



Technical Memorandum

Date: January 21, 2015

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Re: 2014 Interim Measure 15 Inter-laboratory Comparison Memo

Introduction

Four laboratory cross comparisons sampling events occurred during the 2014 Klamath Hydroelectric Settlement Agreement (KHSAs) Interim Measure 15 (IM 15) baseline monitoring program to provide insight into laboratory performance at the principal laboratories employed. Location of the sampling event has changed every two years since program inception, including: Link Dam near Klamath Falls (RM 254.4), Klamath River near the Estuary (RM 0.5) and Klamath River near Weitchpec (RM 43.5), and Klamath River below Seiad Valley (RM 128.5).

On March 31, 2014 several entities involved in the IM 15 baseline monitoring program held a meeting to discuss the progress of the inter-laboratory (henceforth, interlab) cross comparisons. From the meeting, several changes to the program were suggested and approved based on data collected from 2009 to 2013. These changes include:

- Continue laboratory analysis for constituents that were more variable (less consistent between laboratories), limited in data, or important for baseline monitoring program. These constituents include: dissolved organic carbon (DOC), total nitrogen (TN), orthophosphate (OPO₄), total phosphorus (TP), total suspended solids (TSS), volatile suspended solids (VSS), and total chlorophyll-a (CHLOR-A).
- Discontinue analyses for constituents that were consistent between laboratories, were often non-detect, or were cost prohibitive. These constituents include:

alkalinity, nitrite+nitrate, ammonia, and five-day carbonaceous biological oxygen demand (CBOD5).

- Add another sampling event between August and October for comprehensive look at the Klamath River. Instead of three sampling events, another sampling event was added in 2014. The four sampling events include: April, July, September, and October.
- Basic Laboratory was dropped from the cross comparison, reducing the laboratories to: CH2M Hill Applied Sciences Laboratory (Corvallis, Oregon) and Aquatic Research, Inc. (Seattle, WA).

Given these changes, laboratory cross comparison for 2014 included collecting a single surface grab sample in the Klamath River below Seiad Valley on April 16, July 9, September 10, and October 8. Each sample was split into two separate bottles via churn-splitter and sent to the two laboratories: CH2M Hill and Aquatic Research.

Even for an identical sample, laboratories may present different results due to the analytical equipment differences, experience of technicians, and varying methods. The cross comparison exercise is not intended to rate the performance of each laboratory or to determine which laboratory is “best.” Such an undertaking would require a much more comprehensive study. Rather, the comparisons are intended to illustrate the range of results produced by CH2M Hill and Aquatic Research for the identified constituents over a sampling season. This memo presents background information on the inter-laboratory study, overview of each laboratory’s methods, detection limits and reporting limits, cross comparison methods, summary of sampling issues, summary of results, and plots for each constituent.

Background

The IM 15 laboratory comparison, which began in 2009, is now in its sixth year. To explore different water quality conditions as well as share the responsibilities in collecting the cross comparison samples, the IM 15 monitoring group decided to move sampling locations every two years among the four sampling entities. The sampling location for the cross comparison in 2009 and 2010 was Link Dam, near Klamath Falls (RM 254.4) by the United States Bureau of Reclamation. In 2011, three grab samples were collected at the Klamath River near the Estuary (RM 0.5) by the Yurok Tribe. Several constituents were below the detection level at this location. Therefore, the group decided to move the 2012 sampling site further upstream. In 2012, three grab samples were collected at the Klamath River near Weitchpec (RM 43.5) by the Yurok Tribe. In 2013, three grab samples were collected at the Klamath River below Seiad Valley (RM 128.5) by the Karuk Tribe. In 2014, four grab samples were collected at the Klamath River below Seiad Valley (RM 128.5) by the Karuk Tribe. In 2015 and 2016 PacifiCorp will collect cross comparison samples at a location to be determined by the group.

Censored data samples refers to laboratory results with “less than” (<), “non-detect” (ND), and (j) flag data. Data sets with “less than” and “non-detect” are results below the method detection limit (MDL). When censored data is present for a constituent at two laboratories, then the pair is excluded from the cross comparisons. More information on this topic is discussed in the cross comparison methods section. The method detection limit (MDL) is explicitly defined in Standard Methods (APHA 2005) as “the constituent concentration that, when processed through the complete method, produces a signal with a 99 percent probability that it is different than the blank.” The RL is defined as the lowest constituent concentration in a sample that can be quantitatively determined with statistical rigor. Results greater than or equal to the laboratory MDL, but below the method reporting limit (RL)¹ are referred to as (j) flag data.

Overview of Labs: Methods, Detection and Reporting Limits

All methods used by the analytical laboratories were either EPA methods or Standard Methods. While laboratories used the same methods for certain constituent analysis, the method detection limit (MDL) and reporting limit (RL) were not necessarily the same. The analytical methods and associated limits at each constituent at each laboratory are presented in Table A-1 and Table A-2.

Laboratory reporting values for constituents varied. Generally, the RL for each laboratory was within a factor of 5. For example, the RL for ammonia was 0.05 mg/l for CH2M Hill and 0.01 mg/l for Aquatic Research. For TSS and VSS, this maximum difference between the RL was a factor of 10. For several constituents, Aquatic Research did not provide a distinct RL, but set the RL as equal to the MDL.

Table A-1. Laboratory methods, method detection limits (MDL), and reporting limits (RL) for CH2M Hill (2014). N/A = not applicable

Constituent	units	Method	CH2M Hill	
			MDL	RL
DOC	mg/l	SM5310B	0.12	0.5
TN	mg/l	SM4500-N C	0.048	0.2
OPO4	mg/l	E365.1	0.0014	0.01
TP	mg/l	E365.4	0.017	0.05
TSS	mg/l	SM2540D	0.6	5
VSS	mg/l	E160.4	N/A	5
CHLOR-A ^a	0µg/l	EPA 445.0	0.18	N/A

^a CH2M Hill does not analyze for chlorophyll-a. Samples were sent to Chesapeake Biological Laboratory (CBL) for chlorophyll-a analysis.

¹ Certain analytical laboratories are adopting more formal names for MDL, such as the Limit of Detection (LOD), and also for RL, such as the Level of Quantitation (LOQ) or Minimum Level of Quantitation (MLQ).

Table A-2. Laboratory methods, method detection limits (MDL), and reporting limits (RL) for Aquatic Research (2014).

Constituent	units	Method	MDL	Aquatic Research
				RL
DOC	mg/l	SM205310B	0.095	0.25
TN	mg/l	SM204500NC	0.03	0.05
OPO4 ^a	mg/l	SM18 4500PF	0.001	0.001
TP ^a	mg/l	SM18 4500PF	0.002	0.002
TSS	mg/l	SM20 2540D	0.1	0.5
VSS	mg/l	SM20 2540E	0.1	0.5
CHLOR-A ^a	µg/l	SM18 10200H	0.10	0.10

^a The MDL and RL values were set to same concentration.

Cross Comparison Method (RPD & AD)

To compare the results from each laboratory, relative percent difference (RPD) or absolute difference (AD) calculations were applied to paired samples for CH2M Hill and Aquatic Research. CH2M Hill and Aquatic Research reported different significant figures and the data presented herein are directly from respective laboratory reports. The RPD and AD, used for assessing a regular and duplicate sample are calculated as:

$$\text{RPD (percent)} = |(R - D)| / ((R + D) / 2) * 100 \quad (1)$$

$$\text{AD (concentration)} = |R - D| \quad (2)$$

Where: R = Regular sample result
 D = Duplicate sample result

These RPD and AD formulae were adapted for the laboratory comparison as follows:

$$\text{RPD (percent)} = |(X1 - X2)| / ((X1 + X2) / 2) * 100 \quad (3)$$

$$\text{AD (concentration)} = |X1 - X2| \quad (4)$$

Where: X1 = Result sample result from laboratory 1
 X2 = Result sample result from laboratory 2

During each comparison, if the laboratories used different RLs, the larger RL value was selected as the criteria to determine whether to use the RPD or AD. Use of the larger RL value allows the comparison to encapsulate the largest possible uncertainty associated with the data.

If the sample result was equal to or greater than five times the selected reporting limit, the RPD was calculated. The RPD criteria of 20 percent was used to determine if two samples were similar (RPD of less than or equal to 20 percent) or dissimilar (RPD of greater than 20 percent) (USBR, 2009). If the RPD result was less than or equal to 20 percent, the two samples were deemed to be similar and the comparison was labeled with

an “OK” result. If the RPD result was greater than 20 percent, the results were termed dissimilar and the RPD was presented within the table.

If the sample result was less than five times the selected reporting limit, the AD was calculated and a different criteria of the reporting limit was used to determine if two samples were similar (AD less than or equal to the selected reporting limit) or dissimilar (AD greater than the selected reporting limit) (USB, 2009). If the AD was less than the selected reporting limit for the sample comparison, the comparison was labeled with an “OK” result. If the AD was greater than the selected reporting limit for the sample comparison, the results were termed dissimilar and the AD result was presented, along with a footnote of the laboratory reporting limit used. This process is illustrated in Figure A-1.

Censored data refers to sample results without a result (e.g. “<” value, non-detect, and (j) flagged). When censored data is present for a constituent, the sample pair is excluded from the cross comparison analysis. For example, a duplicate sample was sent to the laboratories to be analyzed for total phosphorus (TP). The results were 0.04(j) mg/l and 0.03(j) mg/l and CH2M Hill and Aquatic Research. Data below the laboratory RLs are replaced by the laboratory RLs in the data tables. Thus, both values at the two laboratories would be replaced by the RLs. Cross comparisons are not performed for paired data that consist of two RL values. These comparisons are labeled as “censored” and excluded from the cross comparison.

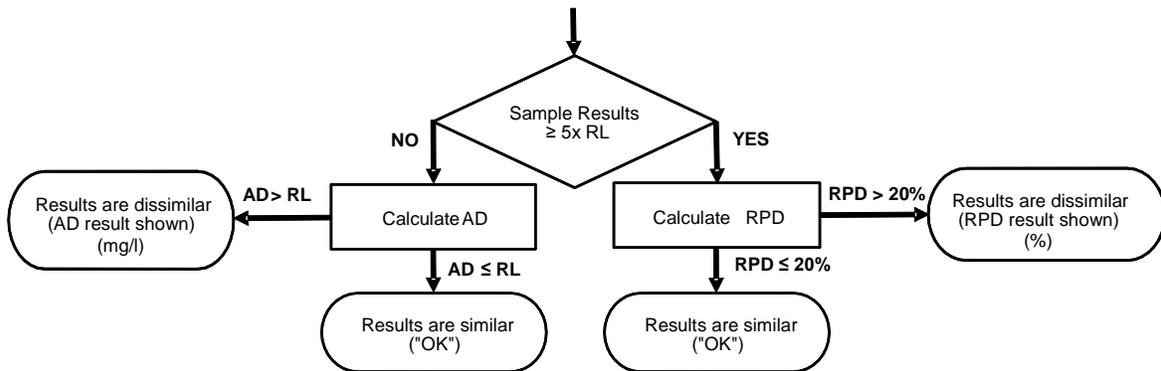


Figure A-1. Flow diagram of the comparison process. RPD = relative percent difference. RL = reporting limit. AD = absolute difference.

2014 Sampling

Sampling was scheduled for April 16, July 9, September 10, and October 8. Samples were collected, shipped, and processed by the laboratory for July 9 and October 8 sampling events. The April 16 sample sent to CH2MHill was lost due to a United Parcel Service (UPS) shipping error. To remedy this condition, the Karuk Tribe collected an additional interlab sample on August 6. On September 10 the interlab sample was not

collected. The Karuk Tribe sent an email out on September 11, notifying several KHSA group members, and a new sample data of September 24 was selected.

The IM 15 baseline monitoring program, including the laboratory cross comparison element, is intended to be adaptive to accommodate challenges that face busy sampling crews, dynamic field conditions, shipping and laboratory issues, and other factors that can affect program results. The following recommendations are made to track samples and react to program problems in a timely manner:

- Shipping or tracking information should be maintained for all interlab samples
- Shipments should be confirmed with either a communication to the laboratory (email, phone call), or confirming via the shipping company website
- If a sampling date is missed, or a sample is lost in shipment, a communication (email, telephone call) to the group should be made as soon as feasible.
- The group, considering the number of remaining interlab samples and sampling dates can identify if there should be an additional sample collected and an appropriate date.

Chlorophyll-a

In 2014, chlorophyll-a was collected and analyzed for all four sampling events. CH2M Hill does not analyze for chlorophyll-a. Therefore, the samples were sent to Chesapeake Biological Laboratory (CBL) in Maryland for analysis. The RPD was applied to CH2M Hill and Aquatic Research when both concentrations were equal to or greater than 5 times the reporting limits. Otherwise, the cross comparison were censored as “non-applicable”.

Results

The comparison of the laboratory results from the two labs was completed as identified above (Figure A-1) based on laboratory data shown in Table A-3, Table A-5, Table A-7, and Table A-9. Data were not complete for the April 16 event and are not included. The cross comparison results for each sampling date are shown in Table A-4, Table A-6, Table A-8, and Table A-10.

Table A-3. Laboratory data used for lab cross comparison: July 9, 2014.

Constituent	Laboratory Units	CH2M Hill (CH2M)	Aquatic Research, Inc. (ARI)
Dissolved Organic Carbon (DOC)	mg/l	3.27	3.95
Total Nitrogen (TN)	mg/l	0.69	0.398
Orthophosphate (OPO4)	mg/l	0.098	0.116
Total Phosphorus (TP)	mg/l	0.11	0.131
Total Suspended Solids (TSS)	mg/l	4.2	2
Volatile Suspended Solids (VSS)	mg/l	0.4	1
Chlorophyll-a (CHLOR-A)	µg/l	0.58	0.1 ^a

^a ARI result for CHLOR-A: "<0.1" mg/l. Value replaced with RL.

Table A-4. Results for paired laboratory comparisons: July 9, 2014.

Constituent	Units	CH2M Hill versus Aquatic Research, Inc.
Dissolved Organic Carbon (DOC)	mg/l	OK
Total Nitrogen (TN)	mg/l	(0.282 mg/l) ^a
Orthophosphate (OPO4)	mg/l	OK
Total Phosphorus (TP)	mg/l	OK
Total Suspended Solids (TSS)	mg/l	OK
Volatile Suspended Solids (VSS)	mg/l	OK
Chlorophyll-a (CHLOR-A)	µg/l	n/a

^a CH2M RL result for TN: 0.2 mg/l.

Table A-5. Laboratory data used for lab cross comparison: August 6, 2014.

Constituent	Laboratory Units	CH2M Hill (CH2M)	Aquatic Research, Inc. (ARI)
Dissolved Organic Carbon (DOC)	mg/l	4.4	3.94
Total Nitrogen (TN)	mg/l	0.82	0.667
Orthophosphate (OPO4)	mg/l	0.15	0.182
Total Phosphorus (TP)	mg/l	0.22	0.232
Total Suspended Solids (TSS)	mg/l	11.6	8.5
Volatile Suspended Solids (VSS)	mg/l	5.4	5.5
Chlorophyll-a (CHLOR-A)	µg/l	19.34	15

Table A-6. Results for paired laboratory comparisons: August 6, 2014.

Constituent	Units	CH2M Hill versus Aquatic Research, Inc.
Dissolved Organic Carbon (DOC)	mg/l	OK
Total Nitrogen (TN)	mg/l	OK
Orthophosphate (OPO4)	mg/l	OK
Total Phosphorus (TP)	mg/l	OK
Total Suspended Solids (TSS)	mg/l	OK
Volatile Suspended Solids (VSS)	mg/l	OK
Chlorophyll-a (CHLOR-A)	µg/l	(25.3%) ^a

^a CH2M and ARI value for CHLOR-A greater than 20 percent RPD.

Table A-7. Laboratory data used for lab cross comparison: September 24, 2014.

Constituent	Laboratory Units	CH2M Hill (CH2M)	Aquatic Research, Inc. (ARI)
Dissolved Organic Carbon (DOC)	mg/l	4.07	5.22
Total Nitrogen (TN)	mg/l	0.69	0.588
Orthophosphate (OPO4)	mg/l	0.13	0.15
Total Phosphorus (TP)	mg/l	0.18	0.199
Total Suspended Solids (TSS)	mg/l	6.2	7.5
Volatile Suspended Solids (VSS)	mg/l	4.6	2.8
Chlorophyll-a (CHLOR-A)	µg/l	3.81	2.9

Table A-8. Results for paired laboratory comparisons: September 24, 2014.

Constituent	Units	CH2M Hill versus Aquatic Research, Inc.
Dissolved Organic Carbon (DOC)	mg/l	(24.8%) ^a
Total Nitrogen (TN)	mg/l	OK
Orthophosphate (OPO4)	mg/l	OK
Total Phosphorus (TP)	mg/l	OK
Total Suspended Solids (TSS)	mg/l	OK
Volatile Suspended Solids (VSS)	mg/l	OK
Chlorophyll-a (CHLOR-A)	µg/l	(27.1%) ^b

^a CH2M and ARI value for DOC greater than 20 percent RPD.

^b CH2M and ARI value for CHLOR-A greater than 20 percent RPD.

Table A-9. Laboratory data used for lab cross comparison: October 8, 2014.

Constituent	Laboratory Units	CH2M Hill (CH2M)	Aquatic Research, Inc. (ARI)
Dissolved Organic Carbon (DOC)	mg/l	3.66	4.82
Total Nitrogen (TN)	mg/l	0.78	0.587
Orthophosphate (OPO4)	mg/l	0.12	0.136
Total Phosphorus (TP)	mg/l	0.14	0.163
Total Suspended Solids (TSS)	mg/l	7.4	6.7
Volatile Suspended Solids (VSS)	mg/l	1.6	2.3
Chlorophyll-a (CHLOR-A)	µg/l	3.3	2.1

Table A-10. Results for paired laboratory comparisons: October 8, 2014.

Constituent	Units	CH2M Hill versus Aquatic Research, Inc.
Dissolved Organic Carbon (DOC)	mg/l	(27.4%) ^a
Total Nitrogen (TN)	mg/l	OK
Orthophosphate (OPO4)	mg/l	OK
Total Phosphorus (TP)	mg/l	OK
Total Suspended Solids (TSS)	mg/l	OK
Volatile Suspended Solids (VSS)	mg/l	OK
Chlorophyll-a (CHLOR-A)	µg/l	(44.4%) ^b

^a CH2M and ARI value for DOC greater than 20 percent RPD.

^b CH2M and ARI value for CHLOR-A greater than 20 percent RPD.

Summary

The 2014 interlab cross comparison, samples were collected in the Klamath River below Seiad Valley (RM 128.5). Comparisons were completed for dissolved organic carbon (DOC), total nitrogen (TN), orthophosphate (OPO4), total phosphorus (TP), total suspended solids (TSS), volatile suspended solids (VSS), and chlorophyll-a (CHLOR-A). 28 laboratory cross comparisons were considered.

In 2014, the study included: 21 similar pairs, 6 dissimilar pairs, 1 non-applicable pair, and no censored pairs. The 6 dissimilar pairs include: (2) DOC, (1) TN and (3) CHLOR-A (Table A-11). The comparisons of non-paired samples were labeled as non-applicable because the pair is not a similar, dissimilar, or censored paired.

Table A-11. Summary of cross comparisons for each constituent. Comparisons include: 71 similar pairs, 14 dissimilar pairs, 17 censored pairs, 6 non-applicable pairs.

	Similar Pairs	Dissimilar Pairs	Censored Pairs	Non-applicable*
DOC	2	2	-	-
TN	3	1	-	-
OPO4	4	-	-	-
TP	4	-	-	-
TSS	4	-	-	-
VSS	4	-	-	-
Chlorophyll-a	<u>0</u>	<u>3</u>	-	<u>1</u>
Total	21	6	0	1

*Data for sample pair not available (e.g. no lab data).

Based on suggestions from the water quality monitoring group, comparison pairs for each constituent are plotted. Trend lines and linear regression equations are included in the graphs which are presented in Appendix A (Figure A-1 through Figure A-7) for the 2014 sampling season.

Acknowledgement

We would like to thank everyone who provided insight and feedback during the project meetings and comments for this technical memorandum.

References

U.S. Bureau of Reclamation (USBR). 2009. *Standard Operating Procedures for Quality Assurance*. Revision 2009-05. Environmental Monitoring Branch, Mid-Pacific Region, Sacramento, CA. May.

American Public Health Assc., American Water Works Assc., and Water Environment Federation (APHA). 2005. *Standard Methods for the Examination of Water and Wastewater*, 21st Ed. Eds. A.E. Eaton, L.S. Clesceri, E.W. Rice, and A.E. Greenberg. Washington D.C.

Appendix A. 2009-2014 Constituent Plots

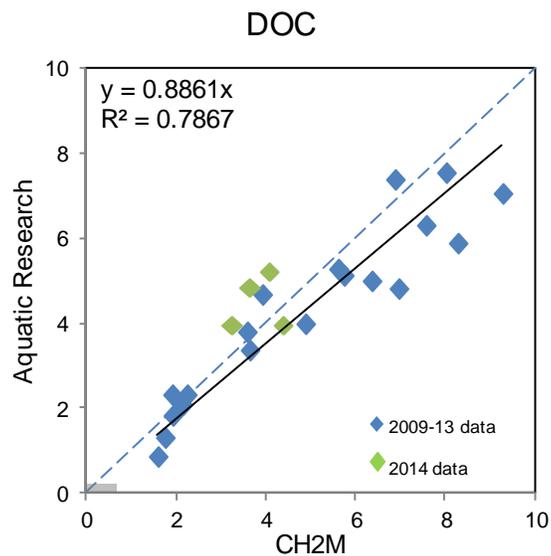


Figure A-1. KHSA inter-laboratory plots from 2009-2014 for Dissolved Organic Carbon (mg/l). Grey region in lower corner represents the region below the RL for the respective laboratories in 2014.

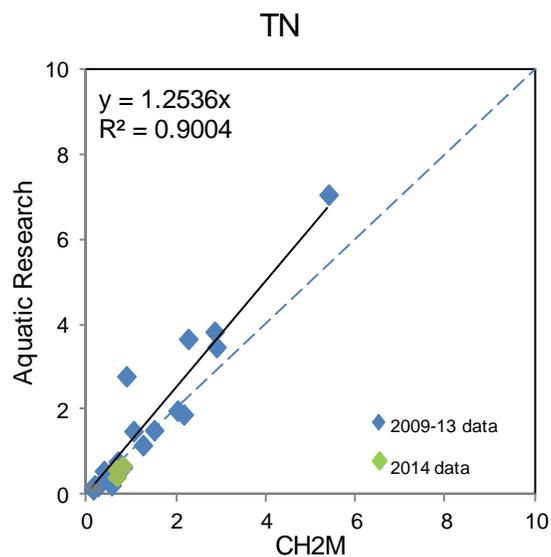


Figure A-2. KHSA inter-laboratory plots from 2009-2014 for Total Nitrogen (mg/l). Grey region in lower corner represents the region below the RL for the respective laboratories in 2014.

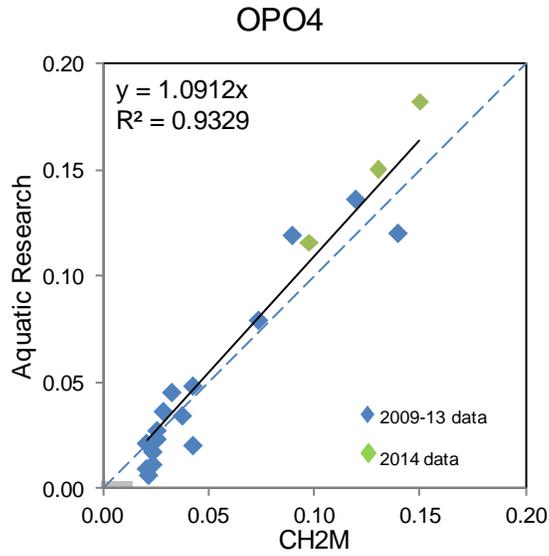


Figure A-3. KHSA inter-laboratory plots from 2009-2014 for Orthophosphate (mg/l). Grey region in lower corner represents the region below the RL for the respective laboratories in 2014.

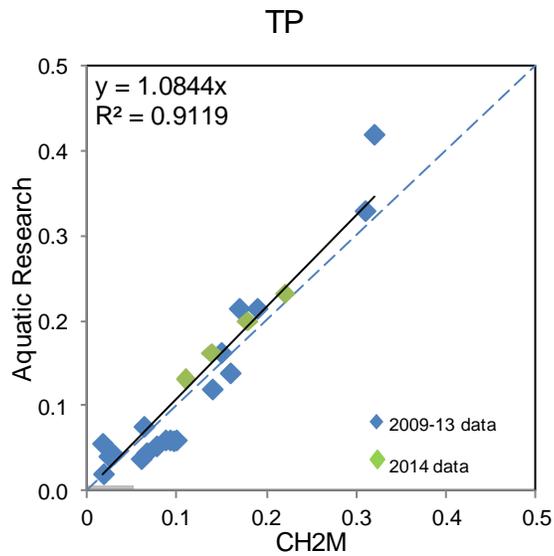


Figure A-4. KHSA inter-laboratory plots from 2009-2014 for Total Phosphorus (mg/l). Grey region in lower corner represents the region below the RL for the respective laboratories in 2014.

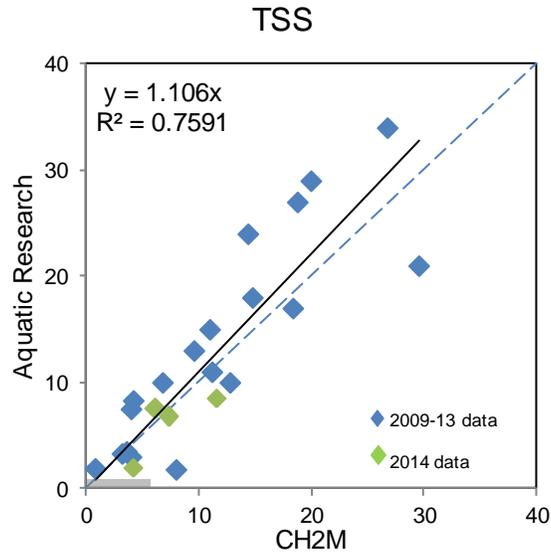


Figure A-5. KHSA inter-laboratory plots from 2009-2014 for Total Suspended Solids (mg/l). Grey region in lower corner represents the region below the RL for the respective laboratories in 2014.

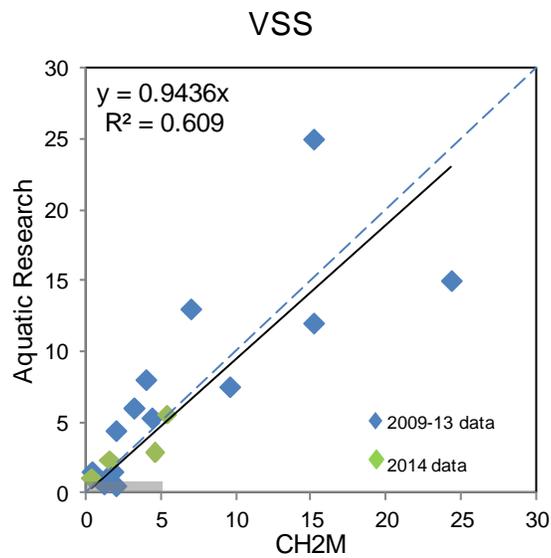


Figure A-6. KHSA inter-laboratory plots from 2009-2014 for Volatile Suspended Solids (mg/l). Grey region in lower corner represents the region below the RL for the respective laboratories in 2014.

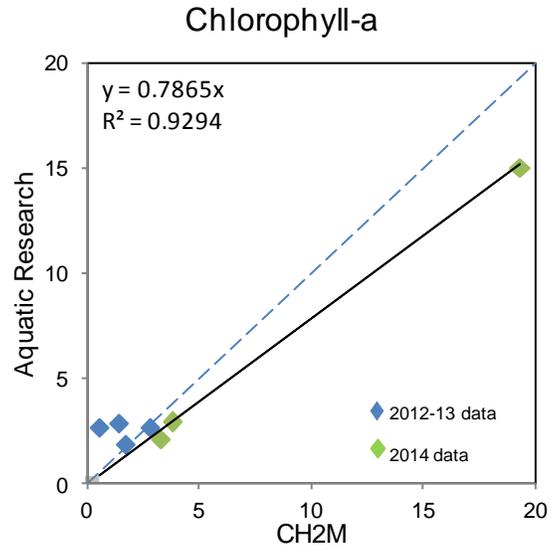


Figure A-7. KHSA inter-laboratory plots from 2009-2014 for Chlorophyll-a ($\mu\text{g/l}$). Grey region in lower corner represents the region below the RL for the respective laboratories in 2014. Note: Chlorophyll-a was not collected from 2009-2011.