Tech Track Work Group Update
July 31, 2014

CLAM Investigations
A conference call was held with AXYS Analytical Services to discuss how an experiment could be set up that would seek answers to the source of the approximately twofold difference between the CLAM and Kaiser's 24 hour composite effluent samples and Ecology's river grab sample. At the conclusion of the call, AXYS agreed to summarize our discussions in the form of a designed experiment scope. The scope has been received and is attached for review and discussion at a later date.

In addition to the analytical side issue above, the CLAM manufacturer also reported that it believes that the tipping bucket device should be usable in the field with sufficient accuracy and that they would be will to work with us on testing it in the field.

Gravity High Volume Sampler
The sampling contract for the synoptic and seasonal sampling events includes sampling with the Gravity high-volume sampler at two locations at two times during the synoptic sampling. The two locations are Nine Mile and the Lake Coeur d'Alene outlet. These locations were chosen on the basis that the Nine Mile grab samples should be well above the method blank noise and could be compared with the range of results from the grab samples. The Lake Coeur d'Alene location should provide the lowest concentrations and therefore provide information on how low a clear environmental signal can be seen before the method blank noise masks it.

Confidence Testing
As a part of the May sampling, one 4-liter grab sample was collected. This sample was sent to AXYS to determine if the sample volume increase from 2.36 liters to 4.0 liters was sufficient to see an environmental signal that was above the method blank noise. AXYS has reported that the sample was involved in a laboratory error and that sample integrity was lost. Since there was only one 4 liter sample (no back-up), there is no additional actions that can be taken with respect to this activity.

Synoptic Sampling Event
All contracts for the sampling event are in place (LimnoTech, Gravity, SVL, and AXYS) for conducting the synoptic sampling event.

Field Training
LimnoTech held training with Gravity, Ecology, and LimnoTech staff on the Quality Assurance Project Plan and the Sampling Analysis Plan on July 28. QAPP, SAP, Health and Safety Plan and Invasive Species procedures were discussed. Richard Grace with AXYS answered some questions about blank contamination and the Confidence Interval testing. The data was appropriately identified and flagged in accordance with the lab's quality assurance plan and was confirmed by LimnoTech. The analysis was still within the specifications required under the

contract. The trip and lab blanks used the same batch of ultrapure water, which is purchased. Results may be scattered, even if they are within an acceptable statistical control range. The lab will have a control range based on is analytical history. The project could establish its own control range but would need to analyze more samples.

The topic of what could have caused contamination was discussed: probably a trace contaminant on glassware or columns. PCBs can bind and adhere to site on glassware and it is not uncommon to “lose” surrogates on glassware to this phenomenon. This can be more pronounced at ultralow concentrations. AXYS was not aware of any process that produces PCBs in the analysis. Not able to specifically identify the source of contamination for a particular congener, some congeners are degradation products due to dechlorination.

Sampling reconnaissance happened on July 29-30. Washington sites (5 discharge locations, 5 gauges were visited on July 29. All Washington sites have public access and sampling is feasible at all locations. Alternative sampling methods may be necessary at some locations due to site access, sample location, and logistics. The goal is to be consistent in sampling techniques at all locations, to the extent possible. Where deviations from the initial sampling plan are necessary, those will be documented. Gravity intends to prepare implementation notes for each site with details about schedule, timing, access, and sampling methods.

QAPP/SAP Update
The Quality Assurance Project Plan and Sampling Analysis Plan will be forwarded for signature next week. All identified parties need to sign next week. QAPP approval is needed prior to the sampling begins.

Following Pages
AXYS Scope and Costs for Designed Experiment Comparing the Analysis of CLAM and Whole Water Grab Sample

July 21, 2014

Spokane River Regional Toxic Task Force
William D. Ruckelshaw Center,
901 Fifth Ave, Suite 2900,
Seattle, WA
98164

Attention: Chris Page

AXYS Analytical Services Ltd. – Proposal for Comparison of PCB Congener Analysis Using C.L.A.M Sampling and Whole Water Sampling in SRRTTF Applications – Outline and Cost Projections

OBJECTIVE

Several projects related to SRRTTF monitoring of PCB Congeners in the Spokane River Basin , conducted in waste water and surface water , have used CLAM samplers to extract large volumes of water (up to 60 L) to provide enough sample to achieve low detection limits and distinguish levels in samples from levels in blanks. In some cases analysis of whole water samples (by sub-sampling 24 hour composites) has also been conducted. Limited comparison of results between CLAM and composite samples has shown a high bias (40 to 60%) in the CLAM results compared to the whole water results. The goal of this work is to identify the source of any differences and to do a systematic comparison of CLAM results to whole water results for low level PCB analyses by Method 1668A/C. This will allow evaluation of either sample collection process, applicable QA limits, and how they affect SRRTTF data quality objectives. This information may then be used for subsequent decisions on sample collection and analysis.

APPROACH

AXYS proposes a two-component project to investigate the discrepancies in PCB results obtained by CLAM sampling versus whole water analyses. One component will involving extensive proofing of the CLAM equipment and the second component will focus on validation of the CLAM results versus whole water results from samples collected in the field. The overall program contains the following key elements;

- All experiments are to be conducted in triplicate to establish variation in results. Results may indicate a need for a greater amount of subsequent replicates.
- All C.L.A.M analysis described in this plan will be performed on C-18 Discs and / or Pre-Filter discs as described in the individual task.
- All C.L.A.M. pre-cleaning described in this plan will be as per manufacturer's instructions.
- All elution of C.L.A.M discs will be as per AXYS SOP SLA-129. Resultant eluents will then proceed to analysis.
- All analysis of whole water, filtered water, C.LA.M. C-18 discs, pre-filter discs (separate or combined) will be performed by AXYS SOP MLA -010 (EPA 1668A/C).

- All water analysis will be reported on a pg/L basis. All C.L.A.M. analysis will be reported on a pg absolute basis as well as a pg/L basis from a measured amount of water. PCB congener values, homologue totals, and Total PCBs will be reported. Flagging conventions and final reporting conventions will be confirmed after determination of scope.
- Existing contractual pricing for analysis of water by AXYS MLA 010 and analysis of C.L.A.M by AXYS SLA 129 and MLA 010 have existing pricing with SRRTTF. Cleaning of C-18 discs and pre-filter discs is included in the unit price for C.L.A.M currently in place. This pricing has been used in these cost estimates. Additional line items for costing will be required for the execution of this work as follows;
    - For both proofing and field experiments, unit prices for C-18 discs and pre-filter discs. Based on ordering volumes in the 20-99 range for each component, the pricing for C-18 discs is anticipated to be $79 each for C-18 discs and $49 for each pre-filter disc. AXYS would apply a 10% surcharge to unit prices for provision of these materials.
    - For proofing experiments only, AXYS has recommended the use of standard CLAM pumping system, using HPLC reagent water (4L per analysis) to create representative C.L.A.M, pre-filter and combined discs after processing of 60L of water. Pricing for creation of these samples (C.L.A.M., pre-filter disc, combo disc) is $300 per run,
    - For field experiments, C.L.A.M unit(s) will be required for collection of samples. These may not be required if currently available through SRRTTF. Complete C.L.A.M kits are currently available for $2,500. Rentals are available on a monthly basis for variable costs, dependent on the number of units required. If these units are sourced through AXYS, cost plus 10% would be applied to this item.

- The overall work is divided into two components as follows;
    - In lab proofing of C.L.A.M materials to establish variation in blank materials and efficacy of cleaning procedures by component (pre-cleaning, after cleaning, for each item and combined pre-filter and C-18 disc. We believe that current knowledge regarding analytical blank levels in MLA 010 water analysis is currently sufficient for this exercise.
    - Field components – Collection on-site of both C.L.A.M. samples and whole water grab samples for comparative analsyis. The current plan has one location (Kaiser Trentwood Facility Final Outfall) recommended for completion of this work. Characterizations of other streams, representing higher analyte or solids loadings may be conducted in parallel or after completion of the final outfall work. The costs associated with Tasks outlined in section 2 would be applied in whole or part to the second site. The current recommended sites discussed have been; Kaiser Trentwood facility prior to Walnut Shell filtration or a lower Dwamish River location yet to be determined.

All potential sources of error that have been identified so far will be carefully controlled in this work. These include;

I. Definition of blank levels for pre-cleaned and cleaned C-18 discs and pre-filters.
II. Accurate determination of the amount of water filtered and flow during collection.
III. Determination of blank levels in C-18 discs and pre-filters from 60L samples.

IV. Determination of comparative PCB levels in whole water samples and C.L.A.M. samplers from actual field location(s) using sampling techniques that are comparable in terms of potential for PCB loss or contribution.

Therefore in the proposed plan all CLAM sampling will include collection of the output water to accurately determine the volume (by mass), all whole water samples will be conducted on individual grab samples to avoid subsampling uncertainty from composites and the potential loss of PCB analytes to container walls, and all bottles containing samples for analysis will be extracted when emptied and the extract included as part of the sample. Unless otherwise specified the default CLAM configuration for these tests will be a C18 cartridge with a pre-filter in the same cartridge. The individual components of the C.L.A.M. system will be examined to determine blank levels.

All analyses will be conducted by Axys' validated SOPs for Method 1668A/C analysis and each analysis batch will contain triplicate procedural blanks to enable distinction of analysis background from project samples. All of the tests described below will be conducted in triplicate.

TASKS

The following tasks are involved with the proposed tests.

1. **Proofing**

1.1 **Establish background PCB level in CLAM media (untreated)** - Proof CLAM C18 discs, pre-filters and filter/C18 combination disks prior to cleaning and pre-conditioning. Collect proof by elution of the CLAM using AXYS SOP SLA 129 for CLAM elution. Analyze proof for PCB congeners by AXYS SOP MLA-010. Perform in triplicate. Completed in conjuction with 1.2.

1.2 **Establish background PCB levels in CLAM Media (treated)** - Proof CLAM C18 disks, pre-filters and filter/C18 combination disks after cleaning and preconditioning as per the manufacturer's instructions. Collect proof by elution of the CLAM using AXYS SLA-129 for CLAM elution. Analyze proof for PCB congeners by AXYS SOP MLA-010. Perform in triplicate. Completed in conjunction with 1.1.

1.3 Proof CLAM Pumping System / Evaluation of Potential Leaching of PCBs from CLAM Housings .

- Under controlled clean lab conditions at AXYS, using a standard CLAM pumping system, pump 60 L of reagent water (HPLC grade "Seastar" Water) through the CLAM system to determine whether PCBs are being leached from individual discs. This 60 L pumped volume will be achieved by recirculating a single 4L aliquot of water to minimize the total volume of water extracted by the CLAM. Elute and analyze the CLAM disk and pre-filter for PCBs by MLA-010. Perform in triplicate.

- Control A: 4 L reagent whole water control sample. Analyze for PCBs by MLA-010. Perform in triplicate.
- Control B: 4 L reagent whole water exposed to the lab atmosphere during pumping of the "60 L" reagent water. Analyze for PCBs by MLA-010. Perform in triplicate.

2. Field Comparison of CLAM results to Whole Water Rsults for PCBs.

The following plan is proposed at a single location for initial work. The Kaiser Trentwood works facility (final outfall) is recommended as the primary choice for effluent monitoring as this system has;

- A history of monitoring by EPA 1668A/C from whole water and CLAM samples.
- PCB levels for major congeners that are sufficient to distinguish from blank levels in whole water samples. Total PCB values from last 20 weeks of sampling range from 1490 pg/L to 3800 pg/L.
- Sufficient residence time to minimize or attenuate variation in PCB levels.
- Defined and low levels of solids (2-5mg/L) for the first phase of this work.
- Defined sample points upstream for further work (example - influent to Walnut Shell filter, representing higher solids loadings with similar water chemistry)

2.1 Testing of C18 /embedded filter (combined)cartridge Perform in triplicate. Analyze C18/embedded filter as one sample.

- Pump 60 L of sample 3X through a separate CLAM system. Collect all water output to measure volume pumped (by mass) and measure at set time increments during pumping.
- Using the same sampling system used to provide effluent for the C.L.A.M. collect 3 2.36 L grab samples (initial, middle, final) during the 60 L C.L.A.M pumping comparative whole water analysis.
- Analyze the CLAM combined disk and each grab sample for PCBs by MLA- 010.

2.2 Testing of CLAM disk plus separate filter cartridge configuration. Perform in triplicate. This test will determine if there is a difference in "whole water" as analyzed by regular liquid-liquid extraction compared to combined CLAM. Ideally this test can be conducted very close in time to those described in Section 2.1 so that the samples and therefore the results can be considered comparable.

- Pump 60 L of sample 3X through CLAM system configured to have a separate filter cartridge in line before the CLAM extraction cartridge. Collect water output to measure volume pumped (by mass) and measure at set increments during pumping. Retain all sample pumped.
- At the beginning, near the middle and near the end of the 60 L pumping cycle collect two (duplicate) 2.3 L grab samples (6 in total) for comparative whole water analysis.
- Analyze the CLAM C-18 disk for PCBs by MLA-010.

- Analyze the pre-filter cartridge from the CLAM assembly for PCBs by MLA-010.
- Analyze (unfiltered as per MLA-010/EPA1668A/C) one of each duplicate pair of grab samples for PCBs by MLA-010.
- Analyze the other duplicate grab samples by first Millipore filtering them to separate any suspended solids and analyzing both the particulate and the filtrate for PCBs by MLA-010.

3.0 Estimated Program Costs – Proofing and Single Location Field Validation

Task	# C-18 Discs @ $87	# Pre-Filters @ $54	# Filter/C18 combination disks	# of MLA 010 Analysis on C.L.A.M. Media @ $765 each	# of MLA 010 Analysis (Whole of Filtered Water or particulate) @ $750 each	# of MLA 010 Incremental QC Samples @ $750 each	# of CLAM pumping runs to create Samples @ $300
1.1	3	3	3	9		2	0
1.2	3	3	3	9			0
1. 3	0	0	3	3	6	2	3
Total Task 1	6 x $87 = $522	6 x $54 = $324	9 x $89 = $801	21 x $765 = $16,065	6 x $750 = $4,500	4 x $750 = $3,000	3 x $300 = $900
2.1			3	3	9	2	3
2.2	3	3		6	18 whole water + 9 filtrates + 9 particulates	4	3
Total Task 2	3 x $87 = $261	3 x $54 = $162	3 x $89 = $267	9 x $ 765 = $6,885	36 x $750 = $27000	6 x $750 = $4500	6 x $300 = $1800
TOTAL	$783	$486	$1287	$22,950	$31,500	$7500	$2700

4.0 DELIVERABLES

This proposal covers the tests that are outlined above. The deliverables include the results of the experiments described above tabulated in Excel document plus Level IV data package.

5.0 TIME FRAME

TO BE DETERMINED UPON FINAILZATION OF SCOPE.