Evaluation of CLAM Sampling Technique
TOF Inlet and Outfall 001

Kaiser Aluminum Trentwood Facility
Spokane Valley, Washington

for
Kaiser Aluminum Washington, LLC

May 15, 2014

GeoEngineers

523 East Second Avenue
Spokane, Washington 99202
509.363.3125

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Prepared for:

Kaiser Aluminum Washington, LLC
15000 East Euclid Avenue
Spokane Valley, Washington 99215-5108

Attention: Bernard P. Leber, Environmental Engineering Manager

Prepared by:

GeoEngineers, Inc.
523 East Second Avenue
Spokane, Washington 99202
509.363.3125

Katie A. Hall
Environmental Engineer

John R. Haney, PE
Senior Environmental Engineer

Stephen C. Woodward
Principal

SHL:JRH:SCW:tlm:mlh

GeoEngineers

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APPENDIX A

Appendix A. Laboratory Reports and Final Report (Provided on CD)

1.0 INTRODUCTION

This report summarizes sampling activities conducted at the Kaiser Aluminum Washington, LLC (Kaiser) Trentwood Works facility (facility) located at 15000 East Euclid Avenue in Spokane Valley, Washington. The location of the facility is shown in Figure 1 and the general layout of the facility is shown in Figure 2. As part of operations, Kaiser produces wastewater that, along with stormwater, is treated and discharged from the facility through Outfall 001 to the Spokane River under a National Pollutant Discharge Elimination System (NPDES) permit.

Wastewater at the facility is treated by several processes prior to entering the industrial wastewater lagoon (IWL). The wastewater then flows into the Trace oil Filters (TOFs) for final treatment prior to discharge at Outfall 001. A schematic of the IWS system is shown in Figure 3. During this study, wastewater samples were collected at two locations: prior to the TOFs and at Outfall 001, which is downstream of the TOFs. The samples were collected using two different methods:

- Continuous low-level aquatic monitoring (CLAM) sampling devices, an emerging sampling technology for detecting ultra-low level polychlorinated biphenyls (PCB); and
- Automated composite wastewater samplers.

The CLAM and composite samples were collected concurrently to compare analytical results between the two methods.

1.1. Background

In 2011 and 2012 GeoEngineers conducted two sampling events to evaluate whether residual sources of PCB were present in the southern portion of the industrial wastewater system (IWS) at the facility (GeoEngineers, 2012a and 2012b). As part of these studies, composite wastewater samples were collected in laboratory-prepared sample containers and submitted for analysis of PCB. In addition, passive wastewater samplers (semipermeable membrane devices [SPMDs]) were simultaneously deployed and analyzed for PCB. The purpose of collecting and analyzing SPMDs along with composite wastewater samples was to evaluate whether SPMD sampling devices could be used to reliably estimate average PCB concentrations in wastewater.

Analytical results from the SPMD samples were used to estimate time-weighted average concentrations of dissolved-phase PCB in wastewater using a mathematical model created by the United States Geological Survey (USGS). SPMD performance was evaluated by comparing calculated PCB concentrations from SPMD samples against PCB concentrations detected in composite wastewater samples. Calculated PCB concentrations from the SPMD results were up to several orders of magnitude greater than PCB concentrations directly measured in the composite wastewater samples.

1.2. Purpose of Study

The purpose of this study was to evaluate whether CLAM sampling devices could be used to reliably measure average PCB concentrations in wastewater. GeoEngineers implemented field activities for this study by concurrently collecting wastewater samples using CLAM sampling devices and automated composite wastewater samplers at the TOF inlet vault and Outfall 001 sample house (see Figure 3). Field activities were conducted in general accordance with a sampling plan (GeoEngineers 2013) that was reviewed and approved by the Washington State Department of Ecology (Ecology). Analytical results derived from the CLAM samples were then compared to results from the composite wastewater samples to evaluate the apparent effectiveness of the CLAM sampling technology. Kaiser intends to use this information when developing sampling plans for future investigations of PCB in the IWS.

1.3. Scope of Services

GeoEngineers completed the following scope of services for the project:

- Researched the applications and deployment techniques of CLAM samplers;
- Prepared a sampling plan describing the sampling activities (GeoEngineers 2013).
- Performed and documented sampling activities and submitted the samples to Axys Analytical Services (Axys) in Sidney, British Columbia for chemical analysis; and
- Evaluated the analytical data and prepared this summary report.

2.0 CLAM SAMPLER OVERVIEW

A CLAM sampling device consists of a battery-powered submersible pump, housed in a nylon body, equipped with solid-phase extraction media cartridges designed to sequester polar or non-polar compounds and other trace organics from water using similar procedures to those described in US Environmental Protection Agency (EPA) Method 3535A. The extraction media is carbon-18 isotope (C-18) and reportedly has a recovery rate of approximately 90–100 percent for non-polar compounds such as PCBs. The CLAM sampling device is deployed directly in the water body being sampled and, theoretically, continuously pumps water at about 60 milliliters per minute (ml/min) through the C-18 solid-phase extraction media (C-18 sample disk) prior to being discharged from the sampler. After the CLAM sampling device is retrieved from the water body, the C-18 sample disk is shipped to the analytical laboratory for solvent elution and analysis.

It is necessary to determine the total volume of water pumped through the extraction media to calculate an average water concentration. The CLAM sampler manufacturer recommends measuring the flow rate of the sampler before and after deployment (in ml/min), averaging the measured flows, and then multiplying the average flow rate by the duration of the deployment (in minutes). The manufacturer of the CLAM sampler claims that the flow rate of the sampler pump decreases linearly over time as battery power declines and, as a result, the average flow rate and deployment duration will yield an adequate estimate of sample volume. However, in order to verify the manufacturer's claims, the water passing through the CLAM sampler deployed at the Outfall 001 Sample House was collected each day and weighed.

3.0 FIELD ACTIVITIES

3.1. Pre-Field Activities

On September 30, 2013 GeoEngineers collected an equipment rinse blank (ERB) from the automated sampler in the TOF sample house using 18-megohm de-ionized water (DI water) supplied by Anatek Labs Inc. (Anatek) located in Spokane, Washington. The ERB was collected by manually activating the automated sampler to pump the DI water through the sampler and into a plastic container lined with a new Teflon® sample bag. The collected sample (ERB-TOF Inlet-093013) was then transferred to a sample container supplied by Axys. A second sample of the DI water (LWB-093013) was transferred directly from the container of DI water supplied by Anatek and into a container supplied by Axys. This sample was intended to serve as a blank of the Anatek DI water used to collect the ERB and was analyzed to assess whether or not the DI water contained PCB prior to using the water to collect the ERB. This sample was referred to as the laboratory water blank (LWB). The ERB and LWB were submitted to Axys for analysis of PCB congeners using EPA Method 1668A.

GeoEngineers removed existing debris/algae buildup within the Outfall 001 sample tank using a scrub brush and the tank was allowed to clear. A 55-gallon polyethylene drum was set up in the Outfall 001 sample house to collect and verify the total volume of water that flowed through the CLAM samplers deployed at this location.

The CLAM C-18 sample disks were prepared at GeoEngineers' Spokane office on September 30, 2013. GeoEngineers "pre-conditioned" the C-18 cartridges (disks) using reagents supplied by Axys and following the manufacturer's protocols:

- Removed each disk (one at a time for pre-conditioning) from the resealable pouch the media was received in from the manufacturer.
- Passed 50 mL methylene chloride through the disks using a graduated glass syringe followed by a 1-minute residence time, and then two syringe volumes of ambient air.
- Passed 50 mL methanol through the disks, followed by a 2-minute residence time and one syringe volume of air.
- Passed 50 mL of deionized water through the disks, followed by one syringe volume of air.
- Returned each disk to the resealable, manufacturer-provided pouch and refrigerated until deployed in the field.

In addition to pre-conditioning the disks intended for deployment, GeoEngineers also pre-conditioned one disk to act as a blank for the solid-phase extraction media to assess whether or not the disks and or conditioning reagents contained PCB prior to deployment.

3.2. Sample Collection

Six C-18 sample disks and six composite wastewater (CWW) samples were collected at the facility between October 1 and 4, 2013 (study period). Three C-18 sample disks and three CWW samples were collected from the TOF inlet vault and three C-18 sample disks and three CWW samples were collected from the sample tank located in the Outfall 001 sample house (sample locations are shown in Figure 4).

3.2.1. Samples Collected Using CLAM Devices

The CLAM samplers were deployed in the TOF inlet vault and Outfall 001 sample house on October 1, 2013. The CLAM samplers were deployed for approximately 24 hour periods at each location, after which the C-18 disks were collected and new C-18 disks were installed in each sampler. The retrieved C-18 disks were placed in the resealable, manufacturer-provided pouch and stored at approximately 4° Celsius (C). This sampling procedure was repeated for three consecutive days, yielding three separate CLAM samples from each of the two sampling locations with the exception noted in Section 3.2.1.1.

At the time the C-18 disks were collected/replaced, new batteries were installed in the CLAM samplers. The pumping rates of the CLAM samplers were measured at the time of deployment and retrieval. Additionally, the total volume of water that passed through the CLAM sampler in the Outfall 001 sample house during each 24-hour sampling period was calculated based on the measured weight and density of water collected in the drum (see Section 3.1).

Sample retrieval times, deployment time period, measured flow rates, calculated sample volumes, weight of sampled water collected, density of sampled water, and associated calculated sample volumes for the CLAM samplers are summarized in Table 1.

At the end of field activities, the deployed C-18 sample disks and the C-18 sample disk blank were shipped in an insulated cooler with ice, under chain-of-custody, to Axys for PCB congener analysis using EPA Method 1668A.

3.2.1.1. CLAM SAMPLER OBSERVATIONS

During the daily retrieval of CLAM samplers deployed in the TOF inlet vault and the Outfall 001 sample house, algae build-up (biofouling) was observed on the C-18 sample disks and within the disk inlets. On October 3, 2013 the inlet to the C-18 disk retrieved from the TOF inlet vault was completely obstructed with algae/particulate and no water was flowing through the sampler (Table 1). Neither the C-18 disk nor the CWW sample collected from this location on October 3, 2013 were submitted for analysis because it would not have been possible to estimate the volume of water that flowed through the CLAM sampler during its deployment.

Final flow rates through the other CLAM samplers at the time of retrieval also were substantially reduced (Table 1), primarily as a result of biofouling.

3.2.2. Samples Collected Using Automated Sampling Devices

CWW sampling was initiated at the TOF inlet vault and Outfall 001 sample house on October 1, 2013. Daily composite wastewater samples were collected using existing, programmable Manning S-5200 Stationary Vacuum Fluid Samplers (automated samplers) already present in the TOF Inlet and Outfall 001 sample house. The automated samplers were started at approximately the same time that the CLAM samplers were deployed and collected composite samples until the CLAM samplers were retrieved (about 24-hours). The automated samplers were configured to collect approximately 50 milliliters (ml) of wastewater every 15 minutes.

Wastewater samples collected by the automated samplers were conveyed through Teflon® tubing and Lexan sampler components and deposited in a Teflon® sample bag housed in a refrigerated compartment. The sample bag was replaced daily prior to collecting a new sample. CWW samples were transferred manually from the Teflon® sample bag into two, unpreserved, 1-liter, amber, borosilicate glass containers with Teflon®-lined lids provided by Axys. CWW samples were refrigerated prior to and during shipment to Axys. Samples were shipped under chain-of-custody to Axys for PCB congener analysis using EPA Method 1668A. The remaining sample volume in the Teflon® sample bags were transported to the on-site Kaiser Aluminum Trentwood Laboratory (Kaiser Lab) in insulated containers for total suspended solids (TSS) analysis by Standard Method (SM) 2540D.

The procedures for CWW sampling were repeated each day during the study (on October 3 and 4, 2013).

3.2.3. Grab Samples

Wastewater grab samples were collected each day of the study (October 2-4, 2013) from both the TOF inlet vault and Outfall 001 sample house locations. Wastewater grab samples were collected at the end of each 24-hour CLAM sampling deployment period and submitted to the on-site Kaiser laboratory for analysis of oil and grease using SM 5520G.

4.0 STUDY RESULTS

4.1. CLAM Pumping Rates

The estimated total volume of wastewater pumped through the CLAM devices based on measurements of the initial and final flow rates ranged from about 42 liters to 64 liters during the approximate 24-hour deployment periods (Table 1). The estimated volumes at Outfall 001 were 74% to 81% of the actual volumes (approximately 70 to 87 liters) collected from the CLAM sampler at Outfall 001. This information suggests that the pumping rate of the CLAM samplers does not decrease linearly, and total flow volumes estimated according to the manufacturer's recommendation would underestimate the total volume of water pumped through the sampling medium. This would produce an overestimate of average PCB concentration in wastewater using the analytical results.

To better understand how the pumping rate of CLAM samplers decreases as battery power declines, a pumping test was conducted using tap water. The test was initiated after installing new batteries and a new C-18 disk, and continued until the batteries died (about 48 hours). Flow rate of the CLAM sampler was generally measured every hour between the hours of 08:00 and 20:00 during each day of the test (Table 2; Figure 6). Data from the pumping test, as illustrated in Figure 6, indicates that the CLAM sampler pumping rate was fairly constant (between approximately 50 and 60 ml/min) for approximately 42 hours and then declined sharply over the last 4 hours of battery life. The decline of the pumping rate was not linear, as shown in Figure 6.

The pumping rates of the CLAM samplers deployed in the TOF inlet vault and Outfall 001 locations declined much more substantially than observed in the tap water test described above. Excluding the one CLAM sampling device that was not pumping upon retrieval, the CLAMs were pumping at rates ranging from 9% to 42% of their initial pumping rates when retrieved. It is anticipated that biofouling was responsible for these more substantial declines in pumping rate.

4.2. Blank Correction of Analytical Results

As-reported analytical results for CWW and CLAM C-18 sample disks were blank-corrected by congener, in accordance with Ecology protocols, to account for the ubiquitous presence of PCB. Blank correction protocols consisted of the following:

- Data was blank corrected if there was a detection of the same PCB congener in both the sample and the laboratory blank.
    - If 10 times the detected laboratory blank concentration was greater than the reported sample concentration, the sample concentration was reduced to zero;
    - If 10 times the detected laboratory blank concentration was less than the reported sample concentration, the sample concentration remained as-reported.

As-reported and blank-corrected analytical results for the C-18 sample disks, CWW samples, ERB sample, and LWB sample are summarized by PCB homolog group and presented in Table 3. Further references to PCB concentrations in this report refer to blank-corrected concentrations.

4.3. Composite Wastewater Sample Results

PCB Analytical results for composite wastewater samples collected during the sampling period are presented in Table 3 and shown graphically in Figures 6 through 11.

4.3.1. TOF Inlet Vault Samples

Concentrations of total PCB in the CWW samples collected from the TOF inlet vault were approximately 7,133 and 7,077 pg/L on October 2 and October 4, 2013, respectively. The CWW sample from October 3, 2013 was not analyzed as described in Section 3.2.1.

4.3.2. Outfall 001 Samples

Total PCB concentrations in the composite wastewater samples collected from the Outfall 001 sample house were approximately 3,333, 3,340 and 3,476 pg/L on October 2, 3, and 4, 2013, respectively.

4.3.1. TSS and Oil and Grease Samples

Oil, grease, and TSS were detected in each of the six samples analyzed. In general, oil, grease, and TSS were detected at lower concentrations in the samples collected from the Outfall 001 sample house compared to the samples collected from the TOF inlet vault. Analytical results are presented in Table 4. There does not appear to be a correlation between oil, grease, and TSS concentrations and PCB concentrations detected in CWW and disk samples.

4.4. C-18 Disk Sample Results

Analytical results for the C-18 disk samples from Axys were reported as picograms per sample (pg/sample). To derive an estimated average PCB concentration in the wastewater that flowed through each CLAM sampling device, the C-18 analytical result was divided by the estimated volume of water that flowed through the CLAM device during the period of deployment. The estimated volume of water used in these calculations was based on the average of the initial and final flow rates of the CLAM device, as recommended by the manufacturer. For the CLAM samples collected at Outfall 001, the calculation was repeated using the actual volume of water that was discharged into the storage drum. The calculated PCB concentrations in wastewater based on these calculations are presented in Table 3.

4.4.1. TOF Inlet Vault Samples

Total PCB in the C-18 sample disks collected at the TOF inlet vault were approximately 583,767 pg/sample on October 2 and 558,974 pg/sample on October 4, 2013. The corresponding average PCB concentrations in wastewater calculated using the manufacturer's protocols were approximately 12,285 pg/L and 12,131 pg/L, respectively (see Table 3). As previously mentioned, the C-18 disk retrieved on October 3, 2013 was not analyzed.

The PCB concentrations detected in the CWW samples from the TOF inlet vault (7,133 pg/L to 7,077 pg/L) were 58% of the calculated average PCB concentration in the time-correlative CLAM samples (12,285 pg/L to 12,131 pg/L).

4.4.2. Outfall 001 Samples

Total PCB in the C-18 sample disks collected at the Outfall 001 sample house were approximately 371,618 pg/sample on October 2, 454,128 pg/sample on October 3, and 392,292 pg/sample on October 4, 2013. The corresponding average PCB concentrations in wastewater calculated using the manufacturer's protocols for sample volume were approximately 6,002 pg/L, 7,118 pg/L, and 7,567 pg/L, respectively. The corresponding PCB concentrations calculated using the actual sample volume collected each day in the storage drum were approximately 4,850 pg/L, 5,239 pg/L, and 5,634 pg/L, respectively. Calculated average PCB concentrations in wastewater were 19% to 26% lower using actual sample volumes as opposed to the sample volumes derived using the manufacturer's recommended method.

The PCB concentrations detected in the CWW samples from Outfall 001 (3,333 pg/L to 3,476 pg/L) ranged between 46% and 56% of the calculated average PCB concentration in the time-correlative CLAM samples (6,002 pg/L to 7,567 pg/L). PCB concentrations in these same CCW samples ranged between 64% and 69% of the calculated average PCB concentrations in the time-correlative CLAM samples (4,850 pg/L to 5,635 pg/L) if the latter concentrations are based on the actual sample volume that flowed through the devices.

4.5. Homolog Profiles

Homolog profiles were developed using analytical results for the composite wastewater and CLAM samples. The purpose of this analysis was to compare the PCB mixture detected in each sample type (CWW versus C-18 sample disk) and to evaluate whether the C-18 sample disks preferentially accumulated certain homolog groups. Homolog profiles were developed by calculating the percentage of each PCB homolog group in a particular sample (Table 3) and plotting that percentage by homolog group. The homolog profiles for the TOF inlet vault samples are presented in Figures 7 and 8; the homolog profiles for the Outfall 001 sample house samples are presented in Figures 9 through 11. The PCB mixtures in both sample locations are dominated by the trichlorinated and tetrachlorinated congeners which compose about 30-35% and 45-50% of the total mixture, respectively. In general, the samples collected by the two methods look very similar to each other, although there is a slight difference in the trichlorinated and tetrachlorinated biphenyl homolog group percentages between the two sampling locations. The reason for this is unclear but might reflect the difference between wastewater composition before and after the TOF.

5.0 CONCLUSIONS

The use of CLAM sampling devices to estimate average PCB concentrations in wastewater requires that the volume of wastewater pumped through the sampling medium be known. The manufacturer of CLAM sampling devices recommends that this volume be determined by averaging the pumping rate at the beginning and end of deployment. The results of this study suggest that this method underestimates the volume of water pumped through the sampling device and thereby overestimates average PCB concentrations in water. Estimated flow volumes calculated during this study in accordance with the manufacturer's recommendation were approximately 74% to 81% of actual total flow volume through the device.

Irrespective of the ability to accurately estimate the total volume of water pumped through the CLAM devices, this study indicates that pumping rates decline substantially during deployment, likely as a result of biofouling. In one sample, the CLAM device was totally plugged and not pumping wastewater at the time of retrieval. Disregarding the effects of decreasing battery power, the effects of biofouling make it difficult to estimate the total volume of water that has flowed through the device during deployment.

Similar to the SPMD sample results from an earlier study, average PCB concentrations calculated from the CLAM sample results are higher than PCB concentrations detected in CWW samples collected at the same time. The CLAM-derived PCB concentrations, however, are closer to the CWW sample results than the SPMD results were. CLAM-derived PCB concentrations calculated using the manufacturer's recommended protocol for estimated total sample volume ranged from about 1.7 to 2.2 times greater than detected concentrations in the correlative CWW samples. CLAM-derived PCB concentrations calculated using the actual volume of water that flowed through the sampling devices ranged from about 1.5 to 1.6 times greater than the correlative CWW sample results.

6.0 REFERENCES

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