

Technical Memorandum

Date: April 2, 2009

| To: | Rick Carlson, U.S. Bureau of Reclamation |
|-------|---|
| | Susan Corum, Karuk Tribe |
| | Clayton Creager, North Coast Regional Water Quality Control Board |
| | Rich Fadness, North Coast Regional Water Quality Control Board |
| | Ken Fetcho, Yurok Tribe |
| | Sue Keydel, U.S. Environmental Protection Agency, Region 9 |
| | Steve Kirk, Oregon Department of Environmental Quality |
| | Linda Prendergast, PacifiCorp |
| | Chantell Royer, Humboldt State University |
| From: | Mike Deas, Watercourse Engineering, Inc. |
| | Jennifer Vaughn, Watercourse Engineering, Inc. |
| Re: | 2009 Klamath River AIP Sampling Lab Cross Comparison (DRAFT) |

Abstract

As there are several sampling crews using different analytical laboratories participating in the monitoring of water quality in the Klamath River, a comparison of laboratory results was undertaken to determine the similarity of the results of the different laboratories. Five sets of triplicate samples were collected by Reclamation staff at Link Dam from June 10 through December 8, 2009 and sent to three different laboratories to be analyzed for the same constituents. The relative percent difference between each laboratory was calculated for each result pair in a triplicate set (the first laboratory compared with the second, the first laboratory compared with the third, and the second laboratory compared with the third), resulting in 231 result pairs for all seven sample sets. The comparison of the result pairs indicated that some constituents were similar at all labs for all seven sampling sets (such as nitrate + nitrite), while other constituents had dissimilar results when the laboratories were compared (such as total nitrogen). A 20 percent relative percent difference (RPD) criteria was applied as a threshold to ascertain differences – this was an arbitrary threshold only for purposes of general comparison. Based on the 20 percent criteria, the total amount of similar result pairs for all seven sampling sets was 168 (73 percent of total result pairs). Of the 63 dissimilar result pairs, 22 percent were from comparisons between Basic Laboratory and CH2MHill Analytical Services Lab, 27 percent were from comparisons between Basic Laboratory and Aquatic Research and 51 percent were from comparisons between CH2MHill and Aquatic Research.

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Introduction

There are multiple stakeholders along the Klamath River, many of whom use different laboratories to analyze the water samples collected for Klamath River water quality monitoring. Laboratory cross comparison was performed during 2009 to provide insight into laboratory performance measures at the three principal laboratories employed in the 2009 sampling season: Basic Laboratory in Redding, California, CH2MHill Applied Sciences Laboratory in Corvallis, Oregon; and Aquatic Research, Inc. in Seattle, Washington. The laboratory cross comparisons were performed by collecting a single sample volume at Link Dam, splitting each volume into a triplicate, and sending a sample set to each of the three laboratories. This was completed throughout the 2009 sampling season. Water quality analysis included alkalinity, ammonia, carbonaceous biological oxygen demand – 5 day (CBOD5), dissolved organic carbon (DOC), nitrate plus nitrite (NO3+NO2), total nitrogen (TN), ortho-phosphate (OPO4) for Basic Laboratory and CH2MHill, or soluble reactive phosphate (SRP) for Aquatic Research, Inc., total phosphorus (TP), total Kjeldahl nitrogen (TKN), 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 Standard Methods. The analytical methods and associated limits for each constituent at each laboratory are presented in Table 1.

The topic of precision (measure of the degree of agreement among replicate analysis of a sample, often expressed as a standard deviation) is an important element of this discussion. This holds for both within lab and between lab comparisons for the same method and where different methods for the same constituent are applied. Standard Methods (2005) and EPA methods identify precision for all methods, typically for a range of constituent concentrations. Not only does precision change among methods, but also laboratory equipment and personnel can further modify precision of methods. A 20 percent relative percent difference (RPD) criteria was applied as a threshold to ascertain differences – this was an arbitrary threshold only for purposes of general comparison and may be overly stringent given the inherent variability within labs, among labs, and among methods. Nonetheless, this approach provides a mechanism to compare laboratories across a wide range of parameters.

| | Basic | | С | CH2MHill | | Aquatic Research | | | | |
|-------------|-------|-------------|--------|----------|------------|------------------|-------|--------------|-------|----|
| Constituent | units | Method | MDL | RL | Method | MDL | RL | Method | MDL | RL |
| Alkalinity | mg/l | SM 2320B | 1 | 5 | E310.1 | 0.55 | 5.00 | SM18 2320B | 1 | - |
| Ammonia | mg/l | EPA 350.1 | 0.02 | 0.05 | E350.1 | 0.0087 | 0.050 | SM184500NH3H | 0.01 | - |
| CBOD5 | mg/l | SM 5210 | 3 | 3 | SM5210B | 2.00 | 2.00 | SM205210B | 2 | - |
| DOC | mg/l | SM5310C | 0.3 | 0.5 | E415.1 | 0.052 | 0.50 | SM205310B | 0.25 | - |
| NO3+NO2 | mg/l | EPA 353.2 | 0.01 | 0.05 | E353.2 | 0.0017 | 0.010 | SM184500N03F | 0.01 | - |
| TN | mg/l | EPA 351.2 | (calc) | 0.2 | SM4500-N C | 0.020 | 0.020 | SM204500NC | 0.05 | - |
| OPO4 | mg/l | SM 4500P-E | 0.01 | 0.05 | E365.1 | 0.0018 | 0.010 | SM18 4500PF | 0.001 | - |
| TP | mg/l | SM 4500P-BE | 0.02 | 0.05 | E365.4 | 0.0078 | 0.050 | SM18 4500PF | 0.002 | - |
| TKN | mg/l | EPA 351.2 | 0.1 | 0.2 | E351.2 | 0.038 | 0.20 | EPA 351.1 | 0.2 | - |
| TSS | mg/l | SM 2540D | 2 (1) | 6 (5) | E160.2 | 0.87 | 2.00 | SM20 2540D | 0.5 | - |
| VSS | mg/l | SM 2540D | 2 (1) | 6 (5) | E160.4 | 0.87 | 2.00 | SM20 2540E | 0.5 | - |

Table 1. Methods and Limits for each laboratory

Notes:

- Only CBOD was analyzed with the same method at all three laboratories, but it had a higher MDL at Basic Laboratories than at the other two laboratories.

- When laboratories used the same method for a constituent analysis, the MDL and RL (if applicable) were not necessarily the same.

- There is not an MDL for TN at Basic, because it is a calculated value.

- The MDL and RL for TSS and VSS were lowered by collecting a larger water sample. The higher values apply to the June 10 and July 14 sampling collections. The lower values apply to all other sample collections.

Results Comparison

To compare the results from each laboratory, the relative percent difference was calculated for each pair of results: Basic and CH2MHill, Basic and Aquatic Research, and CH2MHill and Aquatic Research. The values of the three samples used to determine the relative percent difference (RPD) and criteria values for each day are presented in Table 2 through Table 10. All comparisons are made based on samples collected only at Link Dam.

The RPD was calculated using the following formula:

RPD = ((X1 - X2)/((X1 + X2)/2))Where: X1 = Value of sample from laboratory 1 X2 = Value of sample from laboratory 2

The criteria used to determine if the paired samples were similar was an RPD of 20 percent or less for values greater than five times the reporting limit. For values less than or equal to five times the reporting limit, the RPD criteria was plus or minus the reporting limit (USBR, 2009). If the paired samples had an RPD greater than 20percent (or a difference greater than plus or minus the reporting limit), the samples were considered dissimilar.

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 (except for data from Aquatic Research, which was replaced with the appropriate MDL). When comparing Basic with either CH2MHill or Aquatic Research, Basic reporting limits were used as necessary to determine the RPD criteria. When CH2MHill was compared to Aquatic Research, CH2MHill reporting limits were used. The compliance with the RPD criteria for the pairs of samples for each date is presented below in Table 3 through Table 11. Where RPD was greater than 20 percent, the actual percent was placed in the tables to identify the actual difference.

Under certain circumstances where concentrations were low and/or reporting limits high, calculation of the RPD was not feasible. For example, when assessing similarity/dissimilarity for the June 10, 2009 comparisons for TSS, the RPD was not calculated. As shown in Table 2, the TSS values from Basic, CH2MHill Applied Sciences and Aquatic Research were 6.0 mg/l, 12.8 mg/l, and 10.0 mg/l, respectively. When comparing the results from Basic and CH2MHill, Basic's reporting limit of 6.0 mg/l was used. Neither the Basic nor the CH2MHill Applied Sciences results were greater than five times the reporting limit, therefore the RPD calculation could not be used. Instead, the absolute difference between the two values was determined to be 6.8 mg/l, which was higher than Basic's reporting limit of 6.0 mg/l. As such, this comparison did not meet the assumed criteria and results were not considered similar.

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Similarly, when comparing the results from Basic and Aquatic Research, Basic's reporting limit of 6.0 mg/l was used. Neither the Basic nor the Aquatic Research results were greater than five times the reporting limit, therefore the RPD calculations could not be used. Instead the absolute difference between the two values was determined to be 4.0 mg/l, which was less than the Basic reporting limit of 6.0 mg/l. This comparison did meet the assumed criteria and were considered similar.

When comparing the results from CH2MHill Applied Sciences and Aquatic Research, CH2MHill's reporting limit of 2.0 mg/l was used. The TSS value from CH2MHill was greater than five times the reporting limit, which allowed for the calculation of the RPD. The resulting RPD was 24.5 percent, which was greater than 20 percent. Therefore, this comparison did not meet the assumed criteria and were not considered similar.

| | Laboratory | Basic | CH2MHill Applied Sciences | Aquatic Research, Inc. |
|------------|-------------------|-------------------|---------------------------|------------------------|
| | Sample ID / units | 2009AIP-004 | 2009AIP-006 | 2009AIP-007 |
| Alkalinity | mg/l | 54 | 51.6 | 58.3 |
| Ammonia | mg/l | 0.08 | 0.05 ^d | 0.010 |
| CBOD5 | mg/l | 7 | 6.85 | 7.32 |
| DOC | mg/l | 5.7 | 5.59 | 5.28 |
| NO3+NO2 | mg/l | 0.05 ^a | 0.010 ^e | 0.01 ^g |
| TN | mg/l | 1.36 | 1.23 | 1.16 |
| OPO4 | mg/l | 0.05 ^b | 0.010 ^f | 0.0031 |
| ТР | mg/l | 0.05 | 0.088 | 0.06 |
| TKN | mg/l | 1.3 | 1.72 | 1.33 |
| TSS | mg/l | 6 | 12.8 | 10 |
| VSS | mg/l | 6 ^c | 9.6 | 7.5 |

^a Basic Laboratory reported results for NO3+NO2 was 0.03 mg/l and was replaced with the appropriate RL. .

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

 $^\circ\textsc{Basic}$ Laboratory reported result for VSS was 3.0 mg/l and was replaced with the appropriate RL. .

^d CH2MHill reported result for ammonia was -0.056 mg/l and was replaced with the appropriate RL. .

^e CH2MHill reported result for NO3+NO2 was -0.0044 mg/l and was replaced with the appropriate RL.

^f CH2MHill reported result for OPO4 was 0.004 mg/l and was replaced with the appropriate RL.

^g Aquatic Research reported result for NO3+NO2 was "<0.010 mg/l" and was replaced with the appropriate MDL.

| Constituent | Basic versus CH2MHill Applied Sciences | Basic versus Aquatic Research, Inc. | CH2MHill Applied Sciences versus Aquatic Research, Inc. |
|-------------|---|--|--|
| Alkalinity | OK | OK | OK |
| Ammonia | OK | 0.07 mg/l ^ª | ОК |
| CBOD5 | OK | OK | ОК |
| DOC | OK | OK | ОК |
| NO3+NO2 | OK | OK | ОК |
| TN | OK | OK | ОК |
| OPO4 | OK | OK | ОК |
| TP | OK | OK | ОК |
| TKN | 27.8% | OK | 25.4% |
| TSS | 6.8 mg/l ^b | OK | 24.5% |
| VSS | ОК | ОК | 2.1 mg/l ^c |

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

^b Basic TSS reporting limit was 6.0 mg/l.

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

| | Laboratory | Basic | CH2MHill Applied Sciences | Aquatic Research, Inc. |
|------------|-------------------|-------------------|---------------------------|------------------------|
| | Sample ID / units | 2009AIP-018 | 2009AIP-020 | 2009AIP-021 |
| Alkalinity | mg/l | 53 | 47.3 | 58.1 |
| Ammonia | mg/l | 0.11 | 0.05° | 0.072 |
| CBOD5 | mg/l | 10 | 7.04 | 8.14 |
| DOC | mg/l | 7.9 | 6.86 | 7.39 |
| NO3+NO2 | mg/l | 0.05ª | 0.019 | 0.015 |
| TN | mg/l | 1.86 | 0.86 | 2.78 |
| OPO4 | mg/l | 0.05 ^b | 0.043 | 0.020 |
| TP | mg/l | 0.12 | 0.14 | 0.12 |
| TKN | mg/l | 1.8 | 2.08 | 2.89 |
| TSS | mg/l | 10 | 4 | 7.5 |
| VSS | mg/l | 7 | 3.2 | 6 |

^a Basic Laboratory reported results for NO3+NO2 was 0.02 mg/l and was replaced with the appropriate RL value.

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

 $^{\circ}$ CH2MHill reported result for ammonia was -0.12 mg/l and was replaced with the appropriate RL.

| Constituent | Basic versus CH2MHill Applied Sciences | Basic versus Aquatic Research, Inc. | CH2MHill Applied Sciences versus Aquatic Research, Inc. |
|-------------|---|--|--|
| Alkalinity | OK | ОК | 20.5% |
| Ammonia | 0.06 mg/l ^a | OK | OK |
| CBOD5 | OK | OK | ОК |
| DOC | OK | OK | ОК |
| NO3+NO2 | OK | OK | ОК |
| TN | 73.5% | 39.7% | 105.6% |
| OPO4 | OK | OK | 0.03 mg/l ^b |
| TP | OK | OK | OK |
| TKN | OK | 46.4% | 32.5% |
| TSS | OK | OK | 3.5 mg/l ^c |
| VSS | OK | OK | 2.8 mg/l ^d |

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

^b CH2MHill OPO4 reporting limit was 0.01 mg/l.

^c CH2MHill TSS reporting limit was 2.0 mg/l.

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

| | Laboratory | Basic | CH2MHill Applied Sciences | Aquatic Research, Inc. |
|------------|-------------------|-------------|---------------------------|------------------------|
| | Sample ID / units | 2009AIP-030 | 2009AIP-033 | 2009AIP-034 |
| Alkalinity | mg/l | 58 | 60 | 72 |
| Ammonia | mg/l | 0.16 | 0.05 ^b | 0.028 |
| CBOD5 | mg/l | 23 | 34.2 | 32.5 |
| DOC | mg/l | 7.9 | 8 | 7.55 |
| NO3+NO2 | mg/l | 0.05 | 0.012 | 0.012 |
| TN | mg/l | 5.08 | 5.37 | 7.06 |
| OPO4 | mg/l | 0.05ª | 0.033 | 0.045 |
| TP | mg/l | 0.37 | 0.32 | 0.42 |
| TKN | mg/l | 5.1 | 5.45 | 7.02 |
| TSS | mg/l | 24 | 18.8 | 27 |
| VSS | mg/l | 18 | 15.2 | 25 |

Table 6. Result values used to determine RPD and criteria values, August 11, 2009.

^a Basic Laboratory reported result for OPO4 was 0.02 mg/l and was replaced with the appropriate RL value.

^b CH2MHill reported result for ammonia was 0.013 mg/l and was replaced with the appropriate RL.

| Constituent | Basic versus CH2MHill Applied Sciences | Basic versus Aquatic Research, Inc. | CH2MHill Applied Sciences versus Aquatic Research, Inc. |
|-------------|---|--|--|
| Alkalinity | OK | 21.5% | ОК |
| Ammonia | 0.11 mg/l ^a | 0.13 mg/l ^ª | ОК |
| CBOD5 | 39.2% | 34.2% | ОК |
| DOC | OK | OK | ОК |
| NO3+NO2 | OK | OK | ОК |
| TN | OK | 32.6% | 27.2% |
| OPO4 | OK | OK | 0.012 mg/l ^b |
| TP | OK | OK | 26.1% |
| TKN | OK | 31.7% | 25.2% |
| TSS | OK | OK | 35.8% |
| VSS | OK | 7.0 mg/l ^c | 48.8% |

Table 7. Comparison of similarity criteria compliance (non-compliance noted) for August 11, 2009.

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

^b CH2MHill OPO4 reporting limit was 0.01 mg/l.

^c Basic VSS reporting limit was 6.0 mg/l.

| | Laboratory | Basic | CH2MHill Applied Sciences | Aquatic Research, Inc. |
|------------|-------------------|-------------------|---------------------------|------------------------|
| | Sample ID / units | 2009AIP-043 | 2009AIP-047 | 2009AIP-046 |
| Alkalinity | mg/l | 54 | 53.9 | 61.2 |
| Ammonia | mg/l | 0.22 | 0.05 ^b | 0.053 |
| CBOD5 | mg/l | 17 | 11.2 | 18.7 |
| DOC | mg/l | 9.4 | 9.26 | 7.06 |
| NO3+NO2 | mg/l | 0.05 ^ª | 0.01 [°] | 0.010 ^d |
| TN | mg/l | 3.98 | 2.24 | 3.66 |
| OPO4 | mg/l | 0.06 | 0.074 | 0.079 |
| TP | mg/l | 0.3 | 0.31 | 0.33 |
| TKN | mg/l | 4 | 3.37 | 3.48 |
| TSS | mg/l | 21 | 29.6 | 21 |
| VSS | mg/l | 13 | 24.4 | 15 |

^a Basic Laboratory reported result for NO3+NO2 was ND and was replaced with the appropriate RL value.

^b CH2MHill reported result for ammonia was -0.0079 mg/l and was replaced with the appropriate RL value.

^c CH2MHill reported result for NO3+NO2 was 0.0063 mg/l and was replaced with the appropriate RL value.

^d Aquatic Research reported result for NO3+NO2 was <0.010 mg/l and was replaced with the appropriate RL value.

| Constituent | Basic versus CH2MHill Applied Sciences | Basic versus Aquatic Research, Inc. | CH2MHill Applied Sciences versus Aquatic Research, Inc. |
|-------------|---|--|--|
| Alkalinity | OK | OK | ОК |
| Ammonia | 0.17 mg/l ^a | 0.17 mg/l ^a | ОК |
| CBOD5 | OK | OK | 50.2% |
| DOC | OK | 28.4% | 27.0% |
| NO3+NO2 | OK | OK | ОК |
| TN | 56.0% | OK | 48.1% |
| OPO4 | OK | OK | ОК |
| TP | OK | OK | ОК |
| TKN | OK | OK | ОК |
| TSS | 8.6 mg/l ^b | OK | 34.0% |
| VSS | 11.4 mg/l ^c | ОК | 47.7% |

| Table 9. Comparison of similarity | v criteria compl | liance (non-com | oliance noted) for Se | eptember 8, 2009. |
|-----------------------------------|------------------|-----------------|-----------------------|-------------------|
| | | | | |

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

^b Basic TSS reporting limit was 6.0 mg/l.

^c Basic VSS reporting limit was 6.0 mg/l.

| | Laboratory | Basic | CH2MHill Applied Sciences | Aquatic Research, Inc. |
|------------|-------------------|----------------|---------------------------|------------------------|
| | Sample ID / units | 2009AIP-060 | 2009AIP-063 | 2009AIP-064 |
| Alkalinity | mg/l | 61 | 58 | 63.1 |
| Ammonia | mg/l | 0.4 | 0.39 | 0.340 |
| CBOD5 | mg/l | 3 | 12.9 | 3.32 |
| DOC | mg/l | 7.9 | 7.55 | 6.31 |
| NO3+NO2 | mg/l | 0.33 | 0.28 | 0.300 |
| TN | mg/l | 2.02 | 1.02 | 1.49 |
| OPO4 | mg/l | 0.05ª | 0.01 ^d | 0.010 |
| TP | mg/l | 0.11 | 0.23 | 0.10 ^e |
| TKN | mg/l | 1.7 | 1.74 | 1.49 |
| TSS | mg/l | 6 ^b | 6.8 | 10 |
| VSS | mg/l | 6 ^c | 4.4 | 5.3 |

| Table 10. Result values used to determine RPD and criteria values, O | October 20, 2009. |
|--|-------------------|
|--|-------------------|

^a Basic Laboratory reported result for OPO4 was 0.01 mg/l and was replaced with the appropriate RL value for RPD determination.

^b Basic Laboratory reported result for TSS was 5 mg/l and was replaced with the appropriate RL value for RPD determination.

^c Basic Laboratory reported result for VSS was 2 mg/l and was replaced with the appropriate RL value for RPD determination.

^d CH2MHill reported result for OPO4 was 0.008 mg/l and was replaced with the appropriate RL value for RPD determination.

^e Aquatic Research reported result for TP was 0.096 mg/l and was replaced with the appropriate RL value for RPD determination.

| Constituent | Basic versus CH2MHill Applied Sciences | Basic versus Aquatic Research, Inc. | CH2MHill Applied Sciences versus Aquatic Research, Inc. |
|-------------|---|--|--|
| Alkalinity | OK | OK | ОК |
| Ammonia | OK | OK | OK |
| CBOD5 | 9.9 mg/l ^a | OK | 9.6 mg/l ^b |
| DOC | OK | 22.4% | ОК |
| NO3+NO2 | OK | OK | OK |
| TN | 65.8% | 30.2% | 37.5% |
| OPO4 | OK | OK | OK |
| TP | 0.12 mg/l ^c | OK | 0.13 mg/l ^d |
| TKN | OK | OK | ОК |
| TSS | OK | OK | 3.2 mg/l ^e |
| VSS | ОК | OK | ОК |

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| Tabla 11 | Comparison | of similarity criter | ia compliance (por | n-compliance noted) fo | r October 20, 2000 |
|-----------|------------|----------------------|--------------------|------------------------------|---------------------|
| Table 11. | Comparison | of similarity criter | іа сопірнансе (пог | - сошрнансе поted) то | r October 20. 2009. |

^a Basic CBOD5 reporting limit was 3.0 mg/l.

^b CH2MHill CBOD5 reporting limit was 2.0 mg/l.

^c Basic TP reporting limit was 0.05 mg/l.

^d CH2MHill TP reporting limit was 0.05 mg/l.

^e CH2MHill TSS reporting limit was 2.0 mg/l.

| | Laboratory | Basic | CH2MHill Applied Sciences | Aquatic Research, Inc. |
|------------|-------------------|-------------------|---------------------------|------------------------|
| | Sample ID / units | 2009AIP-068 | 2009AIP-072 | 2009AIP-071 |
| Alkalinity | mg/l | 58 | 58 | 64.2 |
| Ammonia | mg/l | 0.71 | 0.72 | 0.837 |
| CBOD5 | mg/l | 3ª | 3.23 | 2.4 |
| DOC | mg/l | 6.3 | 6.94 | 4.82 |
| NO3+NO2 | mg/l | 0.36 | 0.34 | 0.319 |
| TN | mg/l | 2.11 | 2 | 1.97 |
| OPO4 | mg/l | 0.05 ^b | 0.024 | 0.011 |
| TP | mg/l | 0.08 | 0.1 | 0.06 |
| TKN | mg/l | 1.7 | 1.98 | 2.01 |
| TSS | mg/l | 11 | 9.6 | 13 |
| VSS | mg/l | 6 ^c | 2 | 4.4 |

Table 12. Result values used to determine RPD and criteria values, November 10, 2009.

^a Basic Laboratory reported result for CBOD5 was ND and was replaced with the appropriate RL value for RPD determination.

^b Basic Laboratory reported result for OPO4 was ND and was replaced with the appropriate RL value for RPD determination.

^c Basic Laboratory reported result for VSS was 3 mg/l and was replaced with the appropriate RL value for RPD determination.

| Table 13. Comparison of similarity criteria compliance (non-compliance noted) for November 10 | , |
|---|---|
| 2009. | |

| Constituent | Basic versus CH2MHill Applied Sciences | Basic versus Aquatic Research, Inc. | CH2MHill Applied Sciences versus Aquatic Research, Inc. |
|-------------|---|--|--|
| Alkalinity | OK | OK | ОК |
| Ammonia | OK | OK | ОК |
| CBOD5 | OK | OK | ОК |
| DOC | OK | 26.6% | 36.1% |
| NO3+NO2 | OK | OK | ОК |
| TN | OK | OK | ОК |
| OPO4 | OK | OK | 0.013 mg/l ^a |
| TP | OK | OK | ОК |
| TKN | OK | OK | ОК |
| TSS | OK | OK | 30.1% |
| VSS | OK | OK | 2.4 mg/l ^b |

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^a CH2MHill OPO4 reporting limit was 0.01 mg/l.

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

| | Laboratory | Basic | CH2MHill Applied Sciences | Aquatic Research, Inc. |
|------------|-------------------|-------------------|---------------------------|------------------------|
| | Sample ID / units | 2009AIP-076 | 2009AIP-080 | 2009AIP-079 |
| Alkalinity | mg/l | 59 | 59 | 62.7 |
| Ammonia | mg/l | 0.84 | 0.91 | 0.862 |
| CBOD5 | mg/l | 3ª | 3.53 | 2.72 |
| DOC | mg/l | 6 | 6.34 | 5.00 |
| NO3+NO2 | mg/l | 0.4 | 0.33 | 0.306 |
| TN | mg/l | 2.25 | 2.14 | 1.88 |
| OPO4 | mg/l | 0.05 ^b | 0.022 | 0.006 |
| TP | mg/l | 0.13 | 0.093 | 0.06 |
| TKN | mg/l | 1.8 | 2.02 | 1.88 |
| TSS | mg/l | 27 | 26.8 | 34 |
| VSS | mg/l | 6 ^c | 3.2 | 6 |

 Table 14. Result values used to determine RPD and criteria values, December 8, 2009.

^a Basic Laboratory reported result for CBOD5 was ND and was replaced with the appropriate RL value for RPD determination.

^b Basic Laboratory reported result for OPO4 was ND and was replaced with the appropriate RL value for RPD determination.

^c Basic Laboratory reported result for VSS was 3 mg/l and was replaced with the appropriate RL value for RPD determination.

| 09. | | | | | | |
|-------------|---|--|--|--|--|--|
| Constituent | Basic versus CH2MHill Applied Sciences | Basic versus Aquatic Research, Inc. | CH2MHill Applied Sciences versus Aquatic Research, Inc. OK | | | |
| Alkalinity | OK | OK | | | | |
| Ammonia | ОК | OK | ОК | | | |
| CBOD5 | ОК | OK | ОК | | | |
| DOC | ОК | OK | 23.6% | | | |
| NO3+NO2 | ОК | 26.6% | ОК | | | |
| TN | OK | OK | ОК | | | |
| OPO4 | OK | OK | 0.016 mg/l ^b | | | |
| TP | ОК | 0.068 mg/l ^a | ОК | | | |
| TKN | ОК | OK | ОК | | | |
| TSS | ОК | 23.0% | 23.7% | | | |
| VSS | ОК | OK | 2.8 mg/l ^c | | | |

 Table 15. Comparison of similarity criteria compliance (non-compliance noted) for December 8, 2009.

^a CH2MHill TP reporting limit was 0.05 mg/l.

^b CH2MHill OPO4 reporting limit was 0.01 mg/l.

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

Comparison Summary

For each constituent there were 21 laboratory cross comparisons (three for each of the seven sampling dates). For each comparison, if the RPD was within the assumed 20 percent limit, the result pair was considered similar. If the RPD was outside of 20 percent limit, the result pair of that comparison was considered dissimilar and the percent difference entered in the tables. The number of similar and dissimilar results is presented in Table 16 and Figure 1.

The constituents for which comparisons produced greater than 80 percent similar result pairs were NO3+NO2, Alkalinity and OPO4. Constituents for which comparisons

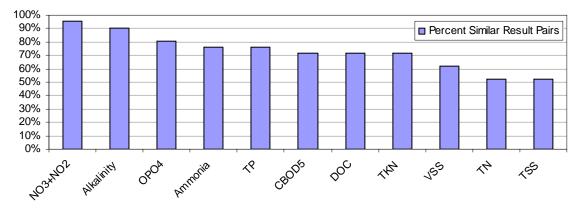
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produced between 71 to 80 percent similar result pairs were ammonia, total phosphorus, CBOD5, DOC and TKN. The constituent for which comparisons produced between 61 to 70 percent similar result pairs was VSS. Constituents for which comparisons produced between 51 and 60 percent similar result pairs were total nitrogen and TSS. A potential reason for the dissilimar results in TSS and VSS was that the reporting limit was notably higher at Basic Laboratory (6 mg/l) than at CH2MHill (2 mg/l) or Aquatic Research (RL not included, MDL = 0.5 mg/l). A potential reason for the dissilimar results in total nitrogen analysis at CH2MHill was the implementation of a new method which produced inconsistent results during portions of 2009.

There were a total of 231 laboratory cross comparisons calculated (33 for each sampling date). There were 63 result pairs that were dissimilar (27 percent). Of those 63 dissimilar result pairs, 22 percent were from comparing results from Basic and CH2MHill, 27 percent were from comparing results from Basic and Aquatic Research, and 51 percent were from comparing CH2MHill and Aquatic Research. These results indicate that when comparing Basic to CH2MHill or Basic to Aquatic Research, the values will be similar more often than when comparing CH2MHill with Aquatic Research. These results do not identify if one laboratory is more "accurate" than another, but rather identify differences or similarities based on RPD among the laboratories.

| | Alkalinity | Ammonia | CBOD5 | DOC | NO3+ NO2 | TN | OPO4 | ТР | TKN | TSS | VSS | Totals |
|---|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|--------------|
| Total Number of similar result pairs (Percent of total results pairs) | 19 (90%) | 16 (76%) | 15 (71%) | 15 (71%) | 20 (95%) | 11 (52%) | 17 (81%) | 16 (76%) | 15 (71%) | 11 (52%) | 13 (62%) | 168 (73%) |
| Total number of dissimilar result pairs | 2 | 5 | 6 | 6 | 1 | 10 | 4 | 5 | 6 | 10 | 8 | 63 |
| Dissimilar Basic and CH2MHill results | 0 | 2 | 3 | 0 | 0 | 3 | 0 | 2 | 1 | 2 | 1 | 14 |
| Dissimilar Basic and Aquatic Research results | 1 | 3 | 1 | 3 | 1 | 3 | 0 | 1 | 2 | 1 | 1 | 17 |
| Dissimilar CH2MHill and Aquatic Research Results | 1 | 0 | 2 | 3 | 0 | 4 | 4 | 2 | 3 | 7 | 6 | 32 |

Table 16. Number of similar result pairs and dissimilar results pairs per constituent and per laboratory comparison



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Figure 1. Percent of similar result pairs from June 10, 2009 through December 8, 2009

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.
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