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MEMORANDUM

Project No.: 110207-004-07

February 13, 2015

To: Andy Kallus, Hun Seak Park, and Pete Adolphson, Department of Ecology

cc: Cindy Jernigan and Bryan Lust, Kimberly-Clark

From: Steve Germiat (Aspect Consulting) and Clay Patmont (Anchor QEA)

Re: **Plan for Supplemental Sampling and Analysis of Sulfide in Intertidal Porewater**
Kimberly-Clark Worldwide Site, Everett, Washington

This memorandum summarizes supplemental sampling and analysis to be conducted for sulfide in intertidal porewater along the downgradient edge of the K-C Worldwide Site Upland Area in Everett, Washington. In accordance with the February 25, 2014, Addendum to the Remedial Investigation/Feasibility (RI/FS) Work Plan, two rounds of intertidal porewater sampling and analysis have been completed to date at the site. Elevated dissolved sulfide concentrations have been detected in one or more samples from four of the porewater sample locations (PW-3, PW-4, PW-5, and PW-7; Figure 1). The detected porewater sulfide concentrations are generally higher than measured in groundwater samples from adjacent upland shoreline monitoring wells, as described in the September 2014 RI Data Report for the Upland Area[1].

As discussed during our meeting/phone call with you on January 29, 2015, we have concerns that the detected concentrations of total dissolved sulfide in the porewater (from field-filtered [0.45 µm] samples) may include significant amounts of colloidal sulfide that can pass through the filter, and therefore not be representative of the free sulfide ion (S^{-2}) concentration. Toxicity to benthic organisms is associated with the free sulfide ion, not the colloidal (mineral) form. Literature values for the effects of sulfides to benthic organisms, as generally summarized in the 2013 Dredged Material Management Program (DMMP) clarification paper (Inouye et al., 2013) and other similar reviews (e.g., Dillon et al., 1993; Knezovich et al., 1996; Weston Solutions, 2006), were based on spectrophotometry or ion-selective electrode measurements of free sulfide.

In addition, the porewater data to date are from discrete grab samples collected at lower low tides, thus representing a short-term (acute) exposure that is distinctly different than the longer-term (chronic) exposure that the most stringent porewater quality criteria are based on. Time-averaged sampling, using passive diffusion sampling techniques, is commonly employed to more accurately

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[1] The August 2014 porewater data were not available for the RI Data Report, but are being incorporated into the draft RI Report.

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represent porewater quality conditions in aquatic environments and thus provide data that are most comparable to porewater benchmarks for sulfide. Water quality benchmarks for sulfide vary depending on whether the exposure is acute (several hours) or chronic (several days). Note that since we will be retrieving the samplers at low tide, and since the samplers to be deployed (described below) equilibrate in less than a day, the resultant measurements are likely to reflect an exposure condition that is intermediate between chronic (long-term average) and acute (short-term) conditions. These issues can be considered as part of the interpretation of the new data.

Because of the importance of accurately characterizing porewater sulfide concentrations for purposes of the Upland Area RI/FS, we propose to conduct an additional round of porewater sampling and analysis to accurately measure time-averaged concentrations of free sulfide. The proposed sampling and analysis approach is outlined below. The results of the supplemental sampling will be shared with Ecology for discussion, and incorporated into the RI/FS as appropriate. The data can also help inform the forthcoming RI/FS for the East Waterway site.

Porewater Sample Collection Procedure

The supplemental porewater sampling will be performed using passive, *in situ* diffusive gradient in thin film (DGT) gels, to obtain accurate 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 will not penetrate the thin film gel, so will not be included in the sample. This methodology is described in Teasdale et al. (1999), a copy of which is being provided under separate cover, and has been successfully applied for porewater sampling at other sediment cleanup sites in Puget Sound. Attachment A includes a schematic of the DGT piston assembly along with a schematic illustrating the diffusion principle.

Sampling probes will be advanced at the four intertidal porewater sampling locations (PW-3, PW-4, PW-5, and PW-7; Figure 1) that had detected dissolved sulfide concentrations during the February and/or August 2014 sampling events. Exposed soft sediment substrate exists at each of these sample locations, which are immediately seaward of the shoreline armoring (rip rap or bulkhead). The SEEP-1 sampling location at the south end of the site is located at a higher elevation, within the rip rap, and has not had elevated sulfide concentrations detected.

The DGT piston (approximately 2.5 cm diameter with 0.78 mm-thick diffusive gel) will be advanced into intertidal sediments targeting a sampling depth interval of approximately 1 to 10 cm below mudline. The sampling assemblies will be inserted into the sediment by hand at lower low tide, and will be left to equilibrate in the field for approximately 48 hours, after which they will be retrieved also by hand at lower low tide. Upon retrieval, the DGT piston will be removed from the sediment and flushed with deionized water, sealed in a clean plastic bag, and shipped under chain-of-custody protocol to an Ecology-accredited analytical laboratory (Analytical Resources, Inc. of Seattle, Washington) in an iced cooler for analysis.

Concentration Determination

At the laboratory, the accumulated sulfide mass in the DGT gel will be measured using purge-and-trap followed by the acid volatile sulfide method (EPA Method 9030). The accumulated sulfide mass measured in the DGT will be used to calculate porewater sulfide concentrations based on diffusive flux relationships. The flux to 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):

$F = M / (A*t)$

Once the sulfide mass is measured, porewater concentrations of sulfide are calculated using Fick's first law of diffusion (Teasdale et al., 1999):

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

where:

Δg = the thickness of the diffusion layer and D is the diffusion coefficient of sulfide in the diffusive gel.

References

Dillon, T.M., D.W. Moore, and A.B. Gibson, 1993, Development of a Chronic Sublethal Bioassay for Evaluating Contaminated Sediment with Marine Polychaete Worm *Nereis (Neanthes) Arenaceodentata*, Environ. Toxicol. Chem. V. 12, pp. 589-605.

Docekalova, Hana, 2011, Characterization of Soils by DGT Technique, Diffusive Gradient in Thin Films Technique, http://www.recetox.muni.cz/coe/sources/workshop_3_soil_sed/Docekalova.pdf

Inouye, L. (Department of Ecology), E. Hoffman (EPA), and D. Fox (Army Corps of Engineers), 2013, Modifications to t5he Ammonia and Sulfide Triggers for Purging and Reference Toxicant Testing, DMMP Clarification Paper, April 29, 2013.

Knezovich, J.P., D.J. Steichen, J.A. Jelinski, and S.L. Anderson, 1996, Sulfide Tolerance for Four Marine Species Used to Evaluate Sediment and Pore-Water Toxicity, Bull. Environ. Contam. Toxicology, v. 57, pp. 450-457.

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, v. 71, pp. 2186-2919.

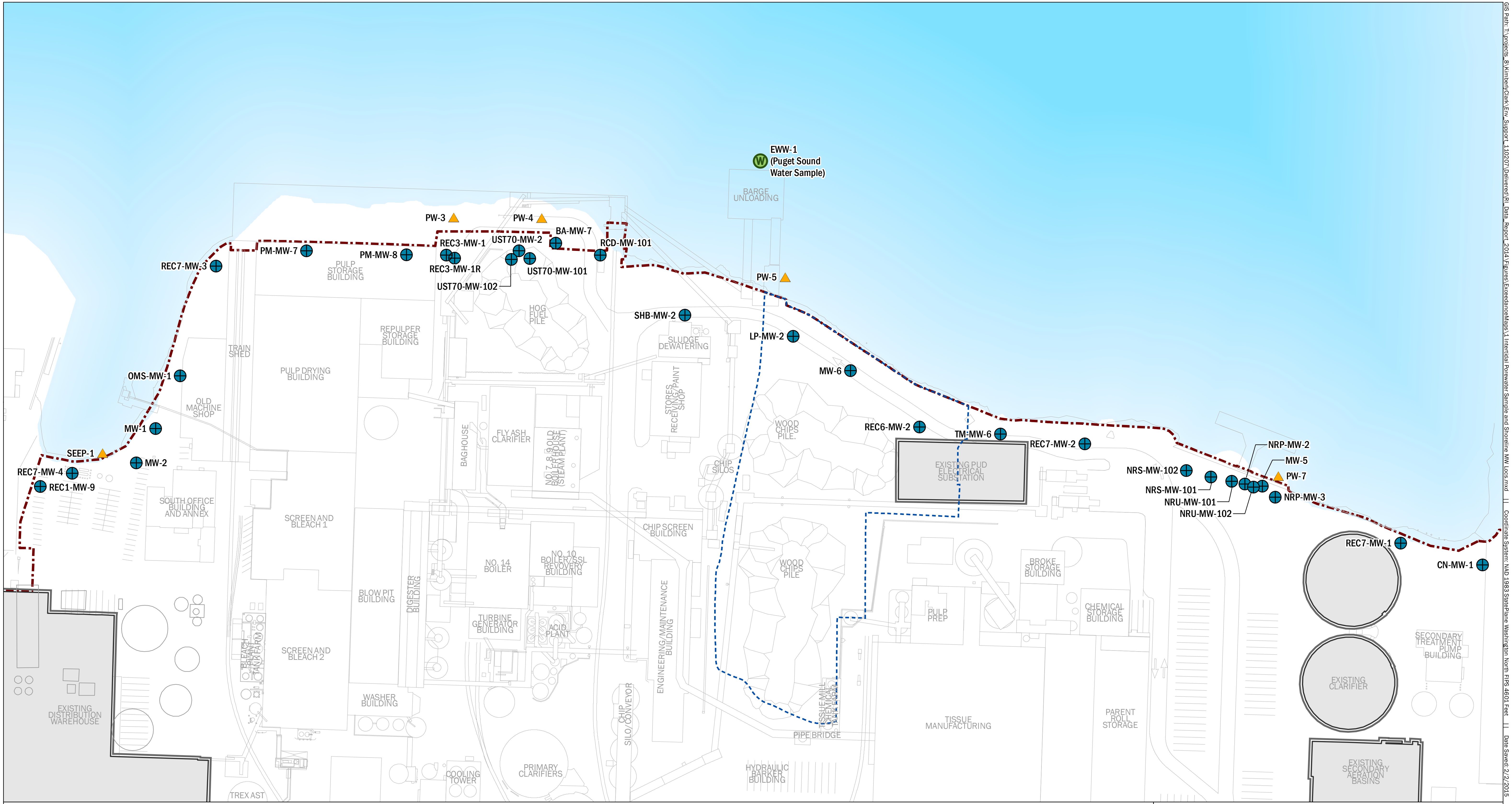
Weston Solutions, 2006, Site-Specific Sulfide Criterion for Produced-Water Discharges at Five California OCS Platforms, Prepared for US EPA Region IX in support of General Permit #CAG280000, Technical Report 427-272.

Attachments

Figure 1 — Intertidal Porewater Sample and Shoreline Monitoring Well Locations

Attachment A — Schematic of DGT piston

FIGURES



▲ 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

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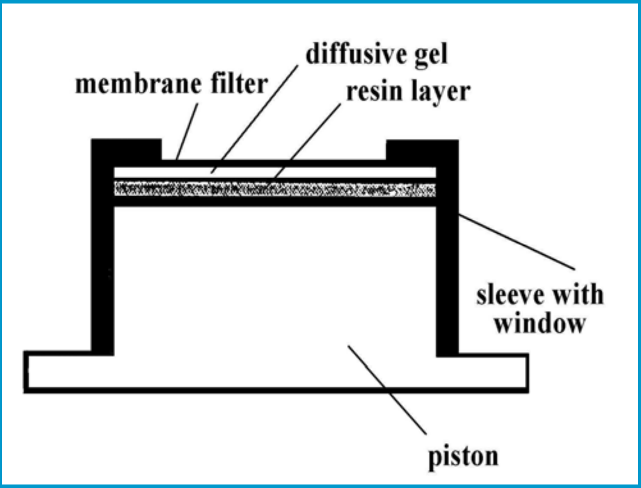
FEB-2015	BY: SJG / PPW	FIGURE NO. 1
PROJECT NO. 070188-001-08	REVISED BY: RAP	

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

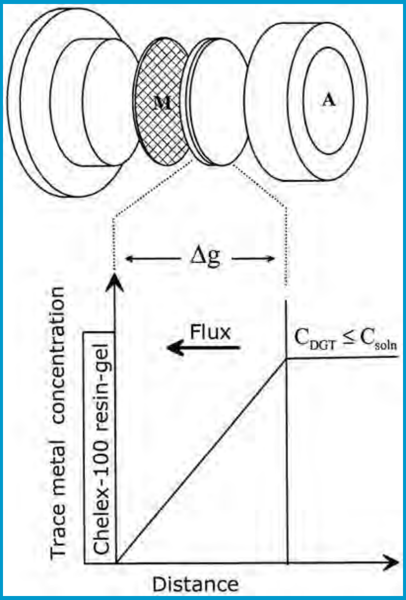
ATTACHMENT A

Schematic of DGT Piston (from Docekalova, 2011)

DGT piston assembly



DGT technique - principle



- *Linear diffusive gradient in a thin layer of acrylamide gel is established in well mixed natural systems (river, sea …)*

  according to

  Fick´s 1st law

  $$F = D \,.\, (c / \Delta g)$$

  metal flux:

  $$F = M / (A \,.\, t)$$

  concentration in liquid phase:

  $$c = (M \,.\, \Delta g) / (D \,.\, A \,.\, t)$$