U (0.42)	nc
1,2,3,6,7,8-HxCDF	U (0.26)	U (0.20)	U (0.29)	nc
2,3,4,6,7,8-HxCDF	U (0.58)	U (0.58)	U (0.53)	nc
1,2,3,7,8,9-HxCDF	U (0.12)	U (0.064)	U (0.061)	nc
1,2,3,4,6,7,8-HpCDF	5.2 J	4.8 J	4.4 J	8%
1,2,3,4,7,8,9-HpCDF	U (0.29)	U (0.32)	U (0.29)	nc
OCDF	18	16	15	9%

RSD=Relative Standard Deviation

U=Undetected at concentration in parentheses

nc=not calculated

J=estimated concentration

Table A-2. Precision of General Chemistry Analysis.

	Laboratory Duplicates			Field Replicates		
	Analysis 1	Analysis 2	RPD	Rep.1	Rep. 2	RPD
DOC (mg/L)	1	1 U	nc	1.1 J	1.6 J	37%
TOC (mg/L)	3.0 J	2.7 J	11%	2.9 J	2.9 J	0%
TSS (mg/L)	4	4	0%	4	4	0%

RSD=Relative Percent Difference

U=Undetected at concentration in parentheses

nc=not calculated

J=estimated concentration