ANCHOR QEA

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MEMORANDUM

To: Andy Kallus and Pete Adolphson, Washington State Department of Ecology
Date: April 2, 2015
From: Clay Patmont and Nathan Soccorsy, Anchor QEA, LLC
Project: 150204-01.01
Cc: Steve Germiat, Aspect Consulting
Cindy Jernigan and Bryan Lust, Kimberly-Clark Corporation
Re: Supplemental Porewater Sulfide Sampling and Analysis, K-C Worldwide Upland Area in Everett, Washington

INTRODUCTION

This memorandum summarizes the results of supplemental sampling and analysis of sulfide in intertidal porewater along the downgradient edge of the K-C Worldwide Upland Area (Site) in Everett, Washington. As described in previous data transmittals and in the *Plan for Supplemental Sampling and Analysis of Sulfide in Intertidal Porewater* (Aspect 2015), total dissolved sulfide concentrations ranging between less than 0.05 and approximately 24 milligrams per liter (mg/L) were previously reported in intertidal porewater samples collected from stations PW-3, PW-4, PW-5, and PW-7 (Attachment A). Porewater sulfide concentrations were generally higher than levels measured in groundwater samples from adjacent upland shoreline monitoring wells, as described in the September 2014 Remedial Investigation (RI) Data Report for the Upland Area.[1]

The supplemental porewater sampling and analysis described herein was conducted to further characterize bioavailable free sulfide ion concentrations in intertidal porewater, removing the influence of colloidal sulfide forms, to provide a more direct comparison with free sulfide-based toxicity benchmarks.

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[1] The August 2014 porewater data were not available for the RI Data Report but have been uploaded to Ecology's Environmental Information Management system and are being incorporated into the draft Remedial Investigation/Feasibility Study Report.

SAMPLE COLLECTION

The supplemental porewater sampling was performed using passive in situ diffusive gradient thin (DGT) film gels to obtain tidally averaged concentrations of free sulfide. In this sampling approach, free sulfide in porewater diffuses through a polyacrylamide hydrogel and then reacts with silver iodide at the surface of a second gel to form solid-phase silver sulfide. The reaction fixes ionic sulfide into a stable form, thereby allowing it to be eluted under controlled conditions in the analytical laboratory. Colloidal forms of sulfide do not penetrate the thin film gel. This sampling and analysis procedure is described in Teasdale et al. (1999) and has successfully characterized porewater free sulfide concentrations at other sediment cleanup sites in Puget Sound (e.g., Port Gamble Bay).

Sampling probes were advanced on February 17, 2015 at the four intertidal porewater sampling locations where total dissolved sulfide concentrations have been previously detected (PW-3, PW-4, PW-5, and PW-7; Attachment A). The sampling probes were allowed to equilibrate in the field for more than 48 hours and were retrieved during low tide conditions. A description of surface sediments at each DGT probe station, along with deployment and retrieval times, is provided in Table 1.

The DGT probe pistons (approximately 2.5-centimeter [cm] diameter and 0.78-mm thickness) were advanced by hand into intertidal sediments targeting a sampling depth interval of approximately 1 to 10 cm below the mudline. Upon retrieval, each DGT piston was removed from the sediment and flushed with deionized water, sealed in a clean plastic bag, and stored in a cooler on ice. Samples were delivered to Analytical Resources, Inc., in Seattle, Washington, for analysis under chain-of-custody protocol.

POREWATER SULFIDE ANALYSIS

At the laboratory, the accumulated sulfide mass in the DGT gel was extracted using the purge-and-trap method followed by the acid volatile sulfide analysis (EPA Method 9030). The accumulated sulfide mass measured in the DGT was used to calculate porewater sulfide concentrations based on diffusive flux relationships. The flux into the DGT equals the mass (M) accumulated by the binding gel divided by the area of the sampling window (A) and the exposure time (t):

$$F = M / (A^*t)$$

Porewater sulfide concentrations were calculated using Fick's first law of diffusion (Table 2):

$$C_{DGT} = (F^*\Delta g) / D = (M^*\Delta g) / (D^*A^*t)$$

where:

Δg = thickness of the diffusion layer

D = diffusion coefficient of sulfide in the gel

POREWATER SULFIDE CONCENTRATIONS

Measured sulfide mass and calculated sulfide concentrations are summarized in Table 2; the original laboratory reports are included as Appendix A. Free sulfide concentrations in all but one of the DGTs (i.e., PW-3, PW-3-duplicate, PW-4, and PW-5) were below the detection limit of 0.06 mg/L. At station PW-7, located along the northern shoreline of the Site, free sulfide was detected above the reporting limit, resulting in a calculated porewater free sulfide concentration of 0.47 mg/L.

Following analysis, the results underwent level 2B data validation. The data validation report is included in Appendix B. All data were determined to be suitable for use in site characterization.

WATER QUALITY BENCHMARKS

The Dredged Material Management Program (DMMP) agencies recently summarized the available literature to develop No Observable Effect Concentrations (NOECs) for free sulfide as a trigger for sediment bioassay purging (Inouye et al. 2013). Converting from hydrogen sulfide (H_2S) to free sulfide (S^{2-}) concentration units, NOECs for the different bioassay tests are summarized in Table 3.

Table 3
Summary of Sulfide NOECs for DMMP Sediment Bioassays

Parameter (mg/L)	Bedded Sediment Tests				Larval Tests	
	Neanthes	***Ampelisca***	***Eohaustorius***	***Rhepoxynius***	**Bivalve**	**Echinoderm**
Free Sulfide	3.2	0.0088	0.11	0.093	0.0024	0.0094

Notes:
DMMP = Dredged Material Management Program
mg/L = milligram per liter
NOEC = No Observable Effect Concentrations
Source: Inouye et al. 2013

Importantly, the NOECs summarized in Table 3 apply to measurements in the overlying water—not porewater (Inouye et al. 2013). The DMMP also notes that sulfide concentrations are often higher in porewater water as compared to overlying water and that porewater represents the most significant exposure medium for many benthic species (e.g., *Neanthes*, *Eohaustorius,* and *Rhepoxynius*).

Relatively little data are currently available to characterize background concentrations of porewater free sulfide concentrations in regional surface sediments (typically 0 to 10 cm below mudline). The available data include investigations of Saanich Inlet, British Columbia (Nissenbaum et al. 1972; Murray et al. 1978) and Puget Sound, Washington (Carr 2010). The data from these studies are summarized as follows:

- Saanich Inlet – Surface sediments present at relatively deep depths in Saanich Inlet contain porewater free sulfide concentrations commonly ranging up to 25 mg/L, with peak concentrations exceeding 100 mg/L (Nissenbaum et al. 1972; Murray et al. 1978)
- Puget Sound – Surface sediments present in relatively pristine areas in Puget Sound contain porewater free sulfide concentrations that range up to approximately 0.1 mg/L (Carr 2010)

The data summarized above reveal that naturally occurring concentrations of free sulfide in surface sediment porewater within the region are highly variable but can be present at levels that exceed the NOECs developed by the DMMP for overlying water.

CONCLUSIONS

The relatively low (below the 0.06 mg/L detection limit) porewater free sulfide concentrations measured in intertidal sediments throughout most of the Site (i.e., at stations PW-3, PW-4, and PW-5) are generally below the NOECs summarized in Table 3 and also appear to be within the natural background range reported for Puget Sound (Carr 2010). Thus, porewater sulfide concentrations in these areas do not pose an environmental risk, including from groundwater discharge pathways from the Upland Area.

While porewater free sulfide concentrations measured at Station PW-7 (0.47 mg/L) are below the NOEC for the benthic polychaete worm *Neanthes*, they exceed other NOECs developed by the DMMP for overlying water. The PW-7 concentration also appears to be slightly above the natural background range reported for Puget Sound, though within the concentration range reported for relatively deep water environments such as Saanich Inlet. Relative to the other DGT probe locations, station PW-7 contained more wood fragments and dimensional lumber on the sediment surface (Table 1), which could reasonably have contributed to the observed sulfide concentrations at this station (i.e., from wood debris degradation). This is supported by the fact that the previously detected porewater sulfide concentrations at PW-7 (up to 15 mg/L) were considerably higher than sulfide concentrations detected in adjacent upland shoreline monitoring wells NRP-MW-2, NRP-MW-3, and MW-5 (groundwater data included in RI Data Report for Upland Area).

Based on these findings, the need for and scope of sediment and/or wood debris cleanup in the PW-7 area can be most effectively addressed as part of the forthcoming remedial investigation/feasibility study of the Everett East Waterway and can be decoupled from the Upland Area.

REFERENCES

Aspect (Aspect Consulting), 2015. Plan for Supplemental Sampling and Analysis of Sulfide in Intertidal Porewater Kimberly-Clark Worldwide Site, Everett, Washington. February 2015. Prepared with Anchor QEA.

Carr, S.R., U.S. Geological Survey, 2010. *Sediment Toxicity Test Results for the Puget Sound Assessment and Monitoring Program (PSAMP) and the Urban Waters Study 2009*. Submitted to the Washington State Department of Ecology. March 12, 2010.

Inouye L., E. Hoffman, and D. Fox, 2013. *Modifications to Ammonia and Sulfide Triggers for Purging and Reference Toxicant Testing*. DMMP Clarification Paper. April 2013.

Murray, J.W., V. Grudmanis, and W.M. Smethie Jr., 1978. Interstitial Water Chemistry in the Sediments of Saanich Inlet. Gehochimica et Cosmochimica Acta. Volume 42: 1011 to 1026. Revised February 28, 1978.

Nissenbaum, A., B.J. Presley, and I.R. Kaplan, 1972. Early Diagenesis in a Reducing Fjord, Saanich Inlet, British Columbia – I. Chemical and Isotopic Changes in Major Components of Interstitial Water. Gehochimica et Cosmochimica Acta. Volume 36: 1007 to 1027. Revised March 30, 1972.

Teasdale, P.R., S. Hayward, and W. Davison, 1999. In situ, High-Resolution Measurement of Dissolved Sulfide Using Diffusive Gradients in Thin Films with Computer-Imaging Densitometry, Analytical Chemistry. Volume 71: 2186-2919.

TABLES

Table 1
Intertidal Sediment Descriptions at DGT Probe Stations

Station ID	Sediment Description	DGT Deployment Date and Time	DGT Retrieval Date and Time
PW-3	The exposed sediment surface was armored with mostly buried angular riprap which was not removed prior to installation of the sediment probe. The surface riprap was surrounded by very soft brown silt and some shells. The underlying sediment layer was very soft silt with some medium angular rocks from the riprap layer. The subsurface was brown to black silt. A duplicate sample was collected at this station.	2/17/15; 21:32	2/19/15; 22:45
PW-4	The exposed sediment surface was armored with 4 to 5 cm of angular riprap which was removed prior to installing the sediment probe. The underlying sediment layer was primarily silt with some coarse shells and medium angular rocks from the riprap layer. The subsurface was brown to black silt and fine shell hash. Large woody debris was present at the surface, overlying the sediment.	2/17/15; 21:48	2/19/15; 22:37
PW-5	The exposed sediment surface was primarily medium to very coarse shell hash with some exposed boulders and large rocks. The subsurface was dominated by 1 to 2 cm of medium shell and then layers of fine sand and dark silt. Shell hash layers were throughout the subsurface. No woody debris or rocks were observed below the surface.	2/17/15; 21:05	2/19/15; 22:25
PW-7	The exposed sediment surface was primarily fine sand with scattered shell hash, a few small and medium rounded rocks, and abundant wood fragments and dimensional lumber on the sediment surface. The subsurface was dominated by fine sand with layers of fine to medium shell hash every few centimeters. Little woody debris was observed below the surface.	2/17/15; 20:42	2/19/15; 21:52

Notes:
cm = centimeter
DGT = diffusive gradient thin

Table 2

Measured and Calculated Porewater Sulfide Concentrations

Station ID	DGT Gel Thickness (mm)	Trap Sample Sulfide Mass (µmol)	Trap Sample Sulfide Concentration (mg/L)	Calculated Porewater Free Sulfide Concentration (mg/L)
Hydrogen Sulfide				
PW-3	0.78	<0.16	<0.003	0.06 UJ
PW-3D	0.78	<0.16	<0.003	0.06 UJ
PW-4	0.78	<0.16	<0.003	0.06 UJ
PW-5	0.78	<0.16	<0.003	0.06 UJ
PW-7	0.78	1.23	0.020	**0.47 J**

Notes:

µmol = micromole

DGT = diffusive gradient thin

J = estimated value

mg/L = milligram per liter

mm = millimeter

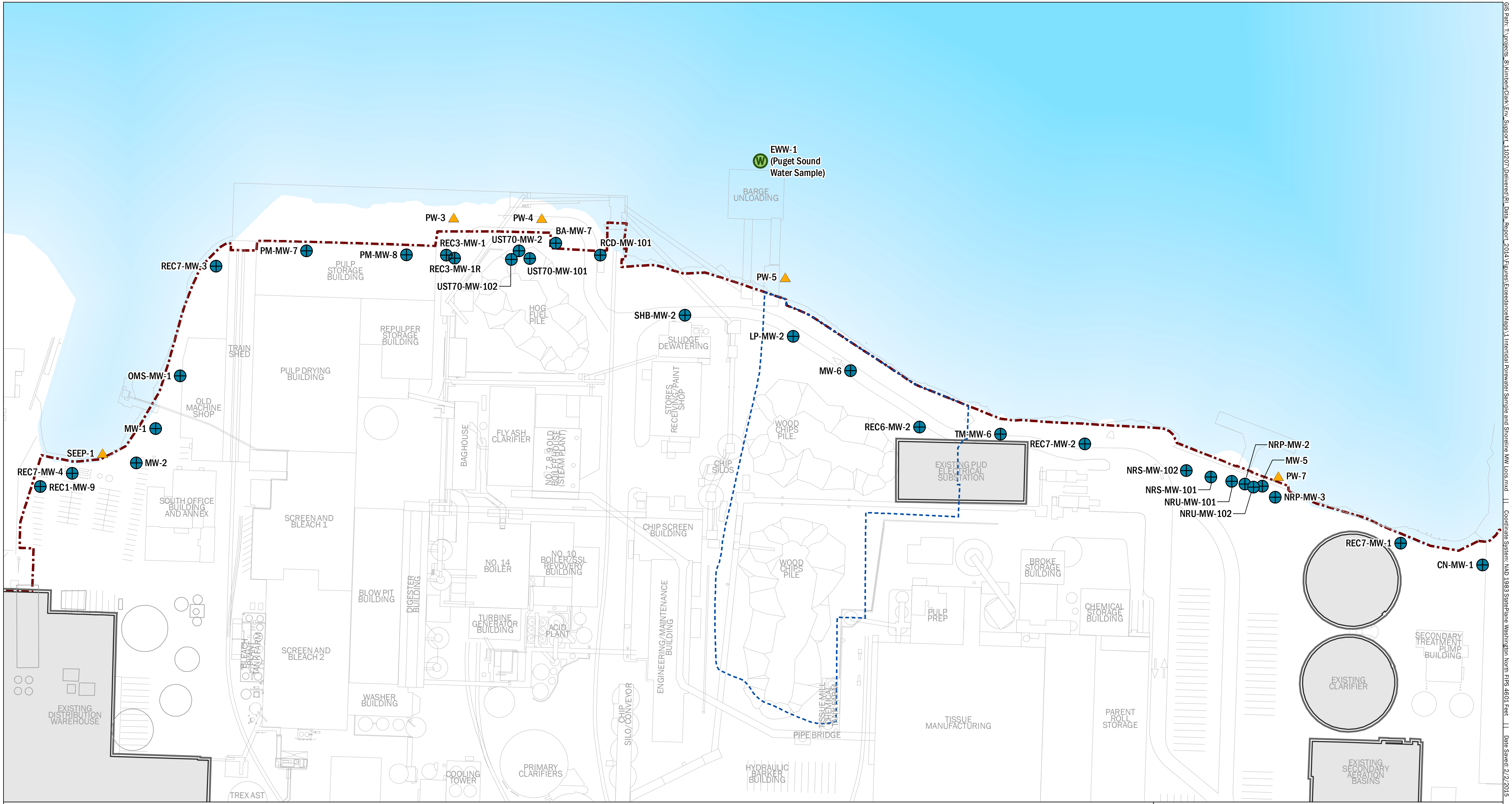
U = not detected above reporting limits

Bold = Detected result

1. Example Calculation:

$$\frac{\text{mass of sulfide sorbed by DGT}(1.23\ \mu\text{mol}) * 0.001\frac{\text{mmol}}{\mu\text{mol}} * 32\frac{\text{mg}}{\text{mmol}} * \text{thickness of diffusion layer } (0.78\text{mm}) * 0.1\ \text{cm/mm}}{\text{Diffusion coefficient of sulfide in gel } (1.48 * \frac{10^{-5}cm^2}{s}) * \text{surface area of the gel } (2.54\ cm^2) * \text{exposure time}(48\text{ hours} = 172800\text{ s}) * \frac{ml}{cm^3} * 0.001L/ml}$$

ATTACHMENT A
SAMPLING LOCATION FIGURE



▲ Intertidal Porewater Sample

⊕ Shoreline Monitoring Well

Ⓦ EWW-1

▨ Existing Structure/Feature

Historical Site Features

Upland Area Boundary

Former Log Pond

Intertidal Porewater Sample and Shoreline Monitoring Well Locations

RI Data Report - K-C Worldwide Site Upland Area
Everett, Washington

Aspect CONSULTING

FEB-2015	BY: SJG / PPW	FIGURE NO. 1
PROJECT NO. 070188-001-08	REVISED BY: RAP	

GIS Path: T:\projects_8\KimberlyClark\Env_Support_110207\Delivered\RI_Data_Report_2014\Figures\ExceedanceMaps\1 Intertidal Porewater Sample and Shoreline MW Locs.mxd || Coordinate System: NAD 1983 StatePlane Washington North FIPS 4601 Feet || Date Saved: 2/2/2015 || User: rpepin || Print Date: 2/2/2015

APPENDIX A
LABORATORY REPORTS

Table of Contents: ARI Job ZX20

Client: Anchor QEA

Project: Everett East Waterway

General Chemistry Analysis

General Chemistry Raw Data

Signature

March-03-2015
Date

Analytical Resources, Incorporated
Analytical Chemists and Consultants

March 3, 2015

Nathan Soccorsy
Anchor QEA
720 Olive Way, Suite 1900
Seattle, WA 98101

RE: Project: Everett East Waterway
ARI Job No.: ZX20

Dear Mr. Soccorsy:

Please find enclosed the Chain of Custody record (COC), sample receipt documentation, and the final data package for samples from the project referenced above.

Sample receipt and details regarding requested analyses are discussed in the Case Narrative.

An electronic copy of this package will remain on file with ARI. Should you have any questions or problems, please feel free to contact me at your convenience.

Sincerely,

ANALYTICAL RESOURCES, INC.

Cheronne Oreiro
Project Manager
(206) 695-6214
cheronneo@arilabs.com
www.arilabs.com

cc: eFile: ZX20

Enclosures

4611 South 134th Place, Suite 100 • Tukwila WA 98168 • **206-695-6200** • **206-695-6201** fax

Chain of Custody Documentation

ARI Job ID: ZX20

Chain of Cust[illegible]ecord & Laboratory Analysis Request

ANCHOR QEA

Laboratory Number:
Date: February 19 2015
Project Name: Everett East Waterway
Project Number:
Project Manager: Nathan Soccorsy
Phone Number: 206-287-9130
Shipment Method: Hand Delivery

					Test Parameters	
Line	Field Sample ID	Collection Date/Time	Matrix	No. of Containers	Sulfide	Comments/Preservation
1	EEW-PW-3-DGT-0-10	2/19/2015 ~~2152~~ 2245 hrs	DGT	1	x	
2	EEW-PW-4-DGT-0-10	2/19/2015 2237 hrs	DGT	1	x	
3	EEW-PW-5-DGT-0-10	2/19/2015 2225 hrs	DGT	1	x	
4	EEW-PW-7-DGT-0-10	2/19/2015 2152 hrs	DGT	1	x	
5	EEW-PW-D-DGT-0-10	2/19/2015 2245 hrs	DGT	1	x	
6						
7						
8						
9						
10						
11						
12						
13						
14						
15						
16						

Notes: Samples have been on ice since the time of collection.

Relinquished By:	Company: Anchor QEA, LLC
Signature/Printed Name	Date/Time 2/19/2015 2305hrs.
Received By: Chris Atwell	Company: ARI
Signature/Printed Name	Date/Time 2-20-15 1009
Relinquished By:	Company:
Signature/Printed Name	Date/Time 2/20/2015 1009hrs
Received By:	Company:
Signature/Printed Name	Date/Time

Distribution. A copy will be made for the laboratory and client. The Project file will retain the original.

Page____of_____

Analytical Resources, Incorporated
Analytical Chemists and Consultants

Cooler Receipt Form

ARI Client: Anchor QEA

Project Name: Everett East Waterway

COC No(s): ______ [✓ NA]

Delivered by: Fed-Ex UPS Courier [✓ Hand Delivered] Other: ______

Assigned ARI Job No: ZX20

Tracking No: ______ [✓ NA]

Preliminary Examination Phase:

Were intact, properly signed and dated custody seals attached to the outside of to cooler? YES [✓ NO]

Were custody papers included with the cooler? [✓ YES] NO

Were custody papers properly filled out (ink, signed, etc.) [✓ YES] NO

Temperature of Cooler(s) (°C) (recommended 2.0-6.0 °C for chemistry) 5.1

Time: 1009

If cooler temperature is out of compliance fill out form 00070F

Temp Gun ID# 91837752

Cooler Accepted by: CA Date: 2-20-15 Time: 1009

Complete custody forms and attach all shipping documents

Log-In Phase:

Was a temperature blank included in the cooler? YES [✓ NO]

What kind of packing material was used? ... [✓ Bubble Wrap] [✓ Wet Ice] Gel Packs Baggies Foam Block Paper Other: ______

Was sufficient ice used (if appropriate)? NA [✓ YES] NO

Were all bottles sealed in individual plastic bags? YES [✓ NO]

Did all bottles arrive in good condition (unbroken)? [✓ YES] NO

Were all bottle labels complete and legible? [✓ YES] NO

Did the number of containers listed on COC match with the number of containers received? [✓ YES] NO

Did all bottle labels and tags agree with custody papers? [✓ YES] NO

Were all bottles used correct for the requested analyses? [✓ YES] NO

Do any of the analyses (bottles) require preservation? (attach preservation sheet, excluding VOCs)... [✓ NA] YES NO

Were all VOC vials free of air bubbles? [✓ NA] YES NO

Was sufficient amount of sample sent in each bottle? [✓ YES] NO

Date VOC Trip Blank was made at ARI [✓ NA] ______

Was Sample Split by ARI : [✓ NA] YES Date/Time: ______ Equipment: ______ Split by: ______

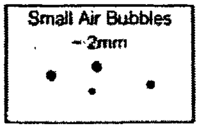
Samples Logged by: JM Date: 2/20/15 Time: 1220

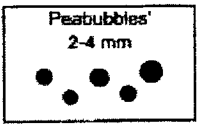
*** Notify Project Manager of discrepancies or concerns ***

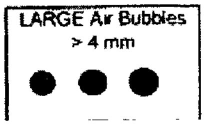
Sample ID on Bottle	Sample ID on COC	Sample ID on Bottle	Sample ID on COC

Additional Notes, Discrepancies, & Resolutions:

By: Date.







Small → "sm" (< 2 mm)
Peabubbles → "pb" (2 to < 4 mm)
Large → "lg" (4 to < 6 mm)
Headspace → "hs" (> 6 mm)

Case Narrative, Data Qualifiers, Control Limits

ARI Job ID: ZX20

Case Narrative

Client: Anchor QEA
Project: Everett East Waterway
ARI Job No.: ZX20

Sample Receipt

Five diffusive gradient thin sheet (DGT) samples were received on February 20, 2015 under ARI job ZX20. The cooler temperature measured by IR thermometer following ARI SOP was 5.1°C. For further details regarding sample receipt, please refer to the Cooler Receipt Form.

Acid Volatile Sulfide by EPA Method 1991

The samples were prepared and analyzed within the method recommended holding times.

The method blank was undetected at the reporting limit.

The LCS percent recovery of AVS fell outside the control limits low. No corrective action was taken.

Sample ID Cross Reference Report

ANALYTICAL RESOURCES INCORPORATED

ARI Job No: ZX20
Client: Anchor QEA
Project Event: N/A
Project Name: Everett East Waterway

	Sample ID	ARI Lab ID	ARI LIMS ID	Matrix	Sample Date/Time	VTSR
1.	EEW-PW-3-DGT-0-10	ZX20A	15-3269	Solid	02/19/15 22:45	02/20/15 10:09
2.	EEW-PW-4-DGT-0-10	ZX20B	15-3270	Solid	02/19/15 22:37	02/20/15 10:09
3.	EEW-PW-5-DGT-0-10	ZX20C	15-3271	Solid	02/19/15 22:25	02/20/15 10:09
4.	EEW-PW-7-DGT-0-10	ZX20D	15-3272	Solid	02/19/15 21:52	02/20/15 10:09
5.	EEW-PW-D-DGT-0-10	ZX20E	15-3273	Solid	02/19/15 22:45	02/20/15 10:09

Printed 02/20/15 Page 1 of 1

Analytical Resources, Inc.

3/3/2015

Analytical Method Information

Sulfide, Acid Volatile (AVS) SM 4500-S2 D-0 in Solid (SM 4500-S2 D-00)

Preservation: None

Container: Glass WM, Clear, 2 oz **Amount Required:** 100 g **Hold Time:** 7 days

Analyte	MDL	Reporting Limit	Surrogate %R	Duplicate RPD	Matrix Spike		Blank Spike / LCS	
					%R	RPD	%R	RPD
Sulfide	0.100	1.00 mg/kg		20	75 - 125		75 - 125	20

General Chemistry Analysis
Report and Summary QC Forms

ARI Job ID: ZX20

ANALYTICAL
RESOURCES
INCORPORATED

INORGANICS ANALYSIS DATA SHEET
Acid Volatile Sulfide by Method EPA 1991

Data Release Authorized:
Reported: 03/02/15
Date Received: 02/20/15
Page 1 of 1

QC Report No: ZX20-Anchor QEA
Project: Everett East Waterway

Client/ ARI ID	**Date Sampled**	**Matrix**	**Analysis Date**	**RL**	**Result**
EEW-PW-3-DGT-0-10 ZX20A 15-3269	02/19/15	Solid	02/26/15	0.16	< 0.16 U
EEW-PW-4-DGT-0-10 ZX20B 15-3270	02/19/15	Solid	02/26/15	0.16	< 0.16 U
EEW-PW-5-DGT-0-10 ZX20C 15-3271	02/19/15	Solid	02/26/15	0.16	< 0.16 U
EEW-PW-7-DGT-0-10 ZX20D 15-3272	02/19/15	Solid	02/26/15	0.16	1.23
EEW-PW-D-DGT-0-10 ZX20E 15-3273	02/19/15	Solid	02/26/15	0.16	< 0.16 U

Reported in µmole

RL-Analytical reporting limit
U-Undetected at reported detection limit

LAB CONTROL RESULTS-CONVENTIONALS
ZX20-Anchor QEA

Matrix: Solid
Data Release Authorized:
Reported: 03/02/15

Project: Everett East Waterway
Event: NA
Date Sampled: NA
Date Received: NA

Analyte	**Date**	**Units**	**LCS**	**Spike Added**	**Recovery**
Acid Volatile Sulfide	02/26/15	mg/kg	0.95	2.04	46.5%

METHOD BLANK RESULTS-CONVENTIONALS
ZX20-Anchor QEA

ANALYTICAL RESOURCES INCORPORATED

Matrix: Solid
Data Release Authorized:
Reported: 03/02/15

Project: Everett East Waterway
Event: NA
Date Sampled: NA
Date Received: NA

Analyte	**Date**	**Units**	**Blank**
Acid Volatile Sulfide	02/26/15	mg/kg	< 0.05 U

General Chemistry Raw Data
Analyst Notes and Raw Data

ARI Job ID: ZX20

ω
2-3-15

SULFIDE BENCHSHEET (Spectrophotometric, EPA 376.2)	Date / Time	Analyst
Aqueous Samples *Distillation*	2/26/15 14:20	APD/EC
Finish	2/26/15 16:47	APD/EC

If distilled, specify procedure: **DGT Conc. Acid Extraction** *zinc acetate:* **D000538**

1. Standardization of sodium thiosulfate titrant *Buret used for titrations:* **S2**

Thiosulfate ID: **D000687**

Bi-iodate ID: **C002718**

Stock bi-iodate = **0.8128** *grams to* 1000 *mL*

Normality = **0.025**

Titration of bi-iodate with thiosulfate

mL bi-iodate =	3.00	3.00	3.00	
mL thiosulfate =	3.07	3.06	3.07	*nthio*
*Normality thiosulfate = (mL bi-iodate*normbio) / mL thiosulfate =*	0.024	0.025	0.024	**0.024**

2. Normality of Iodine

Iodine ID: **C003428**

Titration of Iodine with thiosulfate

mL iodine =	3.00	3.00	3.00	
mL thiosulfate =	3.07	3.06	3.08	*ni*
*Normality iodine = (mL thiosulfate*nthio) / mL iodine=*	0.025	0.025	0.025	**0.025**

3. Standardization of Sodium Sulfide Stock

Stock ID = **D000764**

Approx conc in 60ml

g Na2S = 0.4623 *mg /mL =* 0.123

Titration of standard with thiosulfate

mL Standard =	1.00	1.00	1.00	
mL iodine =	3.00	3.00	3.00	
mL thiosulfate =	1.40	1.39	1.40	*stkconc (mg/mL)*
*Sulfide (mg/mL) = {[(mL iodine*ni)-(mL thio *nthio)]*16} / mL standard =*	0.654	0.658	0.654	**0.655**

Intermediate Standard *mL required for for 0.025 mg/mL* 9.54

Add 9.55 *mL stk to* 250 *mL 0.2N ZnOAc =* **0.025** ***mg/mL***

5.0 Calibration Standard Curve ***spectrophotometer used:*** SPEC #1

Volume Intermediate (ml)	FINAL VOLUME (ml)	CONC (mg S/L)	Absorbance @650 nm 1	Absorbance @650 nm 2	AVG ABS	*mg/L*	RegressionData	
							intercept =	*0.005*
0.00	50	0.000	0.000		0.000	*-0.009*	*slope =*	*0.600*
0.10	50	0.050	0.032		0.032	*E 0.0448*	*r =*	*0.9994*
0.25	50	0.125	0.078		0.078	*0.121*		
0.50	50	0.250	0.159		0.159	*0.256*	*Comment:*	*Calibration OK!*
1.00	50	0.501	0.320		0.320	*0.525*		
2.00	50	1.001	0.598		0.598	*0.988*	*maxabs =*	*0.598*

Calib Verif Std =	*1.0*	*ml int to*	*50*	*ml ZnOAc =*	***0.501***	*mg/L*	***mgS***	***µmole S***
Distillation Prep Std =	*1.0*	*ml Stk to*	*100*	*=*	***6.551***	*mg/L*	***0.655***	***20.4***

SAMPLE DATA *enter dilution factor as ml final/mL sample*

SAMPLE ID	DISTILL DATA Sample Volume	DISTILL DATA Distill Volume (mL)	SPECTROPHOTOMETRIC DATA Dilution factor	SPECTROPHOTOMETRIC DATA ABS @ 650 nm	SPECTROPHOTOMETRIC DATA BKG ABS	SPECTROPHOTOMETRIC DATA Regressed Conc (mg S/L)	SAMPLE DATA Final mg S	SAMPLE DATA Final µmole S	
Cal Blk		n/a	1.00	0.000		-0.009	**< 0.05**		*OK!*
ICV		n/a	1.00	0.305		0.500	**0.500**		*99.85%*
Prep Blk	100	100	1.00	0.000		-0.009	<0.005	**<0.16**	*OK!*
Prep Std	100	100	10.00	0.188		0.305	0.305	**9.506**	*46.52%*
ZX20 A1	1	100	1.00	0.001		-0.007	<0.005	**<0.16**	
ZX20 B1	1	100	1.00	0.000		-0.009	<0.005	**<0.16**	
ZX20 C1	1	100	1.00	0.026		0.035	<0.005	**<0.16**	
ZX20 D1	1	100	1.00	0.242		0.395	0.039	**1.231**	
ZX20 E1	1	100	1.00	0.002		-0.005	<0.005	**<0.16**	
Prep Std	100	100	10.00	0.185		0.300	0.300	**9.350**	*45.76%*
Cal Blk		n/a	1.00	-0.001		-0.010	**< 0.05**		*OK!*
CCV		n/a	1.00	0.293		0.480	**0.480**		*95.85%*

SULFIDE BENCHSHEET (Spectrophotometric, EPA 376.2)
Aqueous Samples

	Date / Time	Analyst
Distillation	2/26/15 14:20	APD/EC
Finish	2/26/15 16:47	SC/APD

If distilled, specify procedure: **DGT Conc. Acid Extraction**

zinc acetate: **D000538**

1. Standardization of sodium thiosulfate titrant

Buret used for titrations: **S2**

Thiosulfate ID: D000687

Bi-iodate ID: C002718

Stock bi-iodate = 0.8128 *grams to* 1000 *mL*

Normality = 0.025

Titration of bi-iodate with thiosulfate

mL bi-iodate =	3.00	3.00	3.00	
mL thiosulfate =	3.07	3.06	3.07	*nthio*
*Normality thiosulfate = (mL bi-iodate*normbio) / mL thiosulfate =*				

2. Normality of Iodine

Iodine ID: C003428

Titration of Iodine with thiosulfate

mL iodine =	3.00	3.00	3.00	
mL thiosulfate =	3.07	3.06	3.08	*ni*
*Normality iodine = (mL thiosulfate*nthio) / mL iodine=*				

3. Standardization of Sodium Sulfide Stock

Stock ID = D000764

Approx conc in 60ml

g Na2S = 0.4623 *mg /mL =* 0.123

Titration of standard with thiosulfate

mL Standard =	1.00	1.00	1.00	
mL iodine =	3.00	3.00	3.00	
mL thiosulfate =	1.40	1.39	1.40	*stkconc (mg/mL)*
*Sulfide (mg/mL) = {[(mL iodine*ni)-(mL thio *nthio)]*16} / mL standard =*				

Intermediate Standard

Add 9.55 *mL stk to* 250 *mL 0.2N ZnOAc =* **mg/mL**

mL required for for 0.025 mg/mL

5.0 Calibration Standard Curve

spectrophotometer used: SPEC #1

Volume Intermediate (ml)	FINAL VOLUME (ml)	CONC (mg S/L)	Absorbance @650 nm 1	Absorbance @650 nm 2	AVG ABS	mg/L	RegressionData
0.00	50		0.000				*intercept =*
0.10	50		0.032				*slope =*
0.25	50		0.078				*r =*
0.50	50		0.159				*Comment:*
1.00	50		0.320				
2.00	50		0.598				*maxabs =*

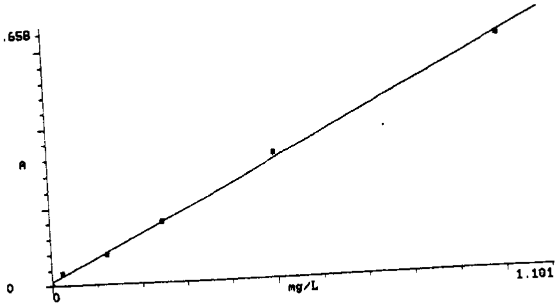
Calib Verif Std =	*1.0*	*ml int to*	*50*	*ml ZnOAc =*	***#VALUE!***	*mg/L*	***mgS***	***µmole S***
Distillation Prep Std =	*1.0*	*ml Stk to*	*100*	*=*	***#VALUE!***	*mg/L*	***#VALUE!***	***#VALUE!***

SAMPLE DATA *enter dilution factor as ml final/mL sample*

	DISTILL DATA		SPECTROPHOTOMETRIC DATA				SAMPLE DATA	
SAMPLE ID	Sample Volume	Distill Volume (mL)	Dilution factor	ABS @ 650 nm	BKG ABS	Regressed Conc (mg S/L)	Final mg S	**µmole S**
Cal Blk		n/a	1.00	0.000				
ICV		n/a	1.00	0.305				
Prep Blk	100	100	1.00	0.000				
Prep Std	100	100	10.00	0.188				
ZX20 A1	1	100	1.00	0.001				
ZX20 B1	1	100	1.00	0.000				
ZX20 C1	1	100	1.00	0.026				
ZX20 D1	1	100	1.00	0.242				
ZX20 E1	1	100	1.00	0.002				
LCS remn	100	100	10.00	0.185				
CCB	ec ~~1~~	100	1.00	-0.001				
CCV	2/27/15 ~~1~~	100	1.00	0.293				
	1	100						
	1	100						
	1	100						
	1	100						
	1	100						
	1	100						
	1	100						
	1	100						
	1	100						
	1	100						
	1	100						
	1	100						
	1	100						
	1	100						
	1	100						
	1	100						

```
;T SETUP
IESYS 10 v2.021 2G2G048006

                                16:47 26Feb15
andard Curve                  SULFIDE[Saved]
st Name                             26Feb15
te Standards Measured                 650nm
velength                                Off
f. Wavelength Correction             Linear
irve Fit                                  6
imber of Standards                     mg/L
iits                                    Off
)# (0=OFF)                      0.050/1.000
ow/High Limits                          Off
tatistics                                On
uto Print
```



```
                                   Linear
Curve Fit                           0.594
Slope                             0.00953
Intercept                           0.010
Std Dev                             0.999
Corr Coeff

  Conc.        Abs
  mg/L        650nm
----------   ------
     0.000    0.000
     0.025    0.032
     0.125    0.078
     0.250    0.159
     0.501    0.320
     1.001    0.598
```

ec

2/26/15

```
TEST SETUP
GENESYS 10 v2.021 2G2G048006

                                16:48 26Feb15
Advanced A-%T-C               SULFIDE[Saved]
Test Name                         Absorbance
Measurement Mode                       650nm
Wavelength                               Off
Ref. Wavelength Correction              0:00
Delay Time (min:sec)                       1
ID# (0=OFF)                      0.000/0.800
Low/High Limits                          Off
Statistics                                On
Auto Print
```

```
ID#    Abs
      650nm
---   ------
 1     0.000

 2     0.305

 3     0.000

 4     0.188

 5     0.001

 6     0.000

 7     0.026

 8     0.242

 9     0.002

10     0.185

11    -0.001

12     0.293
```

]LCS rerun

Sulfide Distillation Log

Analytical Resources, Incorporated

Analyst: APD/EC Date: 2/26/15 Start Time: 14:2

Sample Matrix: DGT discs
Trap Solution: 0.2N ZnOAC
Trap Solution ID:

Distillation Method (circle one)

PSEP soils
5 grams sample
100mL dispersing water
~5mL HCl+Al to pH < 3 by
Bromophenol Blue Indicator, **ID:**
HCL+Al ID:
60 minutes at 90C

9030B waters and soils
100mL / 5 grams sample
Conc. H2SO4 to pH <1
H2SO4 ID:
Pre-test supplement for required acid volumes

AVS soils
5 grams sample
100mL dispersing Water
20mL 1+1 HCl, **ID:**
60 minutes at room Temperature

AVS/SEM: same as AVS, but:
Save acidified solution for metals analysis
Pre-clean all glassware in acid bath
Use trace metals grade 6N HCl

Comments or Modifications:
DGT

Trap #	Sample ID	Sample Weight (g)	Trap Volume	Spike ID	Spike Volume
	BLK	NA	100mL	NA	NA
	LCS			D000764	1mL
	ZX20 A1	1 Disc		NA	NA
	ZX20 B1	1			
	C1	1			
	D1	1			
	E1	1			

APD 2/26/15

Analytical Resources, Incorporated
Analytical Chemists and Consultants

Conventionals Laboratory
Analyst Notes

ZX20

ARI Job No.: ~~Anchor ZU68~~

Client ID: Anchor QEA

Parameter: DGT Sulfide

Client Project: ~~Everett East Waterfr~~

List problems, concerns, corrective actions and any other pertinent information

Method developed internally to extract DGT'S sumarized as follows: 20mL conc. acid to flask with 1 Disc an ~~50~~ no dispearsing water DI Gas washing bottle to catch HCl fumes before sulfide trap. Extract 20minutes with stirring and no heat under nitrogen stream. Sulfide trap solution was modifie from previous projects. Initially ~~0.025~~ 0.25 M NaOH was used to follow ~~At~~ AVS litterature starting point. However, 0.2 N ZnOAc with Ascorbic acid/NaOH pH control was substituted as it is known to give superiorty sample stability and better performance on colorimetry. This enabled the whole Job to be distilled one day and colored another, resulting in less total time required.

Analyst Initials: APD

Date: 2/27/15 2/13/15

Analytical Resources, Incorporated
Analytical Chemists and Consultants

Corrective Actions
Inorganic Analyses

Criteria Flagged:

Unacceptable Blank: ☐
Unacceptable Duplicate: ☐
Unacceptable Spike: ☐
Unacceptable Reference: ☑

ARI Job No.: ZX20
Date of Event: 2/26/15
Client ID:
Method/Element: S
Prep Code:

Details of Problem/Recommended Corrective Action:
Failing LCS at 46.52%

Samples Affected: Prep std

Corrective Action Taken: reran sample and got smlr results.
~~Shows the sample had a~~ ec 2/27/15

Analyst Initials: EC
Date: 2/27/15

Supervisor: w
Date: 3-3-15

5049F

Revision 007
6/11/10

APPENDIX B
DATA VALIDATION REPORTS

ANCHOR QEA

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Seattle, Washington 98101
Phone 206.287.9130
Fax 206.287.9131
www.anchorqea.com

DATA VALIDATION REVIEW REPORT – EPA STAGE 2B

Project:	Everett East Waterway
Project Number:	130105-02.01
Date:	March 16, 2015

This report summarizes the review of analytical results for three diffusive-gradient thin film (DGT) samples and one duplicate collected February 19, 2015. The samples were collected by Anchor QEA, LLC and submitted to Analytical Resources, Inc. (ARI) in Tukwila, Washington. The samples were analyzed for acid volatile sulfides by United States Environmental Protection Agency (USEPA) method 1991.

Sample data group (SDG) number ZX20 was reviewed in this report. Sample IDs are presented in Table 1.

Table 1
Samples Reviewed

Sample ID	Lab ID	Matrix
EEW-PW-3-DGT-0-10	ZX20A	DGT
EEW-PW-4-DGT-0-10	ZX20B	DGT
EEW-PW-5-DGT-0-10	ZX20C	DGT
EEW-PW-7-DGT-0-10	ZX20D	DGT
EEW-PW-d-DGT-0-10	ZX20E	DGT

Data Validation and Qualifications

The following comments refer to the laboratory's performance in meeting the quality assurance/quality control (QA/QC) guidelines outlined in the analytical procedures. Laboratory results were reviewed using *USEPA Contract Laboratory Program National Functional Guidelines for Inorganics Data Review* (USEPA 2004) as a guideline and also by using laboratory and method QC criteria as stated in USEPA (1986; SW 846, Third Edition), *Test Methods for Evaluating Solid Waste: Physical/Chemical Methods*, update 1, July 1992; update IIA, August 1993; update II, September 1994; update IIB, January 1995; update III, December 1996; update IIIA, April 1998. Unless noted in this report, laboratory results for the samples listed above were within QC criteria.

Field Documentation

Field documentation was checked for completeness and accuracy. The chain-of-custody forms were signed by ARI at the time of sample receipt; the samples were received cold and in good condition.

Holding Times and Sample Preservation and Analytical Methods

Samples were appropriately preserved and analyzed within holding times.

Laboratory Method Blanks

The laboratory method blank was analyzed at the required frequency and was free from AVS.

Field Quality Control

Rinse Blanks

No rinse blanks were collected with these sample sets.

Field Duplicates

One field duplicate was collected in association with these sample sets and both results were below detection.

Initial Calibrations and Calibration Verifications

All initial calibrations and calibration verifications met method criteria.

Laboratory Control Sample

One laboratory control sample (LCS) was analyzed at the required. The recovery was below laboratory control limits and the associated sample results have been qualified “J” or “UJ” to indicate a potentially low bias. See Table 2 for qualified results.

Matrix Spike and Matrix Spike Duplicate

Matrix spike (MS) and matrix spike duplicate (MSD) samples were not analyzed in association with these samples due to limited sample mass.

Laboratory Duplicates

Laboratory duplicates were not analyzed in association with this sample set.

Method Reporting Limits

Reporting limits were acceptable as reported. All values were reported using the laboratory reporting limits.

Overall Assessment

As was determined by this evaluation, the laboratory followed the specified analytical method and all requested sample analyses were completed. Accuracy was not acceptable as demonstrated by the LCS recovery. Precision was not evaluated. All data are acceptable as qualified. Table 2 summarizes the qualifiers applied to sample results reviewed in this report.

Data Qualifier Definitions

U	Indicates the compound or analyte was analyzed for but not detected at or above the specified limit.
J	Indicates an estimated value.
UJ	Indicates the compound or analyte was analyzed for but not detected and the specified limit reported is estimated

Table 2
Data Qualification Summary

Sample ID	Parameter	Analyte	Reported Result	Qualified Result	Reason
EEW-PW-3-DGT-0-10	Conventionals	AVS	0.16U µmol	0.16UJ µmol	LCS %R below control limit
EEW-PW-4-DGT-0-10	Conventionals	AVS	0.16U µmol	0.16UJ µmol	LCS %R below control limit
EEW-PW-5-DGT-0-10	Conventionals	AVS	0.16U µmol	0.16UJ µmol	LCS %R below control limit
EEW-PW-7-DGT-0-10	Conventionals	AVS	1.23 µmol	1.23J µmol	LCS %R below control limit
EEW-PW-D-DGT-0-10	Conventionals	AVS	0.16U µmol	0.16UJ µmol	LCS %R below control limit

Notes:
%R = Percent recovery

REFERENCES

USEPA. 1983. Methods for Chemical Analysis of Water and Wastes. U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio. EPA 600/4 79-020.

USEPA. 1986. Test methods for Evaluating Solid Waste: Physical/Chemical Methods. U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response. EPA 530/SW-846.

USEPA. 2004. USEPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review. U.S. Environmental Protection Agency, Office of Superfund Remediation and Technology Innovation (OSRTI). EPA 540-R-04-004. October.