



Technical Memorandum

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Re: 2015 Interim Measure 15 Inter-laboratory Comparison Memo

Introduction

For large monitoring projects involving multiple stakeholders, it is not uncommon to have more than one laboratory involved in the analysis of the environmental samples collected. While external quality assurance and laboratory quality control can offer insight into the accuracy and precision of results reported for environmental samples for a specific laboratory, such procedures do not provide a comparison of the performances of multiple laboratories. Even for an identical sample, laboratories may report different results because of the individual equipment used, the differences in experience of technicians performing the work, and the variety of analytical methods employed.

Therefore, an inter-laboratory comparison procedure has been devised and implemented for the 2015 Klamath Hydroelectric Settlement Agreement (KHSA) Interim Measure 15 (IM 15) baseline monitoring program. The comparison method is not intended to rate the performance of each laboratory or to determine which laboratory is “best” or “right.” Such an undertaking would require a more comprehensive study and is beyond the scope of this project. The comparisons are intended to illustrate the range of results produced by two laboratories for the identified constituents over a sampling season and evaluate the similarities and differences of results from the two laboratories.

Four inter-laboratory comparison sampling events occurred during the 2015 IM 15 baseline monitoring program to provide insight into laboratory performance at the principal laboratories employed. The location of the sampling events has changed every 2 years since program inception in 2009, including: Link Dam near Klamath Falls (River

Mile (RM) 254.4), Klamath River near the Estuary (RM 0.5), Klamath River near Weitchpec (RM 43.5), and Klamath River below Seiad Valley (RM 128.5). During the 2015 IM 15 baseline monitoring season, the inter-laboratory comparison sampling occurred at Klamath River below Iron Gate dam (aka Hatchery Bridge; RM 189.73)

In 2015, six constituents were analyzed at two laboratories to compare laboratory performance. These constituents included dissolved organic carbon (DOC), total nitrogen (TN), ortho-phosphate (OPO₄), total phosphorus (TP), total suspended solids (TSS), and volatile suspended solids (VSS). Samples were collected on May 18, July 8, September 2 and October 20, 2015. Samples were split into two separate bottles using a churn splitter and sent to both CH2M Applied Sciences Laboratory and IEH Analytical Laboratories (formerly Aquatic Research, Inc.).

This memorandum presents background information on the inter-laboratory comparison study; overview of each laboratory's methods, detection limits and reporting limits; inter-laboratory comparison methods; summary of sampling issues, comparison results, and plots for each constituent.

Background

The IM 15 inter-laboratory comparison, which began in 2009, is now in its seventh year. To explore different water quality conditions as well as share the responsibilities in collecting the comparison samples, the IM 15 monitoring group decided to move sampling locations every 2 years among the four sampling entities. Grab sampling locations for the comparison in 2009 and 2010 was Link Dam, near Klamath Falls (RM 254.4) where samples were collected by the United States Bureau of Reclamation. In 2011, three samples were collected at the Klamath River near the Estuary (RM 0.5) by the Yurok Tribe. Several constituents were below detection levels at this location. Therefore, the KHSA stakeholders decided to move the 2012 sampling site further upstream. In 2012, three samples were collected at the Klamath River near Weitchpec (RM 43.5) by the Yurok Tribe.

In 2013, three samples were collected at the Klamath River below Seiad Valley (RM 128.5) by the Karuk Tribe. In 2014, four samples were collected at the Klamath River below Seiad Valley (RM 128.5) by the Karuk Tribe. In 2015, PacifiCorp collected four samples at Klamath River below Iron Gate dam (RM 189.73). As of 2015, a 7 year dataset has been created, through the combined efforts of the monitoring stakeholders, that has allowed a comparison of different laboratories.

In any dataset, there is the possibility that some of the constituents have results which are censored data. Censored data refer to laboratory results of less than (<), non-detect (ND), and (j) flag values. Results given a less than or ND result are those that are below the method detection limit (MDL). The 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 method reporting limit (RL) is defined as the lowest constituent concentration in a sample that can be quantitatively determined with statistical rigor.

However, not all laboratories calculate an RL; some laboratories report values down to the MDL. Results greater than or equal to the laboratory MDL, but below the RL are referred to as (j) flag data.

When censored data is reported by two laboratories for the same constituent in a specific sample, the pair of values is excluded from the comparisons. More information on this topic is discussed in the comparison methods section below.

Overview of Labs: Methods, Detection and Reporting Limits

While different laboratories may use the same method, the differences in equipment and technician experience between the laboratories often produces different MDLs and RLs for the same method. Therefore, the MDL and RL for each laboratory for each method used must be known before any inter-laboratory comparison can be performed. The two laboratories used only EPA methods or Standard Methods in 2015 (Table A-1). Three of the analysis methods were used at both laboratories, but in each case the MDL was different. The RL values could not be compared because IEH Analytical Laboratories did not calculate and utilize an independently defined RL, but rather set the RL equal to the MDL. By setting the RL equal to the MDL, the RL values used by IEH were 2 – 25 times smaller than the RL values used by CH2M.

Table A-1. Laboratory methods, method detection limits (MDL), and reporting limits (RL) for CH2M Applied Sciences Laboratory and IEH Analytical Laboratories (2015). N/A = not applicable

Constituent	unit	CH2M Applied Sciences Laboratory			IEH Analytical Laboratories		
		Method	MDL	RL	Method	MDL	RL
DOC	mg/l	SM5310B	0.2	0.5	SM205310B	0.25	0.25
TN	mg/l	SM4500-N C	0.048	0.2	SM204500NC	0.05	0.05
OPO4	mg/l	E365.1	0.0014	0.01	SM18 4500PF	0.001	0.001
TP	mg/l	E365.4	0.017	0.05	SM18 4500PF	0.002	0.002
TSS	mg/l	SM2540D	0.6	5	SM20 2540D	0.5	0.5
VSS	mg/l	E160.4	N/A	5	SM20 2540E	0.5	0.5

Comparison Method

To compare the results from each laboratory, relative percent difference (RPD) or absolute difference (AD) were calculated for each paired sample result from CH2M and IEH. Censored and non-applicable data was not included in this process. CH2M and IEH reported different significant figures and the data presented herein are directly from respective laboratory reports. The RPD and AD, used for assessing precision from regular and duplicate sample results, 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

If the average of the two sample results was equal to or greater than five times the selected RL, the RPD was calculated (Figure A-1). If the average of the two sample results was less than five times the RL, the AD was calculated (Figure A-1). During comparison of results for each constituent, 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 allowed the comparison to encapsulate the largest possible uncertainty associated with the results.

If the RPD was calculated, a criterion of 20 percent was used to determine if two samples were similar or not (Figure A-1; 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.

If the AD was calculated because the average of the two sample results was less than five times the selected reporting limit, then the RL was used as the criterion to determine if two samples were similar or not (Figure A-1; USBR 2009). If the AD was less than the selected RL for the sample comparison, the comparison was labeled with an “OK” result. If the AD was greater than the selected RL 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.

When censored data was present in the results of one lab for a specific constituent, that censored data was replaced with the appropriate RL and either the RPD or AD was calculated as appropriate based on the average of the RL and the other sample result. When only censored data was present for a constituent, the sample pair was excluded from the comparison analysis. As a hypothetical example, if duplicate samples were sent to two laboratories to be analyzed for TP, and the results were 0.04(j) milligrams per liter (mg/L) and 0.03(j) mg/L, no comparison would be completed for TP as both values would be replaced with the RL for calculations during the comparison. Comparisons were not performed for paired data that consist of two RL values.

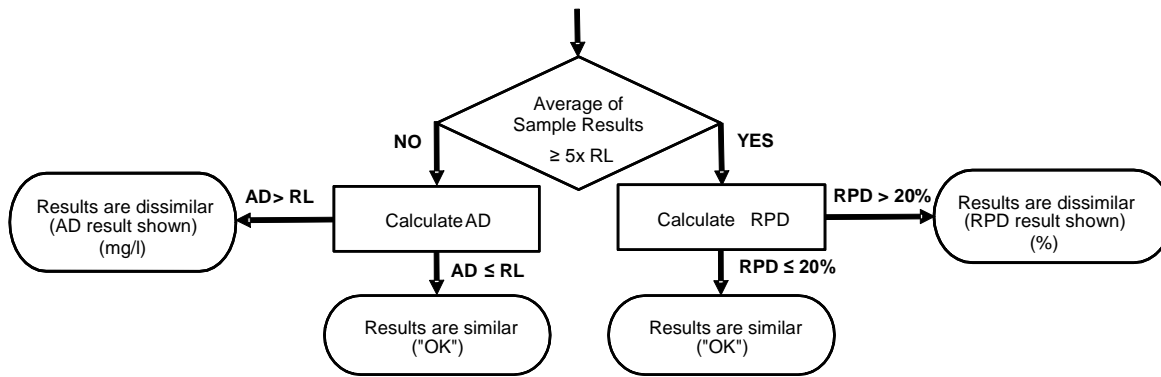


Figure A-1. Flow diagram of the comparison process. RL = reporting limit. RPD = relative percent difference. AD = absolute difference.

2015 Sampling

E&S Environmental Chemistry (E&S) was contracted to carry out the PacifiCorp portion of the IM 15 2015 baseline monitoring program, including the collection of the laboratory comparison samples. E&S collected samples on May 18, July 8, September 2 and October 20, 2015. All samples were received by CH2M and IEH laboratories within 3 days of collection and there were no issues with lost or invalid samples during 2015. However, the May 18 IEH chain-of-custody did not request VSS as a constituent, and therefore VSS has only three comparisons in 2015. Similarly, the July 8 CH2M chain-of-custody did not request TN as a constituent, and therefore TN has only three comparisons in 2015.

Comparison of Laboratory Results

The comparison of the laboratory results from the two labs was completed as identified above (Figure A-1) based on data from the two labs indicates that there was little difference between the results (Table A-3, Table A-5, Table A-7, and Table A-9). From the four 2015 samples collected and analyzed by the two laboratories, there were 18 similar pairs, one dissimilar pair, three censored pairs, and two instances when missing data precluded a comparison (Table A-2). Of the 19 comparisons completed, 18 comparisons were determined to be OK (Table A-4, Table A-6, Table A-8, and Table A-10) only one sample (TP on September 2) was found to have an AD greater than the RL (Table A-8).

Table A-2. Summary of 2015 comparisons for each constituent.

	Similar Pairs	Dissimilar Pairs	Censored Pairs	Not applicable*
DOC	4	0	0	0
TN	3	0	0	1
OPO4	4	0	0	0
TP	3	1	0	0
TSS	3	0	1	0
VSS	1	0	2	1
Total	18	1	3	2

*There is no lab data for sample pair.

Table A-3. Laboratory data used for lab comparison: May 18, 2015.

Constituent	Units	Data Used for Comparison			Average of Data	RL Used in Calculations	Criteria Used
		CH2M	IEH				
Dissolved Organic Carbon (DOC)	mg/l	3.55	3.53	3.54	0.5	RPD	
Total Nitrogen (TN)	mg/l	0.52	0.45	0.49	0.2	AD	
Orthophosphate (OPO4)	mg/l	0.07	0.07	0.07	0.01	RPD	
Total Phosphorus (TP)	mg/l	0.11	0.10	0.11	0.05	AD	
Total Suspended Solids (TSS)	mg/l	5.00 ^a	0.57	5.00	5	AD	
Volatile Suspended Solids (VSS)	mg/l	5.00 ^b	N/A	N/A	5	N/A	

^a The CH2M TSS result was 4.20 mg/l, which is less than the RL of 5.00, and the value was replaced with the RL during calculations.

^b The CH2M VSS result was 0.40 mg/l, which is less than the RL of 5.00, and the value was replaced with the RL during calculations.

Table A-4. Results for paired laboratory comparisons: May 18, 2015.

Constituent	CH2M versus IEH
Dissolved Organic Carbon (DOC)	OK
Total Nitrogen (TN)	OK
Orthophosphate (OPO4)	OK
Total Phosphorus (TP)	OK
Total Suspended Solids (TSS)	OK
Volatile Suspended Solids (VSS)	N/A ^a

^a There was no IEH result for VSS on May 18, 2015, and therefore no comparison was performed.

Table A-5. Laboratory data used for lab comparison: July 8, 2015.

Constituent	Units	Data Used for Comparison		Average of Data	RL Used in Calculations	Criteria Used
		CH2M	IEH			
Dissolved Organic Carbon (DOC)	mg/l	3.46	3.44	3.45	0.5	RPD
Total Nitrogen (TN)	mg/l	N/A	0.611	0.61	0.2	AD
Orthophosphate (OPO4)	mg/l	0.076	0.085	0.08	0.01	RPD
Total Phosphorus (TP)	mg/l	0.13	0.115	0.12	0.05	AD
Total Suspended Solids (TSS)	mg/l	5.00 ^a	6.2	5.60	5	AD
Volatile Suspended Solids (VSS)	mg/l	5.00 ^b	0.83	2.92	5	AD

^a The CH2M TSS result was 3.00 mg/l, which is less than the RL of 5.00, and the value was replaced with the RL during calculations.

^b The CH2M VSS result was 0.00 mg/l, which is less than the RL of 5.00, and the value was replaced with the RL during calculations.

Table A-6. Results for paired laboratory comparisons: July 8, 2015.

Constituent	CH2M versus IEH
Dissolved Organic Carbon (DOC)	OK
Total Nitrogen (TN)	N/A ^a
Orthophosphate (OPO4)	OK
Total Phosphorus (TP)	OK
Total Suspended Solids (TSS)	OK
Volatile Suspended Solids (VSS)	OK

^a There was no CH2M result for TN on July 8, 2015, and therefore no comparison was performed.

Table A-7. Laboratory data used for lab comparison: September 2, 2015.

Constituent	Units	Data Used for Comparison			Average of Data	RL Used in Calculations	Criteria Used
		CH2M	IEH	IEH			
Dissolved Organic Carbon (DOC)	mg/l	3.38	3.91	3.65	0.5	RPD	
Total Nitrogen (TN)	mg/l	0.62	0.693	0.62	0.2	AD	
Orthophosphate (OPO4)	mg/l	0.16	0.183	0.17	0.01	RPD	
Total Phosphorus (TP)	mg/l	0.13	0.198	0.16	0.05	AD	
Total Suspended Solids (TSS)	mg/l	5.00 ^a	0.50 ^b	N/A	5	N/A	
Volatile Suspended Solids (VSS)	mg/l	5.00 ^c	0.50 ^d	N/A	5	N/A	

^a The CH2M TSS result was 1.00 mg/l, which is less than the RL of 5.00, and the value was replaced with the RL during calculations.

^b The IEH TSS result was <0.50 mg/l, and was replaced with the RL of 0.50 mg/l during calculations.

^c The CH2M VSS result was 0.80 mg/l, which is less than the RL of 5.00, and the value was replaced with the RL during calculations.

^d The IEH VSS result was <0.50 mg/l, and was replaced with the RL of 0.50 mg/l during calculations.

Table A-8. Results for paired laboratory comparisons: September 2, 2015.

Constituent	CH2M versus IEH
Dissolved Organic Carbon (DOC)	OK
Total Nitrogen (TN)	OK
Orthophosphate (OPO4)	OK
Total Phosphorus (TP)	(0.068 mg/l) ^a
Total Suspended Solids (TSS)	N/A ^b
Volatile Suspended Solids (VSS)	N/A ^c

^a The average values of TP in September were not greater or equal to five times the selected RL of 0.05 mg/l. Therefore, the AD was calculated and was found to be greater than the selected RL.

^b Both CH2M and IEH TSS results were below the RL, and therefore no comparison was performed

^c Both CH2M and IEH VSS results were below the RL, and therefore no comparison was performed

Table A-9. Laboratory data used for lab comparison: October 20, 2015.

Constituent	Units	Data Used for Comparison			Average of Data	RL Used in Calculations	Criteria Used
		CH2M	IEH	IEH			
Dissolved Organic Carbon (DOC)	mg/l	4.18	3.93	4.06	0.5	RPD	
Total Nitrogen (TN)	mg/l	1.08	1.25	1.17	0.2	RPD	
Orthophosphate (OPO4)	mg/l	0.13	0.135	0.13	0.01	RPD	
Total Phosphorus (TP)	mg/l	0.14	0.152	0.15	0.05	AD	
Total Suspended Solids (TSS)	mg/l	5.0 ^a	1.8	3.40	5	AD	
Volatile Suspended Solids (VSS)	mg/l	5.0 ^b	0.50 ^c	N/A	5	N/A	

^a The CH2M TSS result was 2.2 mg/l, and was replaced with the RL of 5.0 mg/l during calculations.

^b The CH2M VSS result was -0.2 mg/l, and was replaced with the RL of 5.0 mg/l during the calculations.

^c The IEH VSS result was <0.50 mg/l, and was replaced with the RL of 0.50 mg/l during calculations.

Table A-10. Results for paired laboratory comparisons: October 20, 2015.

Constituent	CH2M versus IEH
Dissolved Organic Carbon (DOC)	OK
Total Nitrogen (TN)	OK
Orthophosphate (OPO4)	OK
Total Phosphorus (TP)	OK
Total Suspended Solids (TSS)	OK
Volatile Suspended Solids (VSS)	N/A ^a

^a Both CH2M and IEH VSS results were below the RL, and therefore no comparison was performed.

Summary

The 2015 inter-laboratory comparison samples were collected in the Klamath River below Iron Gate dam (RM 189.73). Comparisons were completed for dissolved organic carbon (DOC), total nitrogen (TN), orthophosphate (OPO4), total phosphorus (TP), total suspended solids (TSS), and volatile suspended solids (VSS). Overall, agreement between the two labs was excellent with 18 out of 19 samples (95 percent) having similar results.

Comparison pairs for each constituent were plotted for 2015 samples, as well as for 2009-2014 samples. Censored pairs or non-applicable data were not included. Trend lines and linear regression equations for the entire 2009 – 2015 dataset (excluding censored data and non-applicable data) were included in the graphs, which are presented in Appendix A (Figure A-1 through Figure A-6).

Acknowledgements

We would like to thank staff from E&S Environmental Chemistry, Inc. for collecting the data required for us to complete the 2015 inter-laboratory comparison. Also, we would like to thank everyone who provided insight and feedback during the project meetings and comments for this technical memorandum.

References

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American Public Health Association., American Water Works Association., 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. Section 1010C p1-3.

Appendix A. 2009-2015 Constituent Plots

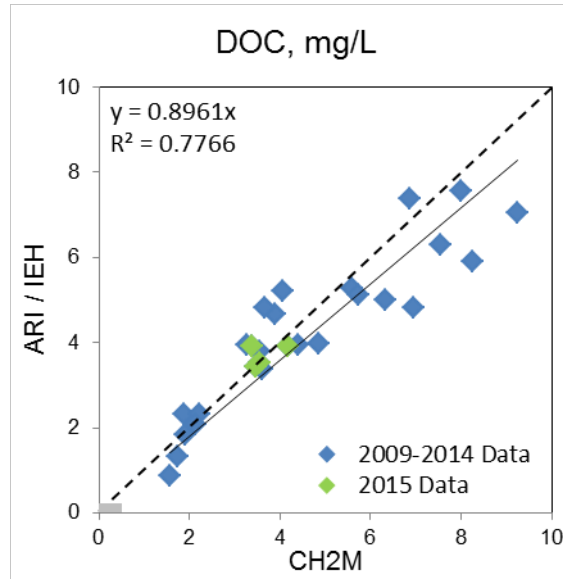


Figure A-1. KHSA inter-laboratory comparison plots from 2009-2015 for Dissolved Organic Carbon (mg/l). Censored and non-applicable data excluded from graph and linear regression formula. Dashed line represents a one to one ratio. Grey region in lower corner represents the region below the RL for the respective laboratories in 2015.

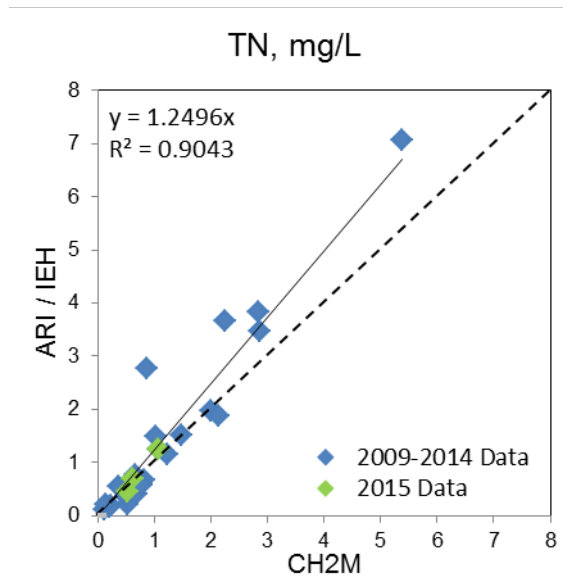


Figure A-2. KHSA inter-laboratory comparison plots from 2009-2015 for Total Nitrogen (mg/l). Censored and non-applicable data excluded from graph and linear regression formula. Dashed line represents a one to one ratio. Grey region in lower corner represents the region below the RL for the respective laboratories in 2015.

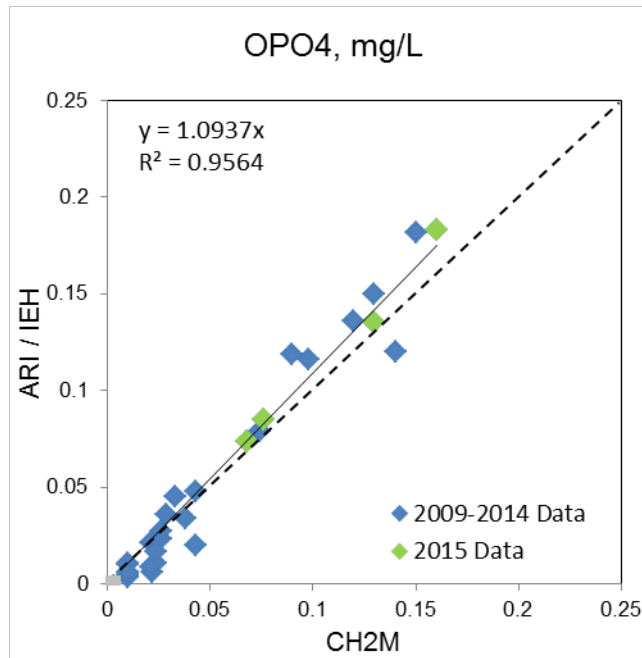


Figure A-3. KHSa inter-laboratory comparison plots from 2009-2015 for Orthophosphate (mg/l). Censored and non-applicable data excluded from graph and linear regression formula. Dashed line represents a one to one ratio. Grey region in lower corner represents the region below the RL for the respective laboratories in 2015.

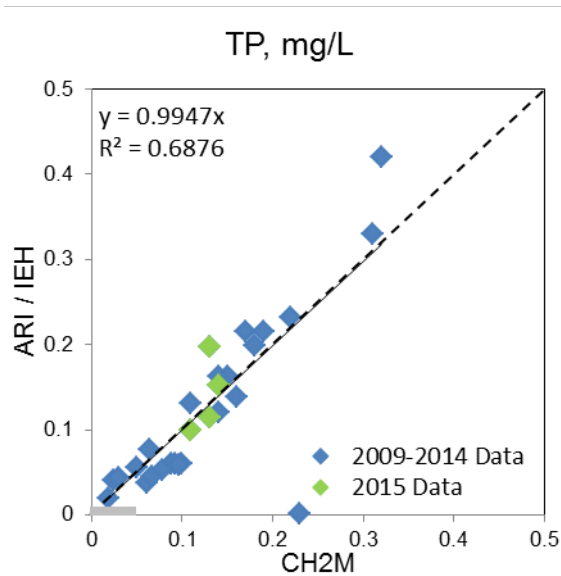


Figure A-4. KHSa inter-laboratory comparison plots from 2009-2015 for Total Phosphorus (mg/l). Censored and non-applicable data excluded from plots and linear regression formula. Dashed line represents a one to one ratio. Grey region in lower corner represents the region below the RL for the respective laboratories in 2015.

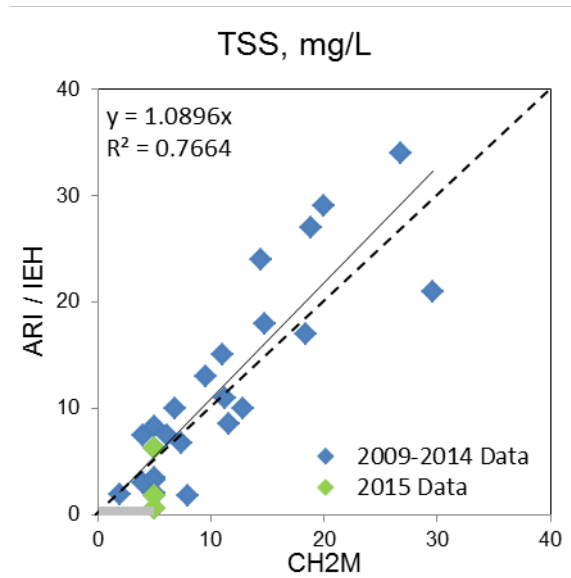


Figure A-5. KHSA inter-laboratory comparison plots from 2009-2015 for Total Suspended Solids (mg/l). Censored and non-applicable data excluded from graph and linear regression formula. Dashed line represents a one to one ratio. Grey region in lower corner represents the region below the RL for the respective laboratories in 2015.

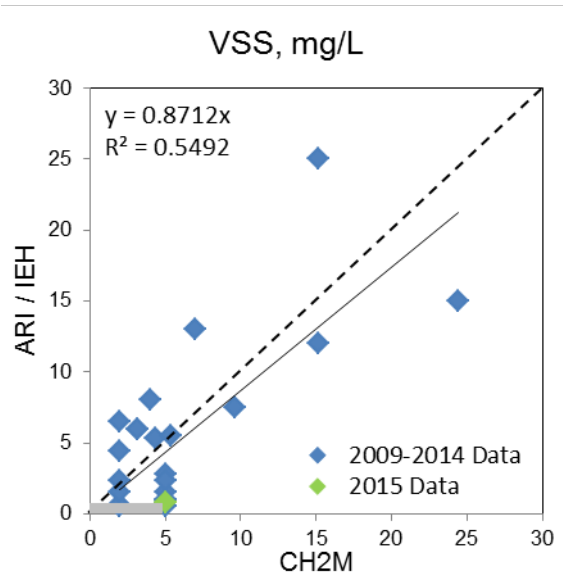


Figure A-6. KHSA inter-laboratory comparison plots from 2009-2015 for Volatile Suspended Solids (mg/l). Censored and non-applicable data excluded from graph and linear regression formula. Dashed line represents a one to one ratio. Grey region in lower corner represents the region below the RL for the respective laboratories in 2015.