



Technical Memorandum

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From: Eric Miao, Watercourse Engineering, Inc.
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Re: 2010 Klamath River KHSA Sampling Lab Cross Comparison

Introduction

Laboratory cross comparison was performed during 2010 KHSA Baseline Sampling to provide insight into laboratory performance measures at the three principal laboratories employed in the 2010 sampling season: Basic Laboratory in Redding, California, CH2MHill Applied Sciences Laboratory in Corvallis, Oregon; and Aquatic Research, Inc. in Seattle, Washington. Laboratory cross comparisons were performed by collecting a single sample volume at Link Dam on select days, splitting each volume into a triplicate, and sending a sample set to each of the three laboratories. Four cross comparison sampling days (February 16th, May 24th, July 20th, and September 21st) have been evaluated. Water quality analysis included alkalinity, carbonaceous biological oxygen demand – 5 day (CBOD5), dissolved organic carbon (DOC), ammonia, nitrate plus nitrite (NO₃+NO₂), total nitrogen (TN), total Kjeldahl nitrogen (TKN), ortho-phosphate (OPO₄)¹, total phosphorus (TP), total suspended solids (TSS), and volatile suspended solids (VSS).

Comparison

Method Comparison

The methods of analysis for the three laboratories were compared along with the associated method detection limits (MDLs). The reporting limits (RLs) were not fully compared between the three laboratories as Aquatic Research does not present reporting limits with their analysis. All methods that were used were either EPA methods or

¹ Soluble reactive phosphorus for Aquatic Research, Inc.

Standard Methods. When laboratories used the same methods for a constituent analysis, the MDL and RL (if applicable) were not necessarily the same. The analytical methods and associated limits for each constituent at each laboratory are presented in Table 1.

Table 1. Methods and limits for each laboratory

Constituent	units	Basic			CH2MHill			Aquatic Research		
		Method	MDL	RL	Method	MDL	RL	Method	MDL	RL
Alkalinity	mg/l	SM 2320B	1.5	5	E310.1	1.5	5	SM18 2320B	0.2	1
Ammonia	mg/l	EPA 350.1	0.03	0.05	E350.1	0.01	0.05	SM184500NH3H	0.006	0.01
CBOD5 ^a	mg/l	SM 5210	3	3	SM5210B	2	2	SM205210B	2	2
DOC	mg/l	SM5310C	0.3	0.5	E415.1	0.052	0.5	SM205310B	0.095	0.25
NO3+NO2	mg/l	EPA 353.2	0.01	0.05	E353.2	0.002	0.01	SM184500N03F	0.005	0.01
TN	mg/l	EPA 351.2	(n/a) ^b	0.2	SM4500-N C	0.02	0.02	SM204500NC	-	0.05
OPO4	mg/l	SM 4500P-E	0.01	0.05	E365.1	0.002	0.01	SM18 4500PF	0.001	0.001 ^c
TP	mg/l	SM 4500P-BE	0.02	0.05	E365.4	0.011	0.05	SM18 4500PF	0.002	0.002 ^c
TKN	mg/l	EPA 351.2	0.1	0.2	E351.2	0.087	0.2	EPA 351.1	-	0.2
TSS	mg/l	SM 2540D ^b	1	5	E160.2	0.95	2	SM20 2540D	0.1	0.5
VSS	mg/l	SM 2540D	1	5	E160.4	0.95	2	SM20 2540E	0.1	0.5

^a MDL and RL for CBOD5 are often equal values at production laboratories such as those used in this study.

^b There is no MDL for TN at Basic Laboratory, because TN is a calculated value at Basic Laboratory.

^c The MDL and RL values were set at the same concentration for both OPO4 and TP at Aquatic Research.

Results Comparison

Because different laboratories use different equipment, different technicians, and sometimes different methods, it is impractical to expect identical results will be produced for a triplicate sample. A comparison of the results is required to determine if the results are similar or dissimilar.

To compare the results from each laboratory, calculations were made for each pair of results: Basic and CH2MHill, Basic and Aquatic Research, and CH2MHill and Aquatic Research. The sample values used to calculate a relative percent difference (RPD) or absolute difference (AD) for each day are presented in Table 2 to Table 8. The three laboratories reported different significant figures and the data presented herein are taken directly from the laboratory reports

The RPD and AD were calculated using the following formulae:

$$\text{RPD (percent)} = |(X1 - X2)| / ((X1 + X2) / 2) * 100 \quad (1)$$

$$\text{AD (concentration)} = |X1 - X2| \quad (2)$$

Where: X1 = Value of sample from laboratory 1

X2 = Value of sample from laboratory 2

For each comparison, if the sample value was equal to or greater than five times the reporting limit, the RPD was calculated. A 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 value was less than or equal to 20 percent, the two samples were deemed to be similar and the comparison was labeled with an “OK” value in Table 3 through Table 9. If the RPD value was greater than 20 percent, the RPD value was presented within the table.

If the sample value was less than five times the reporting limit, the AD was calculated (USBR, 2009) and an AD criteria of the reporting limit was used to determine if two samples were similar (AD less than or equal to the reporting limit) or dissimilar (AD greater than the reporting limit). If the two laboratories used different reporting limits the larger of the two was used as the criteria. If the AD was less than the reporting limit for the sample comparison, the comparison was labeled with an “OK” value in Table 3 through Table 9. If the AD was greater than the reporting limit for the sample comparison, the AD value was presented, along with a footnote of the laboratory reporting limit used. This process is illustrated in Figure 1.

Some of the reported results from the laboratories were presented as non-detects (ND), censored data (i.e., “less than value”), or were less than the RL (i.e., not censored). All of these reported results were replaced with the RL for calculation of the RPD.

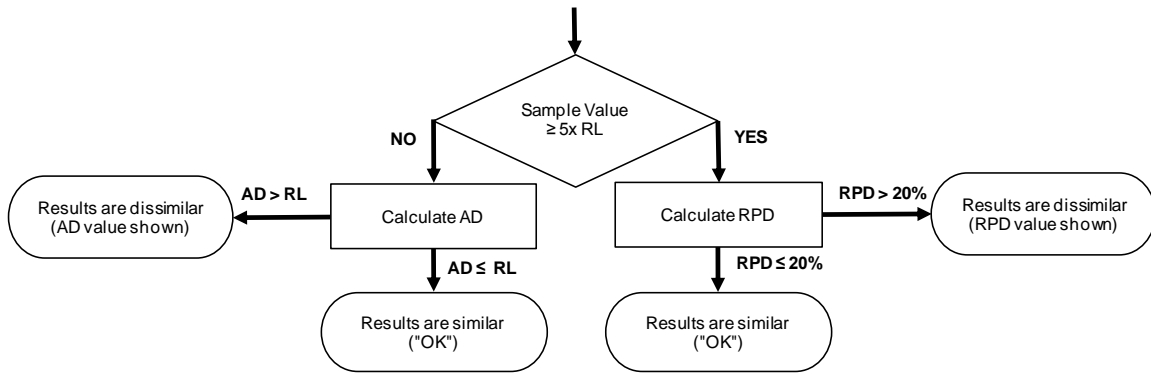


Figure 1. Flow diagram displaying comparison process. RPD = relative percent difference. RL = reporting limit.

Table 2. Result values used to determine RPD or AD for February 16, 2010.

	Laboratory Sample ID:	Basic 2010KHSA-001	CH2MHill Applied Sciences 2010KHSA-005	Aquatic Research, Inc. 2010KHSA-004
	Unit			
Alkalinity	mg/l	50	46	49.5
Ammonia	mg/l	0.38	0.37	0.324
CBOD5	mg/l	3 ^a	3.02	2 ^b
DOC	mg/l	3.6	3.56	3.8
NO3+NO2	mg/l	0.34	0.3	0.279
TN	mg/l	1.4	1.48	1.51
OPO4	mg/l	0.01 ^c	0.01 ^d	0.005
TP	mg/l	0.07	0.078	0.053
TKN	mg/l	1.1	1.17	1.23
TSS	mg/l	17	14.4	24
VSS	mg/l	5 ^e	2 ^f	6.5

^a Basic Laboratory reported result for CBOD5 was "ND" and was replaced with the laboratory RL.

^b Aquatic Research reported result for CBOD5 was "ND" and was replaced with the laboratory RL.

^c Basic Laboratory reported result for OPO4 was "ND" and was replaced with the laboratory RL.

^d CH2MHill reported result for OPO4 was 0.0082 mg/l and was replaced with the laboratory RL.

^e Basic Laboratory reported result for VSS was 3 mg/L and was replaced with the laboratory RL.

^f CH2MHill reported result for VSS was 0.8 mg/l and was replaced with the laboratory RL.

Table 3. Comparison of result pairs for February 16, 2010.

Constituent	Basic versus CH2MHill Applied Sciences	Basic versus Aquatic Research, Inc.	CH2MHill Applied Sciences versus Aquatic Research, Inc.
Alkalinity	OK	OK	OK
Ammonia	OK	OK	OK
CBOD5	OK	OK	OK
DOC	OK	OK	OK
NO3+NO2	OK	OK	OK
TN	OK	OK	OK
OPO4	OK	OK	OK
TP	OK	OK	OK
TKN	OK	OK	OK
TSS	OK	7.0 mg/l ^a	50.0%
VSS	OK	OK	4.5 mg/l ^b

^a Basic Laboratory TSS reporting limit was 5.0 mg/l.

^b CH2MHill VSS reporting limit was 2.0 mg/l.

Table 4. Result values used to determine RPD or AD for May 24, 2010.

	Laboratory Sample ID	Basic 2010KHSA-025	CH2MHill Applied Sciences 2010KHSA-028	Aquatic Research, Inc. 2010KHSA-029
	Units			
Alkalinity	mg/l	53	50.1	56.1
Ammonia	mg/l	0.13	0.05 ^a	0.01 ^b
CBOD5 ^c	mg/l	-	-	-
DOC	mg/l	5.2	4.86	3.99
NO3+NO2	mg/l	0.05 ^d	0.01 ^e	0.011
TN	mg/l	0.77	0.67	0.771
OPO4	mg/l	0.01 ^f	0.01 ^g	0.011
TP	mg/l	0.07	0.064	0.076
TKN	mg/l	0.7	0.75	1.03
TSS	mg/l	20	20	29
VSS	mg/l	5 ^h	4	8

^a CH2M reported result for ammonia was "ND" and was replaced with the laboratory RL.

^b Aquatic Research reported result for ammonia was "ND" and was replaced with the laboratory RL.

^c No CBOD collected for laboratory cross comparison on May 24, 2010.

^d Basic Laboratory reported result for NO3+NO2 was 0.02 mg/l and was replaced with the laboratory RL.

^e CH2MHill reported result for NO3+NO2 was 0.0078 mg/l and was replaced with the laboratory RL.

^f Basic Laboratory reported result for OPO4 was "ND" mg/l and was replaced with the laboratory RL.

^g CH2MHill reported result for OPO4 was 0.0044 mg/l and was replaced with the laboratory RL.

^h Basic laboratory reported result for VSS was 3 mg/L and was replaced with the laboratory RL.

Table 5. Comparison of result pairs for May 24, 2010.

Constituent	Basic versus CH2MHill Applied Sciences	Basic versus Aquatic Research, Inc.	CH2MHill Applied Sciences versus Aquatic Research, Inc.
Alkalinity	OK	OK	OK
Ammonia	0.08 mg/l^a	0.12 mg/l^a	OK
CBOD5	-	-	-
DOC	OK	26.3%	OK
NO3+NO2	OK	OK	OK
TN	OK	OK	OK
OPO4	OK	OK	OK
TP	OK	OK	OK
TKN	OK	0.33 mg/l^b	0.28 mg/l^c
TSS	OK	9.0 mg/l^d	36.7%
VSS	OK	OK	4.0 mg/l^e

^a Basic Laboratory ammonia RL was 0.05 mg/l.

^b Basic Laboratory TKN RL was 0.2 mg/l.

^c CH2MHill TKN RL was 0.2 mg/l.

^d Basic Laboratory TSS RL was 5.0 mg/l.

^e CH2MHill VSS RL was 2.0 mg/l.

Table 6. Result values used to determine RPD or AD for July 20th, 2010.

	Laboratory Sample ID	Basic 2010KHSA-025	CH2MHill Applied Sciences 2010KHSA-028	Aquatic Research, Inc. 2010KHSA-029
	Units			
Alkalinity	mg/l	57	51.4	63.6
Ammonia	mg/l	0.15	0.05 ^a	0.038
CBOD5	mg/l	13	13.2	15.3
DOC	mg/l	7	5.72	5.13
NO3+NO2	mg/l	0.05 ^b	0.012	0.01
TN	mg/l	3	2.83	3.83
OPO4	mg/l	0.02	0.021	0.021
TP	mg/l	0.17	0.17	0.215
TKN	mg/l	3	4.05	3.71
TSS	mg/l	13	11	15
VSS	mg/l	8	7	13

^a CH2MHill reported result for ammonia was "ND" and was replaced with the laboratory RL.

^b Basic Laboratory reported result for NO3+NO2 was 0.01 mg/L and was replaced with the laboratory RL.

Table 7. Comparison of result pairs for July 20th, 2010.

Constituent	Basic versus CH2MHill Applied Sciences	Basic versus Aquatic Research, Inc.	CH2MHill Applied Sciences versus Aquatic Research, Inc.
Alkalinity	21.2%	OK	OK
Ammonia	0.10 mg/l^a	0.11 mg/l^a	OK
CBOD5	OK	OK	OK
DOC	20.1%	30.8%	OK
NO3+NO2	OK	OK	OK
TN	OK	24.3%	30.0%
OPO4	OK	OK	OK
TP	OK	OK	OK
TKN	29.8%	21.2%	OK
TSS	OK	OK	30.8%
VSS	OK	OK	60.0%

^a Basic Laboratory ammonia reporting limit was 0.05 mg/l.

Table 8. Result values used to determine RPD or AD for September 21st, 2010.

	Laboratory Sample ID	Basic 2010KHSA-025	CH2MHill Applied Sciences 2010KHSA-028	Aquatic Research, Inc. 2010KHSA-029
	Units			
Alkalinity	mg/l	58	51	65.9
Ammonia	mg/l	0.19	0.05 ^a	0.02
CBOD5	mg/l	11	11.3	11.7
DOC	mg/l	9	8.26	5.89
NO3+NO2	mg/l	0.05 ^b	0.021	0.01 ^c
TN	mg/l	2.7	2.87	3.47
OPO4	mg/l	0.03	0.026	0.023
TP	mg/l	0.21	0.19	0.215
TKN	mg/l	2.7	2.56	3.52
TSS	mg/l	8	18.4	17
VSS	mg/l	6	15.2	12

^a CH2M reported result for ammonia was 0.04 mg/l and was replaced with the laboratory RL.

^b Basic Laboratory reported result for NO3+NO2 was 0.02 mg/L and was replaced with the laboratory RL.

^c Aquatic Research reported result for NO3+NO2 was "ND" and was replaced with the laboratory RL.

Table 9. Comparison of result pairs for September 21st, 2010.

Constituent	Basic versus CH2MHill Applied Sciences	Basic versus Aquatic Research, Inc.	CH2MHill Applied Sciences versus Aquatic Research, Inc.
Alkalinity	OK	OK	25.5%
Ammonia	0.14 mg/l^a	0.17 mg/l^a	OK
CBOD5	OK	OK	OK
DOC	OK	41.7%	33.5%
NO3+NO2	OK	OK	.011 mg/l^b
TN	OK	25.0%	OK
OPO4	OK	OK	OK
TP	OK	OK	OK
TKN	OK	26.4%	31.6%
TSS	10.4 mg/l^c	9.0 mg/l^c	OK
VSS	9.2 mg/l^d	6.0 mg/l^d	23.5%

^a Basic Laboratory ammonia RL was 0.05 mg/l.

^b CH2MHill NO3+NO2 RL was 0.1 mg/l.

^c Basic Laboratory TSS RL was 5.0 mg/l.

^d Basic Laboratory VSS RL was 5.0 mg/l.

Comparison Summary

A total of 96 samples were collected for laboratory cross comparison in 2010. Comparisons were completed for alkalinity, CBOD, DOC, ammonia, NO₃+NO₂, TKN, TN, OPO₄, TP, TSS, and VSS. Total number of comparisons per constituent are shown in Table 10.

There were 93 similar pairs of results and 36 dissimilar pair of results in 2010. Of those 36 dissimilar pairs, 7 dissimilar pairs were from comparing results from Basic and CH2MHill, 15 dissimilar pairs were from comparing results from Basic and Aquatic Research, and 14 dissimilar pairs were from comparing CH2MHill and Aquatic Research. Of the 36 dissimilar pairs, 13 of the pairs were total suspended solids (TSS) and volatile suspended solids (VSS), 16 of the pairs were related to nitrogen (i.e., ammonia, NO₃+NO₂, TN, TKN). Additional details of the laboratory comparison are presented in Table 10 and Figure 2.

Table 10. Number of total, similar and dissimilar pairs of results per constituent in 2010.

	Alkalinity	CBOD5	DOC	Ammonia	NO3+NO2	TN	TKN	OPO4	TP	TSS	VSS	Totals
Total Number of Comparisons	12	9	12	12	12	12	12	12	12	12	12	129
Total Number of similar pairs of results	10	9	7	6	11	9	6	12	12	5	6	93
Total number of dissimilar pairs of results	2	0	5	6	1	3	6	0	0	7	6	36
<i>Basic and CH2MHill</i>	0	0	1	3	0	0	1	0	0	1	1	7
<i>Basic and Aquatic Research</i>	0	0	3	3	0	2	3	0	0	3	1	15
<i>CH2MHill and Aquatic Research</i>	2	0	1	0	1	1	2	0	0	3	4	14

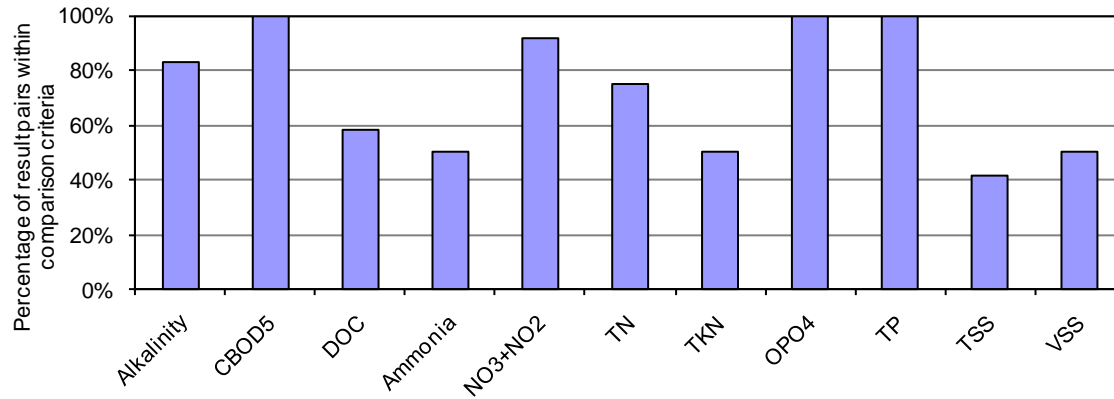


Figure 2. Percentage of result pairs within comparison criteria from February 16, 2010 through September 21, 2010

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.