Quality Assurance Project Plan

Spatial Extent of Dioxin/Furan Contaminated Sediments in Dillenbaugh Creek

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January 2004

Publication No. 04-03-101

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Waterbodies addressed in this study:
Dillenbaugh Creek (WA-23-1027)

Ecology EIM number: RJAC006

Approvals

Approved by:	December 18, 2003
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Rebecca Lawson, Section Manager, Toxics Cleanup Program, SWRO	Date
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Approved by:	December 18, 2003
Will Kendra, Section Manager, Watershed Ecology Section	Date
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Stuart Magoon, Director, Manchester Environmental Laboratory	Date
Approved by:	December 18, 2003
Cliff Kirchmer, Ecology Quality Assurance Officer	Date

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Abstract

This study plan describes the field and laboratory procedures that will be used to investigate the spatial extent of dioxin and furan contamination of sediments in Dillenbaugh Creek, Chehalis, Washington. The investigation will use 22 surface (top 5 cm) sediment stations and four shallow sediment cores to delineate the horizontal and vertical extent of sediment contamination. The sediment cleanup level has not yet been selected, but the analytical methods used provide detection limits down to likely cleanup levels. EPA method 4025, an immunoassay technique, is the principal analytical method for these sediments. These results will be checked for accuracy and false positive and negatives using high-resolution gas chromatography / high-resolution mass spectrometry analysis, EPA method 1613b, on 40% of the samples.

Background and Problem Statement

The American Crossarm and Conduit Company (ACC) operated a wood-treating facility adjacent to Dillenbaugh Creek in Chehalis, Washington from the 1930s to 1983. This site is contaminated with polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/PCDFs), polycyclic aromatic hydrocarbons (PAHs), and pentachlorophenol (PCP) through the discharge of process liquids and wastewaters. In 1986, contamination was dispersed throughout the property when the Chehalis River flooded and spread about 10,000 gallons of PCP mixed with diesel oil to neighboring residences (Figure 1).

In the early 1990s, Roy F. Weston, Inc., under contract with the U.S. Environmental Protection Agency (EPA), determined the nature and extent of residual contamination at the site. These investigations were conducted following remedial actions which had begun after the 1986 flooding events. Weston found up to 0.8 ng/L of PCDD/PCDFs in surface waters of Dillenbaugh Creek and 0.6 ng/L from the nearby stormwater lagoon and in the Chehalis River (Weston, 1992).

In 1998, the Washington State Department of Ecology (Ecology) conducted a follow-up investigation to evaluate contaminant levels in Dillenbaugh Creek fish and sediment (Era-Miller et al., 2002). The results of this study showed that Dillenbaugh Creek sediments within the ACC area of contamination were higher than background stations and sediments in the Chehalis River.

PCDD/PCDF concentrations in cutthroat trout and mountain whitefish fillets and in whole brown bullhead and largescale suckers from Dillenbaugh Creek and the Chehalis River were above the National Toxics Rule fish tissue criterion and EPA screening values for both subsistence and recreational consumers (Era-Miller et al., 2002). Concentrations in fish were also high enough to pose a potential risk to wildlife.

Ecology's Toxics Cleanup Program has requested that Ecology's Environmental Assessment Program identify the horizontal and vertical extent of PCDD/PCDF contamination in Dillenbaugh Creek to allow a cleanup remedy to be designed and implemented. This investigation does not include PAHs or pentachlorophenol, as these possible contaminants are not believed to pose a risk to humans or wildlife. A dioxin/furan cleanup level has not yet been chosen by the Toxics Cleanup Program.

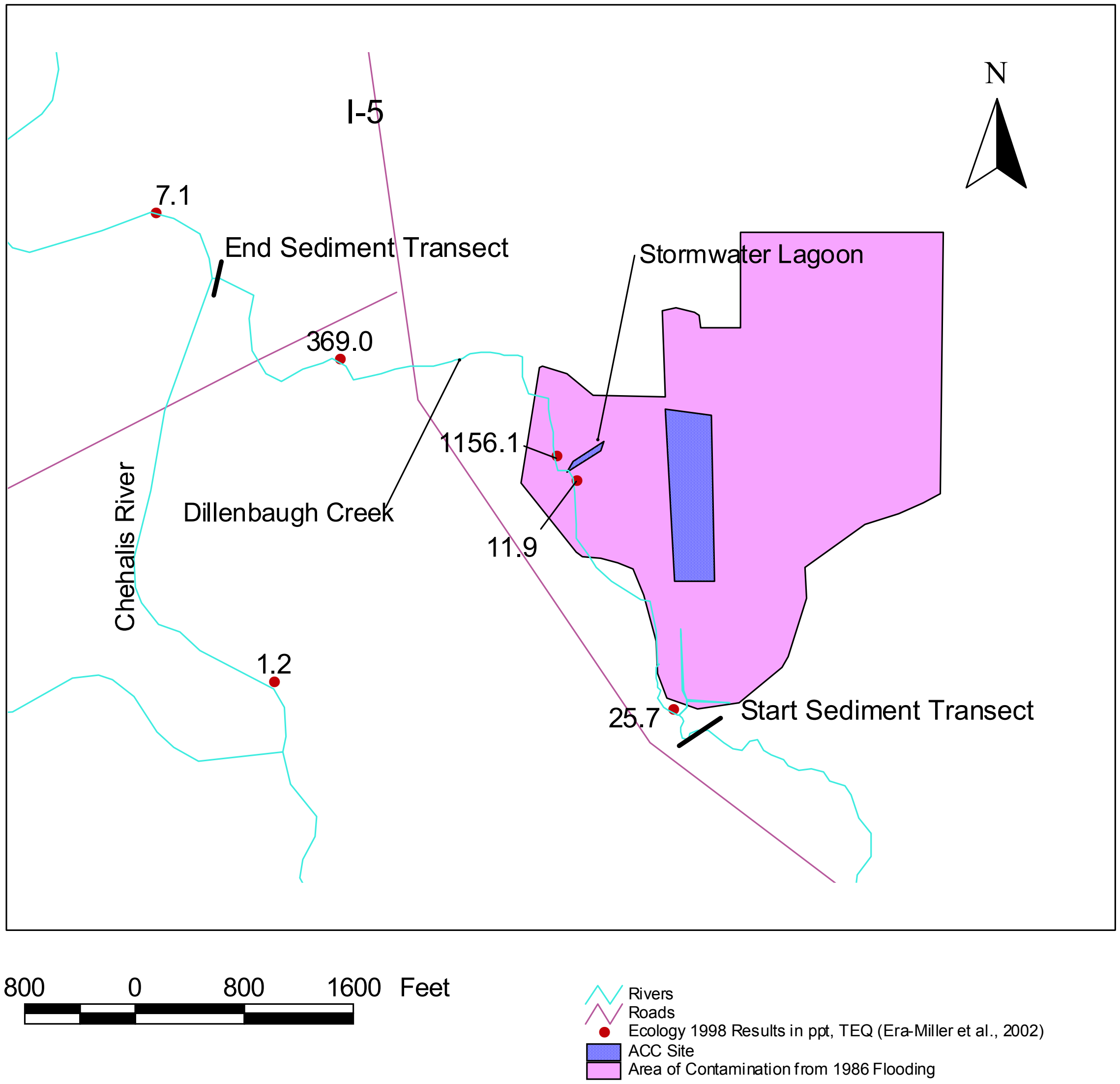

Figure 1. Dillenbaugh Creek with ACC site, Area of 1986 Flooding, and Start and End of Sediment Transect.

Project Description

This project is designed to evaluate the spatial extent of dioxin/furan contamination in Dillenbaugh Creek sediments downstream from the ACC site. A combination of 22 surficial (top 5 cm) samples and four sediment cores (to 76 cm) will be used to construct a two-dimensional map of PCDD/PCDF contamination. This project will use two analytical techniques to measure PCDD/PCDF concentrations:

1. An immunoassay technique will be used to semi-quantitatively assess dioxin toxic equivalent concentrations (TEQs) in approximately 30 samples, 22 surface sediments and 8 core samples. About 12 of these 30 samples will have confirmatory high-resolution gas chromatography / high-resolution mass spectrometry analysis (HRGC-HRMS) conducted.
2. A sediment trap will be used to collect particulates from the stormwater lagoon outfall to confirm that this is not an ongoing source of PCDD/PCDFs to Dillenbaugh Creek.

Responsibilities

Richard Jack, Toxic Studies Unit, Environmental Assessment (EA) Program
Project Manager for Quality Assurance (QA) Project Plan completion and field sampling.

Carolyn Lee, Toxics Studies Unit, EA Program
EIM Data entry

Dale Norton, Supervisor, Toxic Studies Unit, EA Program
Review of draft and final QA Project Plan

Cliff Kirchmer, Ecology Quality Assurance Officer
Review of draft and final QA Project Plan

Stuart Magoon, Ecology Manchester Laboratory Director
Review of draft and final QA Project Plan, scheduling and contracting of contract analytical analysis

Schedule

Final QA Project Plan complete	December 2003
Field sampling begins	January 2004
Field sampling complete	April 2004
Analytical analysis complete	June 2004
Draft report complete	September 2004
Final report complete	November 2004
EIM data entry complete	December 2004

Data Quality Objectives and Decision Criteria

This study will map the spatial extent of PCDD/PCDF contamination in Dillenbaugh Creek downstream from the former ACC woodtreating facility. No cleanup level has been selected. To allow for maximum flexibility in setting any future cleanup level, the lowest possible detection limits for the methods available have been chosen.

The immunoassay analysis, EPA Method 4025, has a detection limit of approximately 5 to 10 parts per trillion TEQ. The immunoassay method uses anti-dioxin antibodies to respond to the toxic PCDD/PCDF congeners in approximate correlation to their toxic equivalency factors (TEFs). There are 75 PCDD congeners and 135 PCDF congeners. The immunoassay test is capable of multiple congener recognition and preferentially targets those congeners with the higher TEF values. The test is most sensitive to 2,3,7,8-TCDD and 1,2,3,7,8-PeCDD, and progressively less sensitive to congeners with lower TEF values. This method has been tested and verified against EPA Method 8290.

The samples analyzed by both immunoassay and HRGC-HRMS should allow an accurate correlation to be developed. An r^2 of 0.80 will be considered suitable for this project. The immunoassay method has a very low false negative rate (<1%) as well as a suitably low false positive rate (9%).

The accuracy, bias, and precision required for the analytical methods of the project are provided in Table 1. Necessary reporting limits are also shown.

Table 1. Analytical Goals by Method for the Dillenbaugh Creek Sediment Investigation

Parameter	Surrogate or Control Sample Recovery Limits	Precision (RPD)	Required Reporting Limit
Dioxins, by Method 4025 – Immunoassay	N/A	40%	10 pg/g, total TEQ
Dioxins, by Method 1613b – HRGC-HRMS	Per Table 7, Method 1613b	30%	1 pg/g, total TEQ
% Solids	90-110%	25%	1%
Total organic carbon	90-110%	10%	0.5%
Grain size	N/A[a]	20%	±1% per size fraction

[a] Evaluated Qualitatively

RPD = Relative percent difference

Study Design

This investigation will use a linear, downstream transect of surficial sediment stations to delineate the extent of PCDD/PCDF contamination in Dillenbaugh Creek. The transect will start approximately at the upstream boundary of the ACC property and continue past the stormwater lagoon, ending at the Chehalis River (Figure 1). Twenty-two sediment stations will be spaced at approximately 250-foot intervals downstream from the upstream property boundary/corner and ending at the confluence of Dillenbaugh Creek with the Chehalis River. The stations will be spaced evenly between the property and the Chehalis River because Era-miller et al. (2002) found high sediment TEQs at least as far downstream as State Highway 6. At four stations, sediment cores will be collected. All stations will be located in the portion of the creek channel with the most fine grained sediment (e.g., bars on the inside of bends) or in the approximate center of the channel.

The above sampling density will estimate the volume of contaminated sediment to plus or minus approximately 150 cubic yards. This estimate is based on an average stream width of about five to seven feet and contamination depth of one to two feet. This sampling intensity is considered appropriate for dry excavation of the contaminated sediment, the most likely remedial design option. Dry excavation, by routing the creek's water into a nearby pipe, would need to be further examined in a detailed engineering report. A comparison of possible remedial design options is outside of the scope of this project.

The stations selected for coring will be located in the field, based on stream and sediment characteristics and likely sediment depths. The four stations will be spaced approximately evenly along the transect. Two sediment depths will be sampled via the cores, 30 to 45 cm, and 60 to 76 cm (12 to 18 inches and 24 to 30 inches). It is anticipated that the deeper core samples will not show elevated dioxin/furan concentrations. If these cores show high levels of PCDD/PCDFs in deeper sediments, further pre-remedy investigation may be required. The only extant information about sediment concentrations (Era-miller et al., 2002) is too widely spaced to make decisions about the limits of contamination, and there is no cleanup level specified.

To confirm that the ACC site is not an ongoing source of PCDD/PCDFs to Dillenbaugh Creek, one sediment trap will be deployed in the site's stormwater outfall during the winter. The sediment trap will be deployed during the winter rainy season for a minimum of eight inches of rainfall as measured by a local weather station. The total suspended solids of the water leaving the stormwater lagoon is unknown. However, based on urban use of the sediment trap in catch basins, 8 inches of rainfall will yield approximately 10 to 200 grams of suspended sediment (dry weight). If insufficient mass is retrieved, the trap will be replaced for additional time and/or rainfall.

Field Procedures

The surficial sediment stations will be located at 250-foot intervals downstream from the upstream limits of the property. At all stations, a petite Ponar ($0.05m^2$) will be used to collect three sediment grabs from a 2-m radius. The top 5-cm of sediment from these grabs will be composited in a stainless steel mixing bowl, mixed thoroughly with stainless steel spoons, and placed into precleaned glass jars.

At four stations, shallow sediment cores will be collected by hand. The cores will be collected using a 1-inch diameter hand corer and will penetrate 76-cm or as deep as possible until refusal. The corer will be fitted with a dedicated stainless steel liner tube. A rubber stopper will be used on the top end of the core tube to help prevent core loss.

The corer will be driven into the stream sediment a minimum of three times within 2 meters of each station. Sediment from the 30 to 45-cm depth, and the 60 to 76-cm depths will be removed from the liner tube separately. Depth will be measured as the penetration depth of the corer. Penetration depth will be corrected for core compression, as measured by the length of sediment column retained in the core, by assuming compression occurs evenly throughout the core length. The shallow (30 to 45-cm) layers from the three penetrations will be composited together and the deep (60 to 76-cm) layers will likewise be composited separately. The two separate depth composites will be mixed in dedicated bowls with dedicated spoons and placed into precleaned jars. Required jar sizes and the required holding times are listed in Table 2.

Table 2. Dillenbaugh Creek Sediment Sampling Containers and Holding Times.

Analysis	Container	Number collected	Holding time and conditions
PCDD/PCDFs by immunoassay	4 oz. glass jar	40	90 days @ 4º C
PCDD/PCDFs by HRGC-HRMS	4 oz. glass jar	12	1 year @ <-10º C
Total organic carbon	2 oz. glass jar	31	28 days @ 4º C
Grain Size	8 oz. plastic jar	31	6 months

All of the stainless steel sampling and compositing implements will be cleaned by sequentially:

1. Washing in Liquinox detergent and hot tap water
2. Rinsing with hot tap water
3. Rinsing with deionized water
4. Rinsing with pesticide-grade acetone
5. Rinsing with pesticide-grade hexane
6. Air-drying
7. Wrapping with aluminum foil until use

For the analysis of suspended sediment potentially released from the stormwater lagoon, a stainless steel sediment trap will be installed in the outfall pipe. The sediment trap is an Environmental Assessment Program designed device, specifically built for deployment in catch basin and other outfalls (Wilson and Norton, 1996). It will use a Teflon bottle as a liner. The liner jar and the sampler will be cleaned per the methods described above.

Field personnel will be trained as described in Appendix A – *Health and Safety Plan*. Personal protective equipment requirements are also described in Appendix A.

Laboratory Procedures

Two analytical methods for determination of PCDD/PCDFs have been selected for this project:

1. All of the sediment samples will be analyzed by SW-846 Method 4025. This immunoassay method uses a polyclonal antibody which responds to PCDD/PCDF congeners in approximate correlation to their TEFs. The method is most specific to 2,3,7,8,-TCDD, 1,2,3,7,8-PeCDD and less sensitive to OCCD and other congeners with lower TEF values. The measured response is proportional to the total TEQ of the sample and is reported in TEQ/ppt units. This method has been validated by EPA and is appropriate for the sediments in this investigation. Detection limits are approximately 5 to 10 ppt TEQ with a rigorous cleanup technique. The preferred technique uses a silica-carbon mini-column as outlined in Cape-Tech Application Note AN-008 (2003). Other comparable cleanup methods may be used with prior notice to the project officer.

   Method 4025 includes a variety of internal and other quality control standards which are described further under Quality Control Procedures. Thirty samples will be analyzed with this method.

2. Of the 30 samples analyzed by immunoassay, 12 (40%) will be analyzed by HRGC-HRMS. These samples will be selected from the range of PCDD/PCDF concentrations reported via Method 4025. Each quartile of immunoassay results will have three samples analyzed by Method 1613b. Method 1613b uses isotope dilution and high-resolution gas chromatography / high-resolution mass spectrometry to detect and quantify tetra through octa-chlorinated PCDD/PCDFs.

Analytical costs for the project are provided in Table 3.

Table 3. Analytical Costs for the Dillenbaugh Creek Sediment Investigation

Method	Number of Samples	Unit Cost	Subtotal
Immunoassay	40	$250.00	$10,000.00
HRGC-HRMS	12	$900.00	$10,800.00
Grain size	31	$100.00	$3,100.00
Total organic carbon	31	$39.00*	$1,209.00
% Solids	31	$10.00*	$310.00
Manchester Lab contracting fees		25% of $20,800	$5,200
		Total	**$30,619**

* Manchester Lab conducted analysis includes a 50% base funding discount.

Quality Control Procedures

Field

Field quality control (QC) will consist of the use of pre-cleaned bottles and sampling equipment which are dedicated to each station. In the case of the hand corer, dedicated stainless steel liners will be used for each core. The corer's stainless steel drive tube will be rinsed with on-site water at each station. Field QC will be checked by performing a blind field duplicate for the immunoassay analysis, total organic carbon, grain size, and percent solids.

Laboratory

For this investigation, standard QC for the immunoassay method will suffice. There will be at least nine QC samples for the 30 sediment samples. The QA samples include replicates, matrix spikes, check standards, standard reference materials, method blanks, and laboratory control samples.

The standard QC for the immunoassay methods will be used for this project. This includes check standards, method blanks, and standard reference materials. There will be six matrix spikes (20% frequency) and three laboratory duplicates (10%). The costs for these measures have been included in the cost quote in Table 3. In addition, at least one standard reference sample, one method blank, and lab control samples will be analyzed. Costs for these QA samples have not been included in the analytical costs in Table 3 and are presumed to be included in the overall analysis.

The HRGC-HRMS methods use isotopic dilution with 15 different C^{13} labeled PCDD/PCDF congeners. These labeled congeners allow for the reported concentrations of target analytes to be based on the recovery of the labeled congeners. For those congeners without an isotopically labeled standard, concentrations of the analyte of interest are quantified using a labeled congener with the same degree of chlorination. The isotopic dilution of every environmental sample analyzed by this method effectively creates a matrix spike within each sample using isotopically labeled analogs of the PCDD and PCDF contaminant congeners, compensating for the varying recovery efficiencies across the chlorination range. Separate matrix spikes and matrix spike duplicates, which only estimate the recovery efficiencies of the homologue groups to the environmental samples, are not referenced in the method and will not be used.

Method 1613b includes guidelines for initial calibration and ongoing precision and recovery, and these provisions will be strictly followed.

Table 4. Laboratory Quality Control Required.

Method	Standard Reference Material Analysis	Laboratory Duplicates	Matrix Spike	Laboratory Control Samples	Method Blanks
Immunoassay	1 per batch, NIST SRM #1944 or equivalent	1 per 10 samples (3 total)	2 per 10 samples (6 total)	1 prior to sample analysis and 1 after, not less than 2 in 20 samples	1 per 20 samples
HRGC-HRMS	None	None	None	Minimum per methods	1 per batch
Total organic carbon	None	1	None	1	1
Grain Size	None	1 triplicate analysis	None	None	None

Data Reduction and Management Procedures

Contract laboratories will be required to submit results electronically in a form suitable for entry into Ecology's Environmental Information Management (EIM) database. All data will be entered into EIM and Ecology's SedQual databases according to the schedule above.

Data Verification and Validation

Data Review

Samples for both method 4025 and 1613b will be analyzed by contract laboratories. As part of the contracting process, a Quality Assurance chemist at Ecology's Manchester Environmental Laboratory will evaluate all of the data and contract laboratory narratives for compliance with method specifications and quality. This evaluation will include a review of the calibration data and the ongoing precision and recovery results.

Data Validation

Data validation will use Manchester's standard data qualifiers to describe any excursions from optimum precision or recoveries. The project officer will further review the data as qualified to ensure that the results meet the objective of delineating the nature and extent of PCDD/PCDF contamination.

Data Quality Assessment

Precision

Precision will be evaluated by reviewing laboratory and field replicates. The precision goals expressed in Table 1 above are maximums, with consideration of the low detection limits requested in this study. For samples with higher concentrations of PCDD/PCDFs, it is expected that the precision of replicates will be superior.

Bias

Bias will be evaluated by comparison of immunoassay results with HRGC-HRMS results. A correlation equal to or greater than $r^2=0.80$ will be considered acceptable. Because the HRGC-HRMS samples are internally spiked with at least 15 isotopically labeled congeners, and the results for autochthonous compounds are calculated relative to the recovery of the sample's labeled standards, this method is considered to present no systematic bias.

Completeness

The completeness goal for this project is 100 percent. This goal is necessary to fully describe the nature and extent of PCDD/PCDF contamination.

Project Reports

The final report for this project will present the results of both the immunoassay and confirmatory HRGC-HRMS analysis. Any discrepancies between the results will be provided in numeric terms, and the magnitude of impact on possible remedial designs will be described.

The report will include maps of the areal extent of PCDD/PCDF contamination using at least three potential cleanup concentrations. These maps will include volume estimates and conceptual remedial strategies which might be elaborated upon in future detailed engineering reports.

References

Cape-Tech. 2003. Application Note AN-008: Analysis of ppt (pg/g) range PCDD/Fs in soil and sediment using rapid extraction and rapid cleanup (modified Method 4025). Available directly from Cape-Tech, email: cape-tech@ceemaine.org

EPA. 2002. Screening for Polychlorinated Dibenzodioxins and Polychlorinated Dibenzofurans (PCDD/Fs) by Immunoassay. EPA Method 4025. Available online at: http://www.epa.gov/SW-846/pdfs/4025.pdf

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Appendix

Health and Safety Plan

HEALTH AND SAFETY SITE PLAN/CHECKLIST

Name of Ecology inspector(s) Richard Jack and at least one other

Training requirements for this inspection 40hr. Hazwoper + refresher

Medical monitoring requirements participant

Date January 2004 (start) Arrival time various

Total anticipated time on site 4 days

Site name Dillebaugh Creek, American Crossarm + Conduit

Site location Chehalis, WA

Nearest city Chehalis, WA Nearest hospital Providence Centralia

Emergency numbers Statewide - 911 Hospital 360-736-2803 Ambulance__________

Name of contractor (if on site) none

Is the site currently active? Yes___ No X Will the buddy system be used? Yes X No______

Site description Dillenbaugh Creek, a wadable stream

Scope/objective of work Sampling of sediments and suspended sediment in storm runoff for design of cleanup remedy

Known contaminants on site Dioxins, furans, pentachlorophenol, PAHs

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Routes of chemical exposure: Inhalation_______ Dermal X No exposure_________

Overall risk of chemical exposure: Serious____ Moderate_____ Low_____ Unknown X

Physical hazards: Confined space______ Noise______ Heat/cold stress______

(continued on next page)

Describe any area on site that could function as a confined/enclosed space none known

Was air monitoring conducted? Yes___ No X

Personal protection level required A B [✓ C] D

Personal protective equipment required rubber boots, nitrile or butyl rubber gloves,

Other (specify) tyvek or other similar overgarment (disposable), duct tape to seal boots + glove to suit.

Overall risk of physical hazards: Serious_____ Moderate_____ Low \ Unknown X

Expected parameters/contaminants to be sampled sediment via sediment trap and sediment via surface + coring for dioxins

Sampling matrix: Air______ Surface water______ Groundwater______ Soil______
Sediment X Containers______________ Other___________________________