Northern Water's Water Quality Monitoring Program Quality Assurance and Quality Control Report: Water Year 2015

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1. Introduction

Quality assurance and quality control measures form an important, integral component of Northern Water's Water Quality Monitoring Program. Quality assurance and quality control (QA/QC) measures are applied to sample collection, laboratory analysis, and data processing and management to ensure that the data are scientifically valid, defensible, accurate, and representative of actual conditions. Quality assurance (QA) is achieved through consistent adherence to the program requirements outlined in Northern Water's Standard Operating Procedures (Northern Water, 2015) including requirements for staff training, calibration and maintenance of equipment and instrumentation, collection of quality control (QC) samples, and standardized procedures for sample collection, sample handling/processing, data review/validation, and database management. Quality control samples are used to measure and maintain the program's data quality, limit error, and ensure that the data quality objectives are being met. Quality control samples include several types of blank and replicate samples.

The purpose of this document is to review the QC samples that were collected and to discuss data quality concerns for Northern Water's Water Quality Monitoring Program in water year 2015 (October 2014 – September 2015).

2. Sampling Summary

In water year 2015, water quality samples were collected by three entities: Northern Water, the U.S. Geological Survey (USGS) and Pinyon Environmental. Northern Water collected the majority of the samples at the flowing sites (canals, rivers and streams), all the samples on the reservoirs on the East Slope, and most of the samples on the reservoirs on the West Slope. The USGS collected samples at two canal sites on the East Slope and for a winter sampling event on the reservoirs on the West Slope. Pinyon Environmental performed supplemental sampling in support of mitigation efforts for the Northern Integrated Supply Project and the Windy Gap Firming Project.

There are some slight differences between Northern's and the USGS's sampling protocols, but both entities adhere to strict and similar QAQC procedures. The USGS sampling protocols are documented in the USGS's "National Field Manual for the Collection of Water-Quality-Data" (U.S. Geological Survey, variously dated). One of Northern Water's important data quality objectives is to collect data that are comparable to those collected by the USGS (and other sampling entities).

The data for all samples collected by the USGS are shared with Northern Water. All samples collected are sent to Northern Water's USGS-certified private laboratories for analysis. Northern Water and the USGS work cooperatively to troubleshoot any instances of suspect data. If it is agreed that there are instances where there are data quality issues, Northern Water and the USGS process and flag the data in the same manner to ensure consistency between the two datasets. These data are available on Northern Water's website and on the USGS's National Water Information System (NWIS) website.

Pinyon Environmental has been trained by Northern Water and utilizes sampling protocols outlined in Northern Water's SOP (Northern Water, 2015). In addition, Northern Water field services staff shadowed Pinyon Environmental for one sampling event during the 2015 sampling season to verify consistency with Northern Water's SOP. During shadowing events, concurrent replicate samples were collected (one sample collected by Northern Water and one by Pinyon Environmental) and the data were compared.

Field QC samples are collected by Northern Water, USGS and Pinyon Environmental. At minimum, 10% of all samples collected on the West Slope and 5% of all samples collected on the East Slope are QC samples. Field QC samples are split equally between blanks and replicates, which will be discussed in detail in subsequent sections of this report. Table 1 is a summary of the percentage of field QC samples collected in water year 2015 for the east and west slopes.

TABLE 1 - FIELD QC SUMMARY

Location	Number of Samples			Percentage Samples		
	Environmental	Blanks	Replicates	Blanks	Replicates	Total
East Slope	273	15	11	5.5%	4.0%	9.5%
West Slope	495	27	25	5.4%	5.1%	10.5%

Various groups of analytes are included in the baseline monitoring program that are specific to site and season. Therefore, the analytes included in each field QC sample vary and are representative of the analytical group of the environmental sample(s) being collected at that time.

3. BLANK SAMPLES

Blank QC samples provide an estimate of bias (systematic error) due to sample contamination that could occur during sample collection, processing, preserving and shipping. Samples can be contaminated by many sources including the field staff (dirty hands, etc), from improperly cleaned sampling devices, from contaminated preservatives or sample bottles, and from dust particles or atmospheric deposition during filtering and preserving (Cavanagh, N., R.N. Nordin, L.W. Pommen and L.G. Swain, 1998). However, the strict adherence to the protocols presented in Northern Water's SOP (Northern Water, 2015) minimizes these sources of sample contamination. Blank samples are used to demonstrate that contamination of the environmental samples has not occurred or, if it did, where in the sampling process it occurred.

Blank samples are made up of de-ionized (D.I.) water produced at Northern Water's Berthoud laboratory, free of the analytes of interest. D.I. water is tap water that has been treated by passing through a standard de-ionizing resin column filter.

Routine blank samples collected for Northern Water's program include laboratory D.I. water blanks, equipment blanks, and field blanks. If chronic sample contamination is suspected, additional blank samples are collected at various additional points in the sample collection and processing sequence to help determine exactly where the contamination is occurring.

The acceptance criteria for blank QC samples are outlined on Table 2. Analytical results for blank samples should be less than the laboratory reporting limit (RL). If the blank samples indicate that sample contamination has occurred, the source of contamination is investigated, eliminated and documented.

TABLE 2 - CRITERION FOR BLANK SAMPLES

Field QC Sample Type	Collection Frequency	Acceptance Criterion	Corrective Action
Laboratory DI Water Blank (LDI)	Once/ quarter	≤ RL	Investigate & eliminate source of contamination: improperly cleaned sample bottles, contamination of sample bottles, contamination of the blank water, lab error; flag suspect data.
Laboratory Equipment Blank (LEB)	Once/ year	≤ RL	Investigate & eliminate source of contamination: improperly cleaned equipment or sources as above for Lab Water Blank; flag suspect data.
Field Blank (FEB)	5% for West Slope sites & 2.5% for East Slope sites, of total annual sample count	≤ RL	Investigate & eliminate source(s) of contamination; flag suspect data.

3.1 2015 FIELD BLANK SAMPLES

Field blanks are collected by taking analyte-free D.I. water out to the field and processing it as if it were a sample, including filtration and sample preservation (Figure 1). Field blank samples are collected to determine if contaminants are introduced to the sample in the field during collection, processing, preserving and shipping of samples. Field blanks are collected randomly and at different sites throughout the sampling season. Field blank samples constitute approximately 5% of the total sample load from the West Slope sites and approximately 2.5% of the total sample load from the East Slope sites during any given year.

FIGURE 1 – POURING A FIELD BLANK SAMPLE

Table 3 provides a summary of the field blank samples collected for each analyte in water year 2015. The number of samples and percentages presented are based on samples collected from both the East and West Slope combined and from all three sampling entities (Northern Water, USGS and Pinyon Environmental). All of the data for the field blank QC samples are presented in time series format in the Appendices, Appendix 1.

TABLE 3 - SUMMARY OF FIELD BLANK RESULTS BY ANALYTE

Analyte	Units	Number of Samples		Percent Blank Samples	Reporting Limit (RL)	Number of Blank Samples > RL	Value of Blank Samples > RL	
		Blank	Field				Median	Max
Ammonia as N	mg/L	42	768	5.5%	0.004	2	--	0.006
Nitrate plus Nitrite as N	mg/L	42	768	5.5%	0.004	--	--	--
Total Kjeldhal Nitrogen	mg/L	42	767	5.5%	0.07	--	--	--
Ortho Phosphate as P	mg/L	42	768	5.5%	0.002	--	--	--
Phosphorus, Total	mg/L	42	768	5.5%	0.003	--	--	--
Organic Carbon, Dissolved	mg/L	20	299	6.7%	0.6	--	--	--
Organic Carbon, Total	mg/L	32	494	6.5%	0.6	--	--	--
Suspended Solids, Total	mg/L	32	587	5.5%	0.3	--	--	--
UV Absorbance	cm^{-1}	11	182	6.0%	0.002	--	--	--
Arsenic, Dissolved	µg/L	15	180	8.3%	0.06	--	--	--
Arsenic, Total	µg/L	15	179	8.4%	0.8	--	--	--
Boron, Dissolved	µg/L	15	180	8.3%	0.5	--	--	--
Cadmium, Dissolved	µg/L	15	180	8.3%	0.02	--	--	--
Chromium, Dissolved	µg/L	15	180	8.3%	0.1	--	--	--
Chromium, Total	µg/L	15	180	8.3%	2	--	--	--
Copper, Dissolved	µg/L	25	383	6.5%	1	--	--	--
Iron, Dissolved	µg/L	25	383	6.5%	4	--	--	--
Iron, Total	µg/L	17	234	7.3%	14	--	--	--
Lead, Dissolved	µg/L	15	180	8.3%	0.03	--	--	--
Manganese, Dissolved	µg/L	25	383	6.5%	0.2	--	--	--
Manganese, Total	µg/L	2	54	3.7%	0.4	--	--	--
Nickel, Dissolved	µg/L	15	180	8.3%	0.12	--	--	--
Selenium, Dissolved	µg/L	17	234	7.3%	0.06	--	--	--
Silver, Dissolved	µg/L	15	180	8.3%	0.01	--	--	--
Uranium, Dissolved	µg/L	15	180	8.3%	0.01	--	--	--
Zinc, Dissolved	µg/L	15	180	8.3%	1	--	--	--
Alkalinity, Total	mg/L	15	180	8.3%	5	--	--	--
Calcium	mg/L	17	234	7.3%	0.02	1	--	0.033
Chloride	mg/L	17	234	7.3%	0.12	1	--	0.64
Magnesium	mg/L	17	234	7.3%	0.012	--	--	--
Sodium	mg/L	15	180	8.3%	0.12	--	--	--
Potassium	mg/L	15	180	8.3%	0.06	--	--	--
Sulfate	mg/L	17	234	7.3%	0.18	--	--	--

There were 33 compounds analyzed with the field blanks. There were a total of 4 occurrences for 3 analytes where values were reported at a concentration above the RL. Discussion follows for these occurrences:

- Ammonia – There were two instances where ammonia was reported above the RL of 0.004 mg/L for a FEB. The sampling occurred within one day of one another, August 12 and 13, 2015. The concentrations were 0.005 and 0.006 mg/L, just above the RL. Both samples were collected by Northern Water. For verification, a rerun analysis was conducted at the laboratory, which resulted in the same values. The cause of contamination is not known. No action was taken on these data since the values were just slightly above the RL and subsequent FEBs did not result in values over the RL.

- Calcium and Chloride – There was one FEB where both calcium and chloride were reported with values above the RLs of 0.02 mg/L and 0.12 mg/L respectively. The sample was collected by Pinyon Environmental. The values were verified by internal QAQC checks by Huffman Laboratory. The likely cause was contamination in the field. The environmental sites that were sampled that day had relatively high calcium and chloride concentrations, which may have contributed to the contamination. Magnesium was also elevated in this FEB sample although it was not above the RL. These data are noted with the remark "Possible field contamination" in Northern Water's database.

3.2 2015 Laboratory Blank Samples

Laboratory water blanks are collected prior to leaving for the field and consist of pouring analyte-free D.I. water, without processing, directly from the D.I. water faucet into sample bottles and then shipping these bottles with the environmental samples to the laboratory for analysis. If analytes of interest are found in the lab water blanks, this can indicate improperly cleaned sample bottles, contamination of the sample bottles, or contamination of the D.I. water. Laboratory D.I. water blanks (LDI) are collected approximately once per quarter.

In 2015, five LDI samples were submitted; one each in October, January, February, April and May. The results for all the samples and analytes were below the RL with the exception of one analyte in the sample submitted in April 2015 shown in Table 4, which was just slightly above the RL.

Table 4 – Laboratory D.I. Water Blank Reported Value above the RL

Date	Analyte	Unit	Value	RL
4/6/2015	Uranium, Dissolved	µg/L	0.02	0.01

Laboratory equipment blanks are collected to determine if the sampling equipment is being thoroughly cleaned and decontaminated before it leaves the lab. Laboratory equipment blanks (LEB) are collected in the same manner as the laboratory water blanks except that the analyte-free D.I. water is poured into the sampling equipment prior to pouring into the sample bottle. At minimum, one round of equipment blanks is collected annually for each piece of sampling equipment (Van Dorn used in lake sampling and DH-81 used in flowing site sampling, Figure 2). Laboratory equipment blanks are generally paired with a LDI.

In water year 2015, Northern Water did not submit a LEB. Given the low occurrence of compounds detected above the RL in the FEB samples, there was likely little to no equipment contamination in 2015. LEB samples will be submitted in subsequent years.

Pinyon Environmental submitted one LEB in March 2015, just prior to the beginning of their sampling period (April-September). This sample was submitted for nutrients only. All the results were below the RL.

FIGURE 2 – VAN DORN SAMPLING EQUIPMENT (LEFT) DH-81 SAMPLING EQUIPMENT (RIGHT)

4. REPLICATE SAMPLES

Replicate samples are two samples collected and processed together and should produce essentially identical results when analyzed. Replicate samples or measurements are used to assess precision (random error). Precision is a measure of how well repeated measurements agree, and how consistent and reproducible the field and laboratory measurements are. The consistent adherence to the protocols presented in Northern Water's SOP (Northern Water, 2015) is the best way to achieve high precision. Imprecision is the result of inconsistent field techniques and/or laboratory analysis.

Field replicate samples included in Northern Water's Program include:

- **Split replicates (SR)** are samples obtained by splitting one sample into two subsamples and are collected to determine variability in sample processing and laboratory analysis. Split samples are collected like a normal sampling event, but enough water must be collected to fill two sets of sample bottles. Split replicates are sent to the same laboratory for analysis.

- **Concurrent replicates (CR)** are two separate sets of samples collected as close as possible to the same location and time to determine variability in space and time of the sample site as well as variability in the collection, processing and analysis of samples. Since concurrent replicates include natural variability, they are somewhat less precise than split replicates from a single sample, but this variation should be small. Concurrent replicates are collected at the flowing sites by setting up two churns, one designated churn A and the other churn B. Each vertical in the stream cross-section is sampled twice with the sub-samples alternated between churn A and churn B.

- **Sequential replicates (SQR)** are two samples collected consecutively at the same location (one right after the other) to determine variability in the collection, processing and analysis of samples. Sequential replicates are collected during lake and reservoir sampling when a replicate sample is desired, but the volume of water needed is too large to process as a split replicate sample (i.e., the volume of water needed is more than what is contained in the Van Dorn or other sampling device), and a concurrent replicate sample is not feasible.

Field replicates are collected randomly and at different sites throughout the sampling season. Field replicate samples constitute approximately 5% of the total sample load from the West Slope sites and approximately 2.5% of the total sample load from the East Slope sites during any given year.

The relative percent difference (RPD) between two replicate determinations is used to assess the precision of the sampling and analytical methods and is calculated using the following equation:

$$RPD = 100 \times \frac{(Xs - Xd)}{[(Xs + Xd)/2]}$$

where:

RPD	=	relative percent difference, expressed in percent
Xs	=	analytical result obtained for the sample
Xd	=	analytical result obtained for the replicate sample

A low RPD reflects high precision. The maximum acceptable RPD depends on the concentration and the RL. Concentrations below the RL are all considered acceptable even if there is a very large calculated RPD since the concentrations are all very low and the magnitude of the difference is very small from a practical standpoint. When results are above the RL for both the environmental and replicate sample, the RPD must be ≤ 25%. The acceptance criteria and corrective action taken by Northern Water for replicate field QC samples are outlined in Table 5.

TABLE 5 – CRITERION FOR REPLICATE SAMPLES

Field QC Sample Type	Collection Frequency	Acceptance Criterion	Corrective Action
Split Replicates (SR)	SR + CR + SQR = 5% for West Slope sites and = 2.5% for East Slope sites, of total annual sample count	For concentrations > RL: Relative Percent Difference (RPD) ≤ 25%	Investigate & eliminate cause: inconsistent field techniques & sample processing, laboratory error; request re-analysis of sample; flag suspect data.
Concurrent Replicate (CR) & Sequential Replicate (SQR)			Investigate cause: natural variability in space and/or time, inconsistent field techniques & sample processing, laboratory error; request re-analysis of sample; flag suspect data.

4.1 2015 Field Replicate Samples

Table 6 provides a summary of the field replicate samples collected for each analyte in water year 2015. The summary combines all three types of replicates; the number of samples and percentages presented are based on samples collected from both the East and West Slope combined and from all three sampling entities (Northern Water, USGS and Pinyon Environmental). The percentages highlighted in yellow are those that fall outside of the acceptance criteria. All field replicate data are presented graphically in the Appendices, Appendix 2.

Table 6 - Summary of Field Replicate Samples by Analyte

Analyte	Unit	Number of Samples		Percent Replicate Samples	Reporting Limit (RL)	Number Replicate Samples > RL	Relative Percent Difference for Replicate Samples above RL		Difference in Concentration Field and Replicate Samples above RL	
		Replicate	Field				Median	Maximum	Median	Maximum
Ammonia as N	mg/L	36	768	4.7%	0.004	14	5%	29%	0.001	0.005
Nitrate plus Nitrite as N	mg/L	36	768	4.7%	0.004	24	1%	18%	0.001	0.019
Total Kjeldhal Nitrogen	mg/L	36	767	4.7%	0.07	36	2%	11%	0.0035	0.019
Ortho Phosphate as P	mg/L	36	768	4.7%	0.002	18	0%	35%	0	0.003
Phosphorus, Total	mg/L	36	768	4.7%	0.003	36	2%	11%	0.001	0.004
Organic Carbon, Dissolved	mg/L	15	299	5.0%	0.6	15	1%	4%	0.02	0.12
Organic Carbon, Total	mg/L	24	494	4.9%	0.6	24	1%	4%	0.03	0.13
Suspended Solids, Total	mg/L	28	587	4.8%	0.3	28	0%	59%	0	1
UV Absorbance	cm^{-1}	7	182	3.8%	0.002	7	0%	13%	0	0.014
Arsenic, Dissolved	µg/L	8	180	4.4%	0.06	8	10%	33%	0.03	0.06
Arsenic, Total	µg/L	8	179	4.5%	0.8	--	--	--	--	--
Boron, Dissolved	µg/L	8	180	4.4%	0.5	8	2%	10%	0.115	0.32
Cadmium, Dissolved	µg/L	8	180	4.4%	0.02	--	--	--	--	--
Chromium, Dissolved	µg/L	8	180	4.4%	0.1	4	6%	20%	0.02	0.04
Chromium, Total	µg/L	8	180	4.4%	2	--	--	--	--	--
Copper, Dissolved	µg/L	17	383	4.4%	1	2	15%	25%	0.19	0.31
Iron, Dissolved	µg/L	17	383	4.4%	4	17	4%	109%	3.1	52.45
Iron, Total	µg/L	10	234	4.3%	14	10	2%	7%	6.5	12
Lead, Dissolved	µg/L	8	180	4.4%	0.03	6	6%	13%	0.003	0.008
Manganese, Dissolved	µg/L	17	383	4.4%	0.2	17	9%	176%	0.4	10.1
Manganese, Total	µg/L	2	54	3.7%	0.4	2	3%	4%	1.9	1.9
Nickel, Dissolved	µg/L	8	180	4.4%	0.12	8	8%	27%	0.02	0.07
Selenium, Dissolved	µg/L	10	234	4.3%	0.06	6	9%	25%	0.02	0.3
Silver, Dissolved	µg/L	8	180	4.4%	0.01	--	--	--	--	--
Uranium, Dissolved	µg/L	8	180	4.4%	0.01	8	2%	20%	0.0075	0.033
Zinc, Dissolved	µg/L	8	180	4.4%	1	1	27%	27%	0.4	0.4
Alkalinity, Total	mg/L	8	180	4.4%	5	8	0%	5%	0	1
Calcium	mg/L	10	234	4.3%	0.02	10	1%	23%	0.06	1.52
Chloride	mg/L	10	234	4.3%	0.12	10	0%	6%	0.005	0.01
Magnesium	mg/L	10	234	4.3%	0.012	10	1%	22%	0.02	1.3
Sodium	mg/L	8	180	4.4%	0.12	8	1%	19%	0.03	0.39
Potassium	mg/L	8	180	4.4%	0.06	8	2%	22%	0.01	0.14
Sulfate	mg/L	10	234	4.3%	0.18	10	0%	5%	0.01	8

There were 33 compounds analyzed for the replicate samples. There were a total of 15 occurrences for 8 different analytes where the acceptance criteria were not met. The data for these occurrences are shown in Table 7. In all but five instances, the replicate results that fell outside of the acceptable criteria range were SQRs that were collected from the bottom depth at a lake/reservoir site. The highlighted rows group together occurrences that will be discussed together.

TABLE 7 - REPLICATE SAMPLE DATA OUTSIDE OF ACCEPTABLE CRITERIA RANGE (COLORS GROUP OCCURRENCES THAT WILL BE DISCUSSED TOGETHER)

Date	Sampler	Analyte	Unit	RL	Reported Value			RPD
					Environ-mental	Replicate	Difference	
3/4/2015	USGS	Iron, Dissolved	µg/L	4	39.8	23.9	15.9	50%
3/4/2015	USGS	Manganese, Dissolved	µg/L	0.2	1.14	0.67	0.47	52%
3/4/2015	USGS	Nickel, Dissolved	µg/L	0.12	0.21	0.16	0.05	27%
3/4/2015	USGS	Suspended Solids, Total	mg/L	0.1	1.1	0.6	0.5	59%
5/20/2015	Northern	Manganese, Dissolved	µg/L	0.2	13.8	23.9	10.1	54%
5/20/2015	Northern	Zinc, Dissolved	µg/L	1	1.3	1.7	0.4	27%
5/27/2015	Northern	Ammonia as N	mg/L	0.004	0.006	0.008	0.002	29%
6/8/2015	Northern	Arsenic, Dissolved	µg/L	0.06	0.15	0.21	0.06	33%
7/7/2015	Northern	Iron, Dissolved	µg/L	4	21.75	74.2	52.45	109%
7/7/2015	Northern	Manganese, Dissolved	µg/L	0.2	0.44	6.955	6.515	176%
8/10/2015	Northern	Iron, Dissolved	µg/L	4	22.1	33.5	11.4	41%
8/10/2015	Northern	Manganese, Dissolved	µg/L	0.2	0.46	1.67	1.21	114%
8/10/2015	Northern	Orthophosphate	mg/L	0.002	0.007	0.010	0.003	35%
9/3/2015	Northern	Iron, Dissolved	µg/L	4	57.90	29.45	28.45	65%
9/3/2015	Northern	Manganese, Dissolved	µg/L	0.2	15.1	9.74	5.36	43%

- Sample Collected on 3/4/2015 – This replicate sample was a SQR that was collected at the bottom depth in Grand Lake at the Adams Tunnel site (GL-ATW). Although only three dissolved metals fell outside of the acceptance criteria, all of the reported results for dissolved metals were suspect. Some of the reported concentrations were consistent with the sample collected at the bottom depth and some were consistent with samples collected at the 1-meter depth.

  Extensive investigation was done to try to determine the cause of the discrepancies, by both the USGS (as they collected the sample) and Northern Water. All values were verified by the laboratory. Sample bottle labels were checked. The cause of the discrepancies was unclear. The cause could have been a mix-up in the sample collection/labeling process or it could have been a mix-up in the analysis/reporting process. Given the randomness of the data reported for the replicate, it was also not possible to determine what sample the mix-up occurred for; the environmental sample collected at 1-meter, the environmental sample collected at the bottom or the replicate sample.

  All the dissolved metals data collected on 3/4/2015 at GL-ATW (1-meter, bottom and replicate) were disqualified from Northern Water's database. These data include the remark "Possible dissolved metals sample bottle mix-up. All values for dissolved metals for top, bottom and SQR samples DQ'd."

- Dissolved Manganese collected on 5/20/2015 - This replicate sample was a sequential replicate that was collected at the bottom depth in Horsetooth Reservoir at the Spring Canyon site (HT-SPR). All other data for the replicate sample were consistent with the environmental sample. The value was verified at the laboratory by duplicate analyses, which was performed at the same time as the original analysis. There was not sufficient sample to perform a rerun analysis.

  The cause of the discrepancy is unknown. Bottom disturbances or collecting the samples at slightly different depths can both be factors when collecting sequential replicates which may contribute to the differing concentrations. This seems likely in this case as the reported concentration for the environmental sample was consistent with dissolved manganese concentrations at the bottom depth at the other sites in Horsetooth Reservoir during this sampling event. In addition, there have been documented issues with dissolved manganese in the past, including several replicates that were above the acceptable RPD of 25% that were discussed in both the 2013 and 2014 Quality Assurance and Quality Control Report (Northern Water, 2014; Northern Water, 2015).

  The environmental and replicate dissolved manganese data for this sample are indicated in Northern Water's database with the remark "Replicate sample significantly higher than environmental sample. Not sufficient sample to verify results through rerun analysis."

- Dissolved Zinc, Ammonia and Dissolved Arsenic – Each of these parameters had one instance where the RPD between the replicate and the environmental sample was above the acceptable threshold of 25%. Zinc and ammonia occurred at flowing sites; arsenic occurred in Shadow Mountain Reservoir at the 1-meter depth. For all occurrences, the concentrations were very low resulting in a high RPD for a small difference. The values were not verified at the laboratory.

- Sample Collected on 7/7/2015 – This sample was a sequential replicate collected at the bottom of Granby Reservoir at the site near the dam (GR-DAM). Although manganese and iron were the only parameters with values that fell outside the acceptable criteria range, there were several other parameters with considerably higher concentrations for the replicate sample compared to the environmental sample including: dissolved copper, orthophosphate and UVA.

  The reported concentrations for iron, manganese, copper and orthophosphate were verified by a rerun analysis; the results were consistent with the values reported for the original analysis. UVA was verified by duplicate analysis that was done as part of the laboratories internal QA/QC. The concentrations for the replicate sample were significantly elevated compared to the environmental sample and the concentrations at the bottom depth at the two other sites in Granby Reservoir also sampled on 7/7/2015. The replicate sample concentrations were also elevated compared to samples collected at the same site in preceding and subsequent months (Jun, Aug and Sep). The recorded bottom dissolved oxygen on 7/7/2015 was 6.53; this concentration does not support elevated concentrations due to anoxic conditions.

Bottom disturbances or collecting the samples at slightly different depths can both be factors when collecting sequential replicates which may contribute to the differing concentrations. This is likely in this case considering the elevated concentrations in the replicate sample are atypical and do not appear to be representative of water quality in the hypolimnion as a whole.

The data for the dissolved metals, orthophosphate and UVA for the replicate sample at GR-DAM at the bottom depth were disqualified from Northern Water's database. These data include the remark "Significant difference between environmental and replicate samples. Replicate likely collected very close to sediment and not representative of water column."

- Sample Collected 8/10/2015 – This sample was a sequential replicate collected at the bottom of Carter Lake at the site near the dam (CL-DAM1). Although manganese, iron and orthophosphate were the only parameters with values that fell outside the acceptable criteria range, there were several other parameters that had considerably higher concentrations for the replicate sample compared to the environmental sample including: dissolved copper, UVA, total kjeldhal nitrogen and total suspended solids.

  The reported concentrations for manganese, iron and orthophosphate were verified at the laboratories through duplicate analyses. There are no other sampling sites in Carter Lake to compare the data to, therefore it was unknown which values (environmental or replicate) most closely represented the actual water quality. The cause of the discrepancy is unknown. Bottom disturbances or collecting the samples at slightly different depths can both be factors when collecting sequential replicates, which may contribute to the differing concentrations.

  The manganese, iron and orthophosphate data for the environmental and replicate sample include the remark "Significant difference between environmental and replicate samples. Replicate likely collected very close to sediment and not representative of water column. Verified at laboratory."

- Sample Collected 9/3/2015 – This sample was a split replicate collected on the Poudre River upstream of the Hansen Supply Canal (HSC-PRU). Although manganese and iron were the only parameters with values that fell outside the acceptable criteria range, there were several other dissolved metals with considerably lower concentrations for the replicate sample compared to the environmental sample including: arsenic, copper, lead and selenium.

  The reported concentrations for manganese and iron were verified at the laboratory through duplicate analyses. The cause of the discrepancy is unknown. The cause could have been related to the filter used in the field to process the dissolved metals or the analytical process in the laboratory. It is unknown which values (environmental or replicate) most closely represented the actual water quality.

  The dissolved manganese and iron data for the environmental and replicate sample include the remark "Split replicate result significantly different than environmental sample result. Verified by duplicate analysis at the lab."

4.2 2015 Northern Water and Pinyon Concurrent Sampling Events

Northern Water's staff shadowed Pinyon Environmental for one sampling event in April to verify proper sampling protocols were being implemented in the field consistent with Northern Water's SOP. During the event, a concurrent replicate sample was collected (one sample collected by Northern Water and one by Pinyon Environmental) and the data were compared. Laboratory data for this sampling is limited to nutrients. In 2015, the laboratory data compared well and are shown in Figure 3. This indicates that Pinyon Environmental was preparing the sampling equipment and collecting and processing samples properly according to Northern Water's SOP.

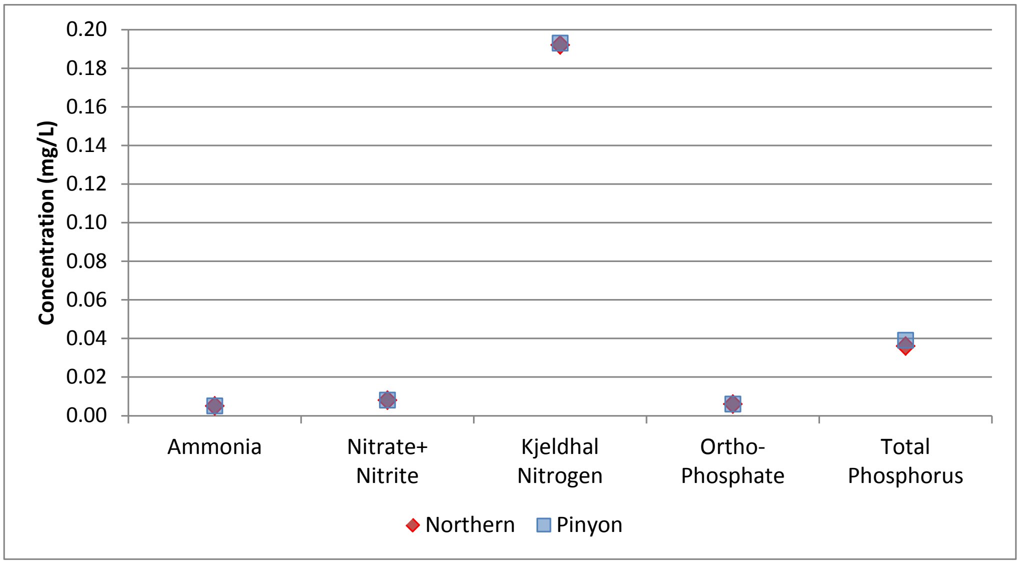

Figure 3 - Laboratory Results for Concurrent Sampling, April 2015

Data collected in the field with a water quality probe are also compared during these sampling events. Comparing these data ensure proper procedures are being followed during equipment calibration. Pinyon Environmental uses one of Northern Water's YSI 6820 multi-parameter probes to collect this data. In 2015, these data compared well as shown in Table 8.

Table 8 - Field data for Concurrent sampling Event

Parameter	April 2015	
	Northern	Pinyon
Dissolved Oxygen (mg/L)	10.8	9.7
pH	7.7	7.8
Specific Conductivity (uS/cm)	102	102
Temperature (Deg C)	4.4	4.4
Turbidity (NTU)	8	8.3

5. Laboratory QA/QC

Northern Water uses two different laboratories for the analysis of the various water quality parameters presented in this report:

- High Sierra Water Lab (Tahoe City, CA): Nutrients, TSS
- Huffman Hazen Laboratories (Golden, CO; http://www.huffmanlabs.com/): Metals, major ions, DOC, TOC

Each of these laboratories is responsible for the accuracy of its data. Each laboratory has its own set of internal QA/QC procedures and conducts its own internal data review and verification prior to submitting data to Northern Water. The primary quality control procedures used by each of the laboratories are outlined in Northern Water's SOP (Northern Water, 2015).

High Sierra Water Lab and Huffman Hazen Laboratories are USGS-certified laboratories. These laboratories participate in the USGS "Round Robin" program, an inter-laboratory comparison study where Standard Reference Samples are submitted to approximately 150 laboratories (USGS and non-USGS labs) in the spring and fall to evaluate and compare analytical performance. More information and results for the Round Robin program can be found on the USGS website under the USGS Standard Reference Sample Project.

These laboratories also undergo annual QC audits that include the analysis of proficiency evaluation samples submitted to them by the USGS. The proficiency evaluation sample has known concentrations for parameters of interest that are within the typical range of concentrations found in the environmental samples submitted to the laboratory. When the proficiency sample is submitted, it is labeled as an environmental sample therefore there is no indication that it is a QA/QC check (aka 'blind' sample). Generally, there is a range of acceptable values provided for each parameter; the value obtained by the laboratory should fall within this range.

5.1 2015 Proficiency Evaluation Results

In March 2015, a proficiency evaluation sample was submitted to High Sierra and Huffman Laboratories by the USGS. The proficiency samples were obtained from two sources:

- ERA, A Waters Company – provided the samples for nutrients, TSS, TOC, DOC, UVA, alkalinity and major ions. ERA provides acceptable upper and lower concentration limits to be used as guidelines for acceptable analytical results. The limits take into consideration limitations of methodologies and instrumentation used for analyses.

- USGS Standard Reference Sample Project (SRS) – provided samples for metals. The SRS samples generally have a higher concentration than what is typically seen in the environmental samples that Northern Water submits. Therefore, low-level dilutions of the samples were prepared by the USGS Colorado Water Science Center in Lakewood, CO. Acceptable concentration limits were not provided for the diluted SRS samples. Analytical performance was evaluated using the

RPD between the certified value and the laboratory value. A RPD of 25% or less was considered acceptable.

The results of the proficiency testing are presented in Table 9. Overall, the laboratory data compared very well to the certified values. All but three of the parameters met the acceptable criterion. Of those three, phosphorus was just above the upper limit, which could be attributed to rounding. The certified value for chromium of 0.7 µg/L was below Huffman's MDL for chromium (1µg/L) which likely had an effect on the laboratory result. UV Absorbance was reported at a value that was significantly lower than the certified value. Most (98%) of the environmental samples collected in WY2015 that were analyzed for UV Absorbance had values less than 0.20 cm-1, with a maximum value of 0.22 cm-1. These values are much lower than the certified value of 0.7 cm-1 that was used in the proficiency testing, and the implications of this 2015 laboratory proficiency result with respect to the much lower WY2015 environmental sample UV Absorbance data is not known.

TABLE 9 - 2015 LABORATORY PROFICIENCY RESULTS

Laboratory	Analyte	Unit	Lab Value	Certified Value	QC Performance Acceptable Limits or RPD
High Sierra	Ammonia as N	mg/L	0.006	0.005	0.0043 - 0.0057
	Nitrate plus Nitrite as N	mg/L	0.021	0.02	0.0175 - 0.0223
	Kjeldhal Nitrogen as N, Total	mg/L	0.212	0.22	0.178 - 0.260
	Ortho Phosphate as P	mg/L	0.005	0.005	0.0045 - 0.0056
	Phosphorus, Total	mg/L	0.023	0.0199	0.0176 - 0.0224
	Suspended Solids, Total	mg/L	3	3.33	2.69 - 3.53
Huffman	Organic Carbon, Dissolved	mg/L	3.41	3.2	2.78 - 3.71
	Organic Carbon, Total	mg/L	3.39	3.2	2.59 - 3.91
	UV Absorbance	cm^{-1}	0.433	0.7	0.554 - 0.896
	Arsenic, Dissolved	µg/L	1.13	0.97	15%
	Arsenic, Total	µg/L	1.3	1.29	1%
	Boron, Dissolved	µg/L	4.57	4.53	1%
	Cadmium, Dissolved	µg/L	0.59	0.52	13%
	Chromium, Dissolved	µg/L	0.6	0.53	12%
	Chromium, Total	µg/L	1	0.7	35%
	Copper, Dissolved	µg/L	1.18	0.97	20%
	Iron, Dissolved	µg/L	33.9	31.26	8%
	Iron, Total	µg/L	42.6	41.68	2%
	Lead, Dissolved	µg/L	6.75	6.6	2%
	Manganese, Dissolved	µg/L	74.8	76.2	2%
	Nickel, Dissolved	µg/L	0.23	0.24	4%
	Selenium, Dissolved	µg/L	0.38	0.33	14%
	Silver, Dissolved	µg/L	1.69	1.66	2%
	Uranium, Dissolved	µg/L	0.454	0.45	1%
	Zinc, Dissolved	µg/L	25.1	21.6	15%
	Alkalinity, Total	mg/L	31	30	27.4 - 33.9
	Calcium	mg/L	7.05	6.66	6%
	Chloride	mg/L	1.41	1.55	1.38 - 1.72
	Magnesium	mg/L	0.794	0.75	6%
	Sodium	mg/L	6.92	6.48	7%
	Potassium	mg/L	0.8	0.73	9%
	Sulfate	mg/L	4.43	4.42	3.79 - 4.93

6. Data Quality

All data collected in the field and received from the laboratories are subject to a thorough QA/QC review and validation by Northern Water prior to being uploaded to Northern Water's databases. Data validation and review of the field data are conducted by both Field Services staff and Water Quality Department staff, while data validation and review of the laboratory data are conducted by Water Quality Department staff. Also note that data validation and review are an ongoing process even after data are uploaded to the databases since some data quality issues may not be apparent until detailed data analyses and assessment are performed while producing reports, conducting water quality modeling, or for other tasks. The data validation and review process is documented in Northern Water's SOP (Northern Water, 2015).

When data quality is found to be unacceptable, one of the following actions are taken:

- **Flagging of Suspect Data -** Data quality issues may not be totally resolved during the data validation process. Data are flagged as "suspect" if there is still a remaining data quality issue (i.e., unexplained outlier or violation of logic check or exceedance of RPD criteria for field replicates), but the data are not of sufficiently poor quality to be rejected. Data flagged as "suspect" in Northern Water's database can be returned during data queries and are available for use, but with caution, if desired.

- **Rejection of Data -** Careful consideration is made on a case-by-case basis to determine if data quality (due to sample contamination, error in sample collection, and/or error in laboratory analyses) has been reduced to a level where the data must be rejected. For example, in cases where sample contamination values (assessed from field blanks) approach the environmental data values, the data collected for that parameter during that particular sample trip is concluded to be invalid and is rejected. Data may also be rejected if a combination of factors are not met (violations of logic checks, poor comparisons with historical data and spatially related sites, poor comparisons with data from outside sampling programs (USGS or other entities), sample hold time violations, etc). Rejected data are flagged as "disqualified" in Northern Water's databases. "Disqualified" data are stored in the database, but are not returned during data queries, are not used during data analyses and data assessments, and are prevented from public release.

The following documents in detail the data that were either rejected/disqualified from or marked as suspect in Northern Water's databases and any other notable data quality issues that occurred in WY2015.

- <u>Dissolved Metals at GL-ATW Collected on 3/4/2015</u> – There was a sequential replicate collected at the bottom depth in Grand Lake at the Adams Tunnel site (GL-ATW), where the replicate data did not compare well with the environmental sample collected at the bottom depth. Some of the reported concentrations were consistent with the sample collected at the bottom depth and some were consistent with samples collected at the 1-meter depth. This is discussed in detail in the 2015 Field Replicate Samples section of this report.

As a result, all the dissolved metals data collected on 3/4/2015 at GL-ATW (1-meter, bottom and replicate) were disqualified from Northern Water's database. These data include the remark "Possible dissolved metals sample bottle mix-up. All values for dissolved metals for top, bottom and SQR samples DQ'd." In total, 51 records were disqualified.

- Discharge Measurements Taken by Pinyon Environmental – After close inspection of field sheets, it was determined that the method that Pinyon Environmental used to collect discharge measurements did not follow Northern Water's discharge measurement protocol (Northern Water, 2015), which follows standard protocol used by the Colorado Division of Water Resources and others. Pinyon Environmental's protocol utilized a set number of verticals regardless of the stream width, which often resulted in more than 10% of the total flow in a given section. In addition, there were instances on the Aquacalc log sheets where many verticals had recorded measurements that were taken under the required 40 seconds. Pinyon Environmental referred to these instances as 'forced' or 'partial' measurements.

  In a few instances, it was possible to compare the discharge measurement taken by Pinyon Environmental to discharge at a gaging station. In most cases, the discharge measurement did not compare well to the recorded discharge at the gage.

  All of the Pinyon Environmental flow data collected in the field from 2011-2015 was flagged as suspect in the database with the remark "Standard discharge measurement procedure not followed." 172 records were flagged.

- Dissolved Boron Change in RL – Dissolved boron was added as a parameter for analysis beginning in WY2014. In WY2014, there were six instances where dissolved boron was detected above the RL in a FEB, one instance for a LDI, and one instance for a LEB. It was suspected that the source water was the cause of the detections (Northern Water, 2015).

  The RL for dissolved boron was low, 0.05 µg/L. Most of the environmental values are above 1 µg/L and none are below 0.5 µg/L. Since detections of boron in the blank samples were a reoccurring problem, the RL was raised from 0.05 µg/L to 0.5 µg/L beginning in WY2015. This better accommodates field blank values without affecting environmental values.

7. SUMMARY

This report provides documentation as well as insight on data quality issues. It can be used as a tool to focus on areas where data quality can be improved. In 2015, 768 samples were collected, 78 of which were QC samples. Given the magnitude of the sampling effort, the results of this report show a small number of occurrences where there were data quality issues. In addition, many of the occurrences noted did not result in a loss of data and/or did not compromise data quality in general. This indicates that Northern Water's data quality objectives for accuracy, bias, and precision are being met.

8. References

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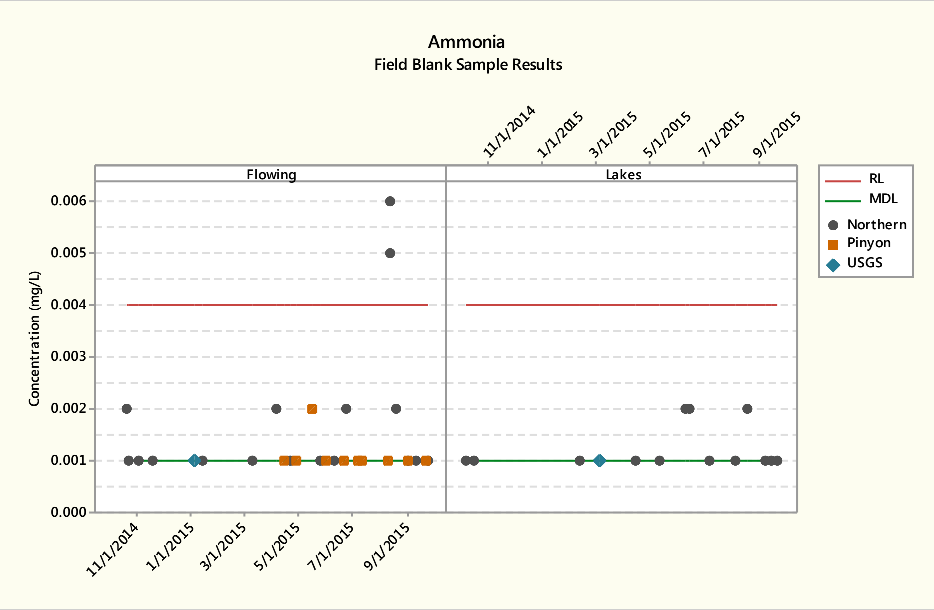
9. Appendices

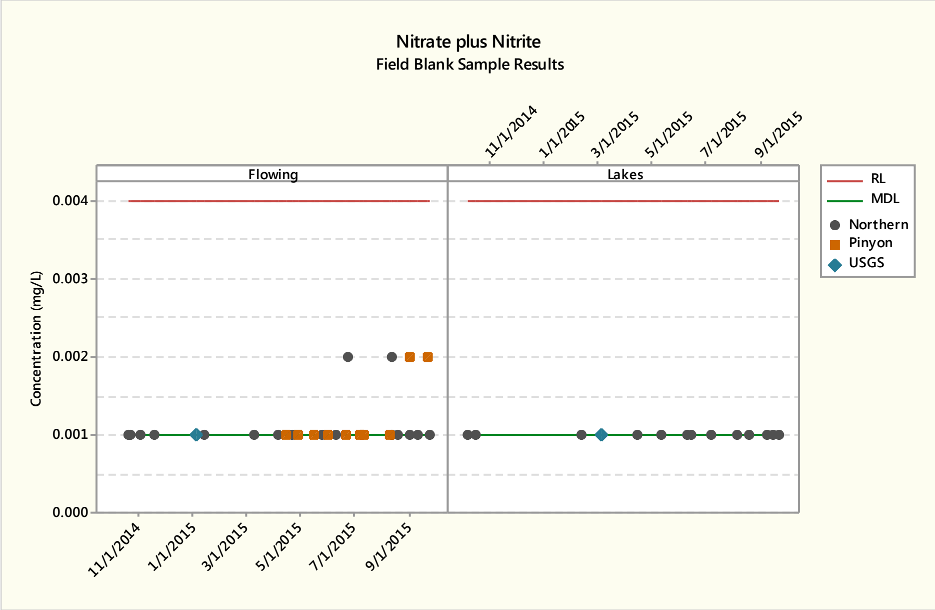
Appendix 1 – Field Blank Time Series Plots

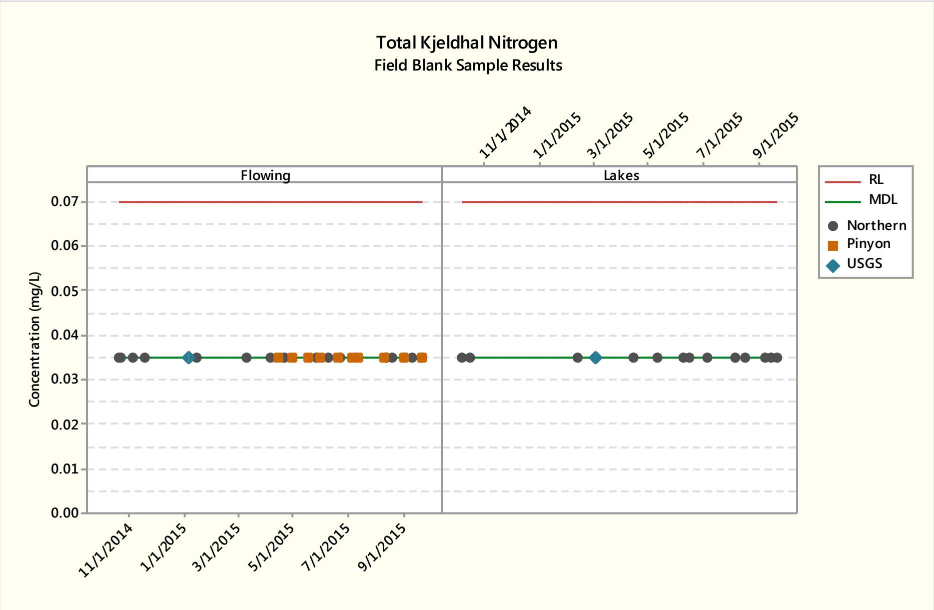
Appendix 2 – Field Replicate Results

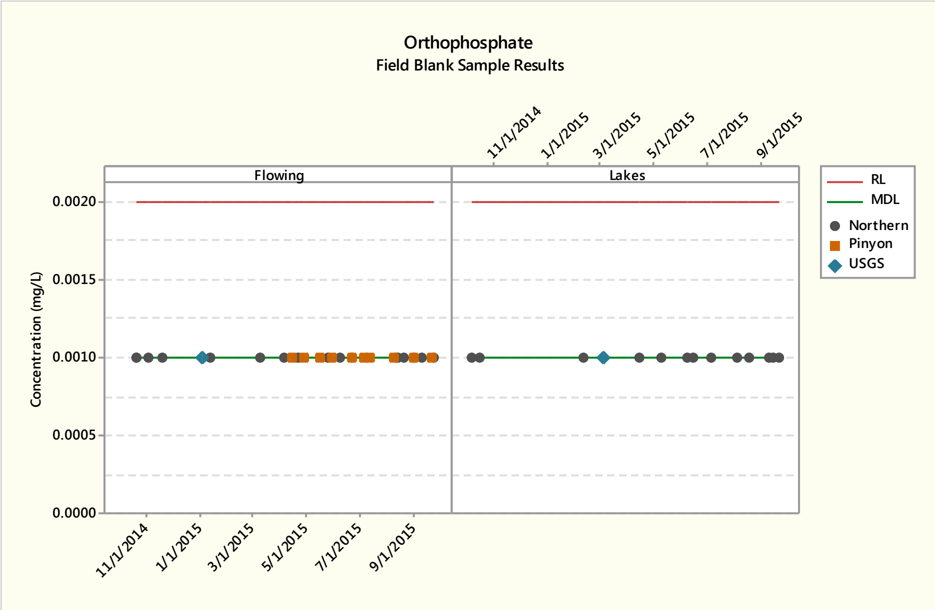
Appendix 3 – Memo, Total Suspended Solids Analysis

Appendix I – Field Blank Time Series Plots









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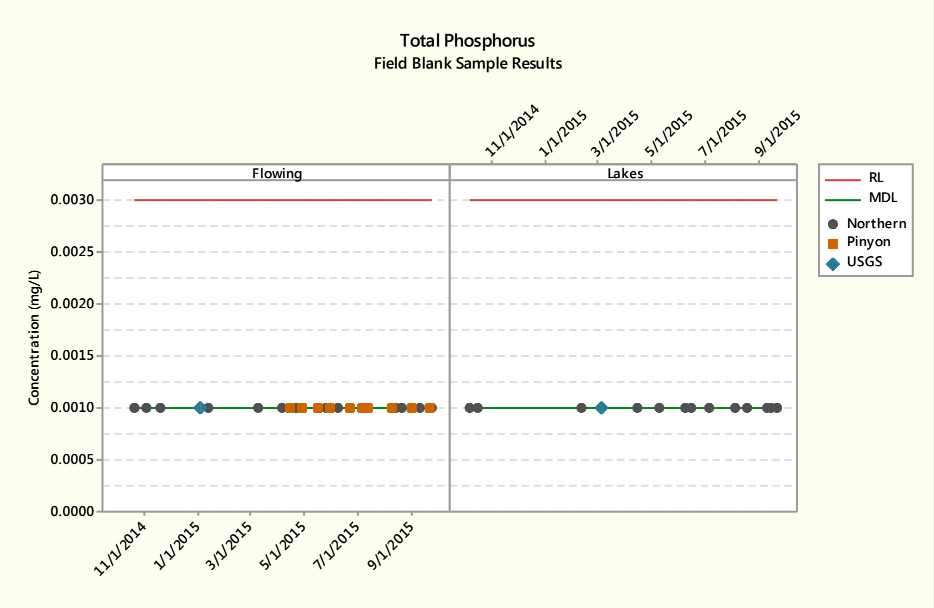

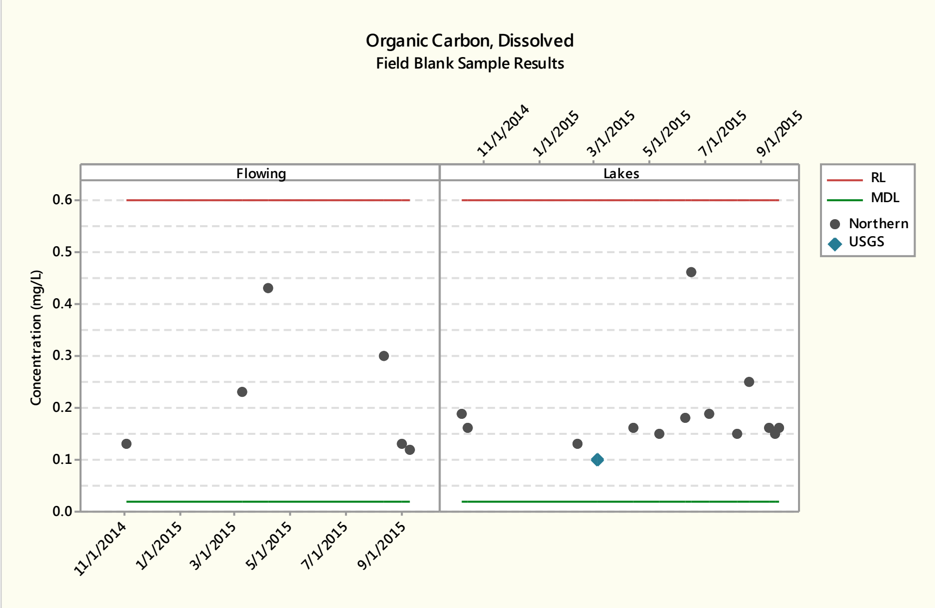

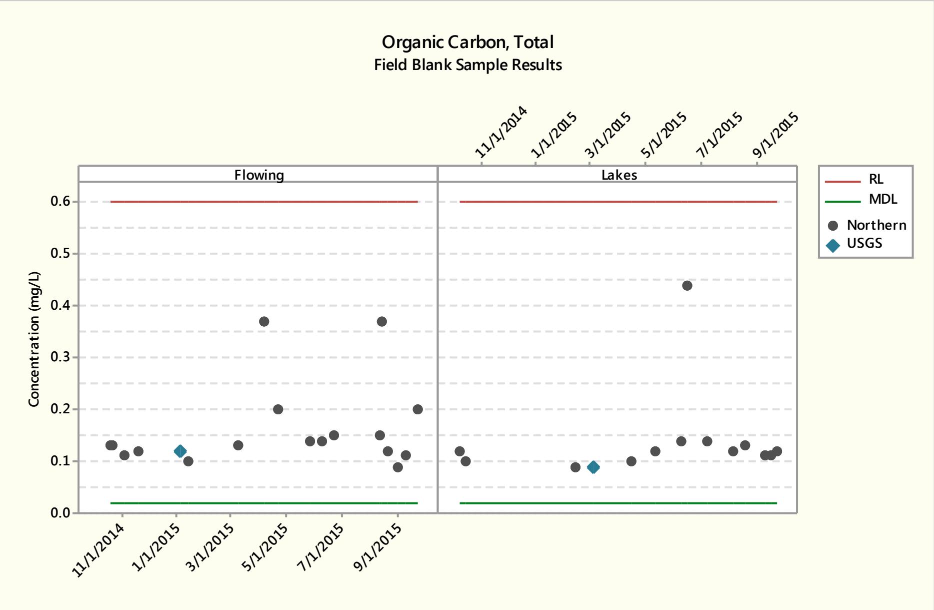

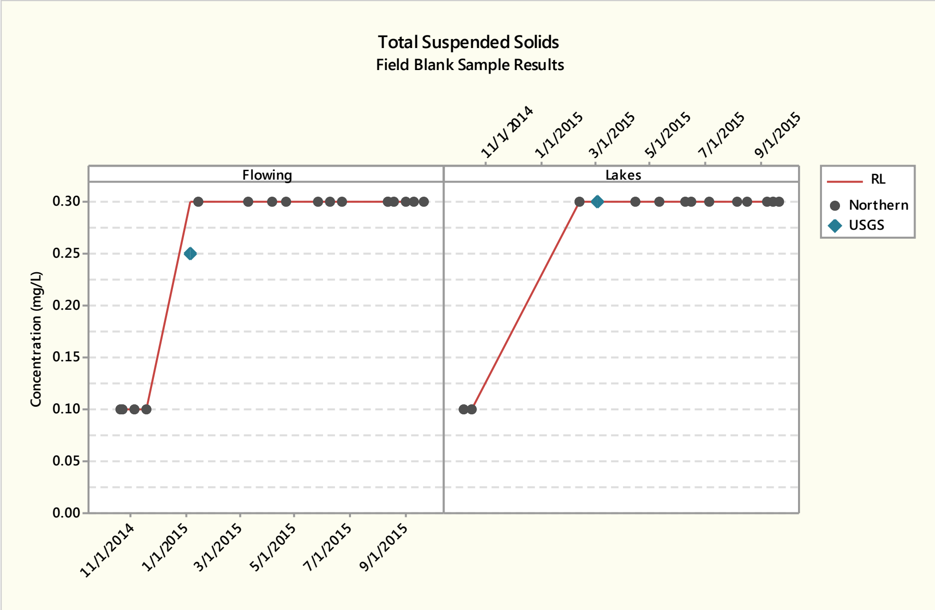

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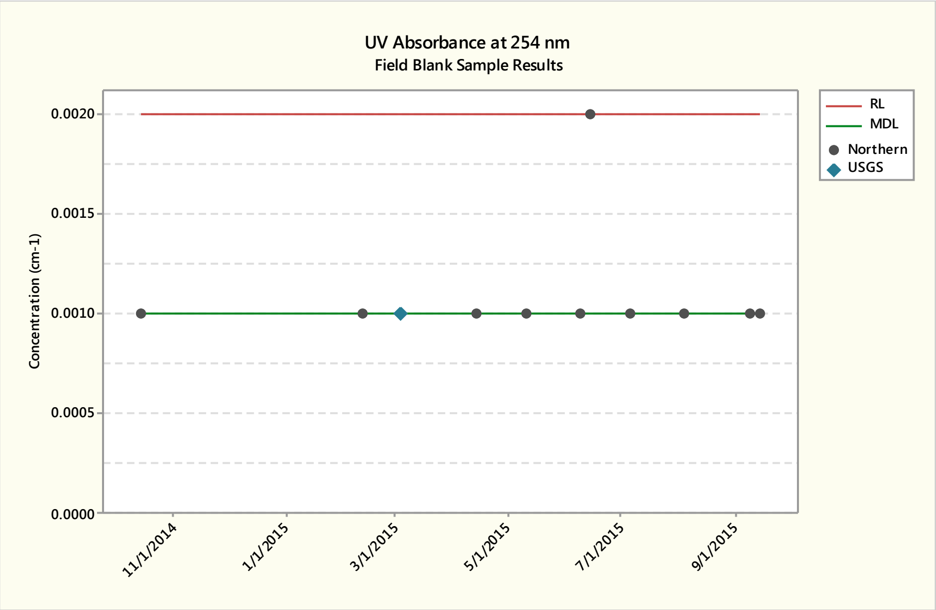

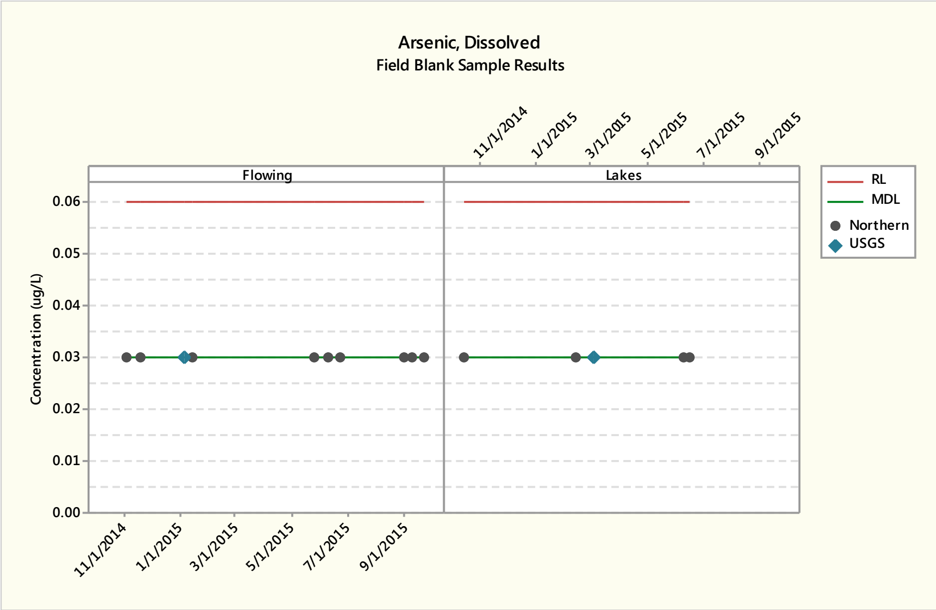

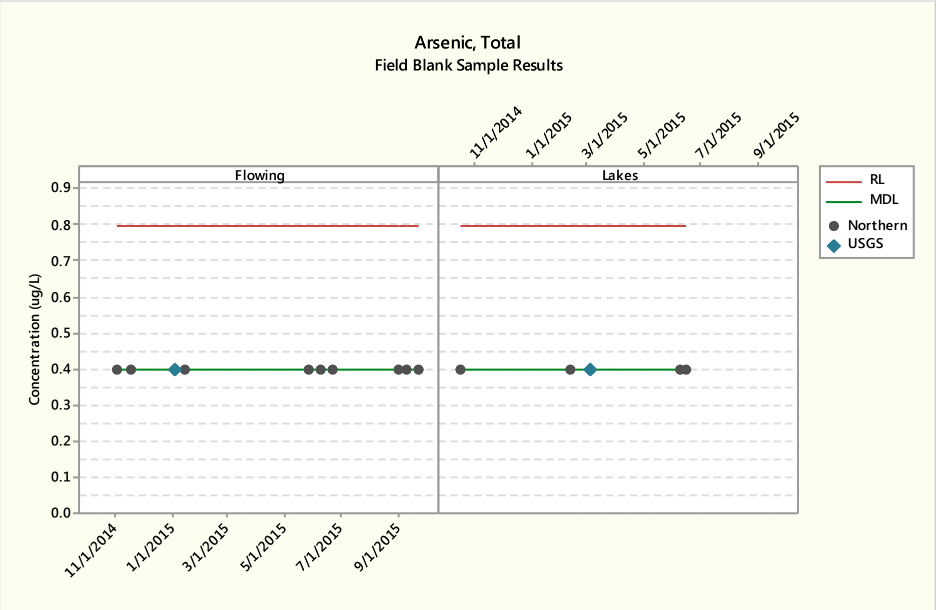

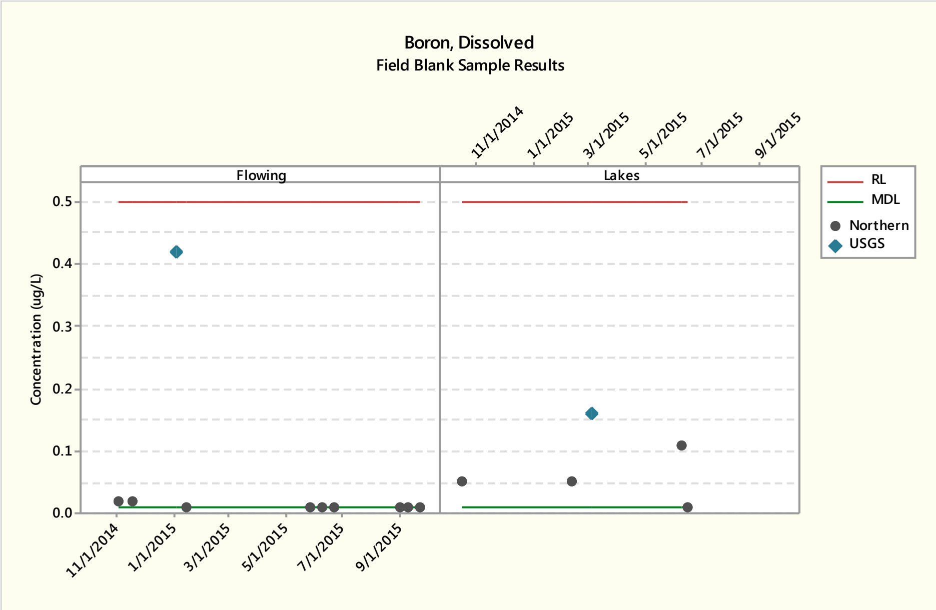

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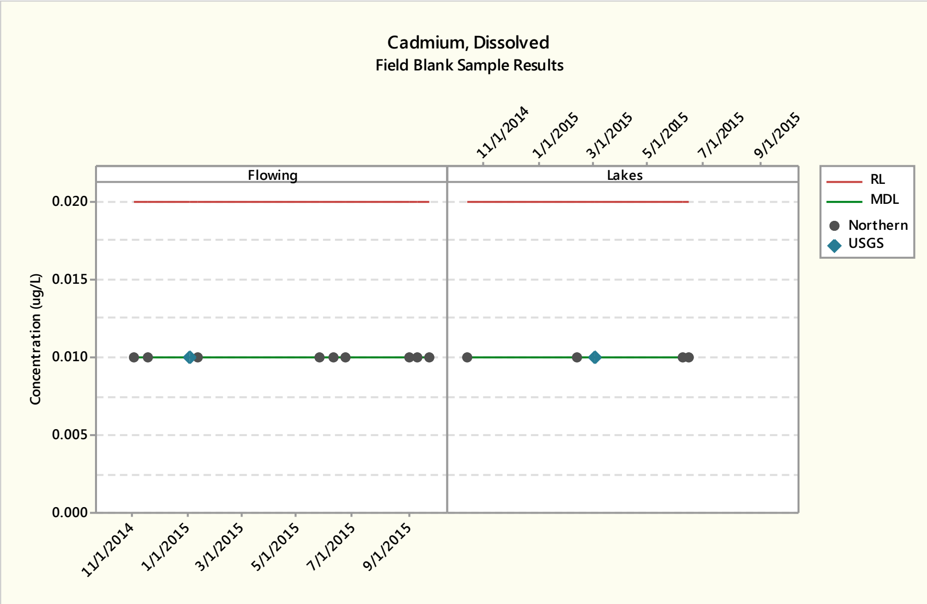

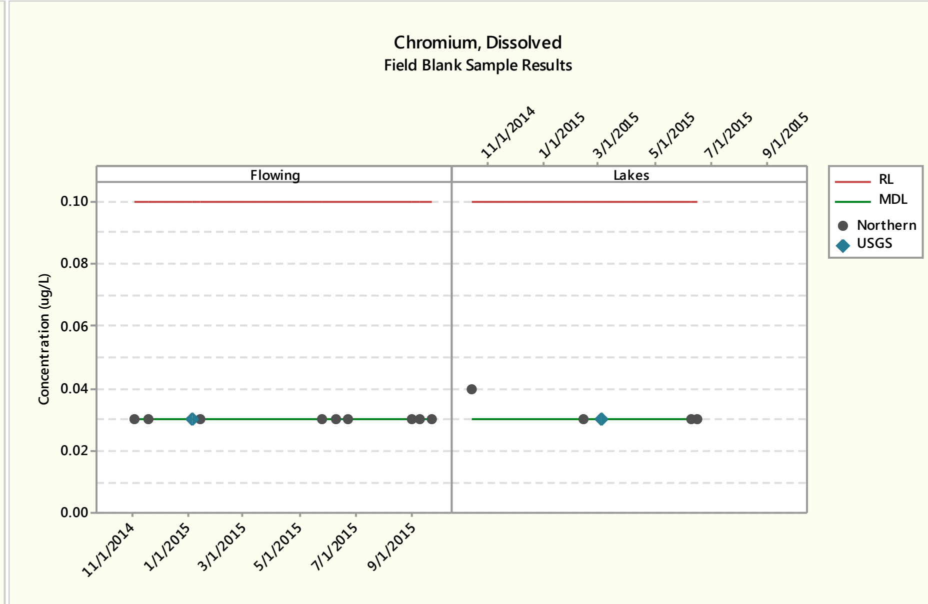

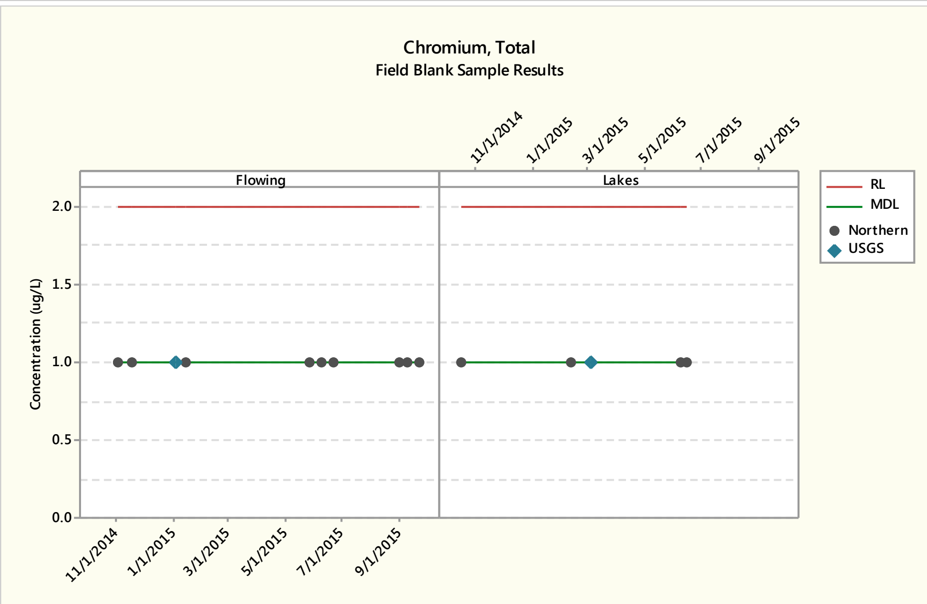

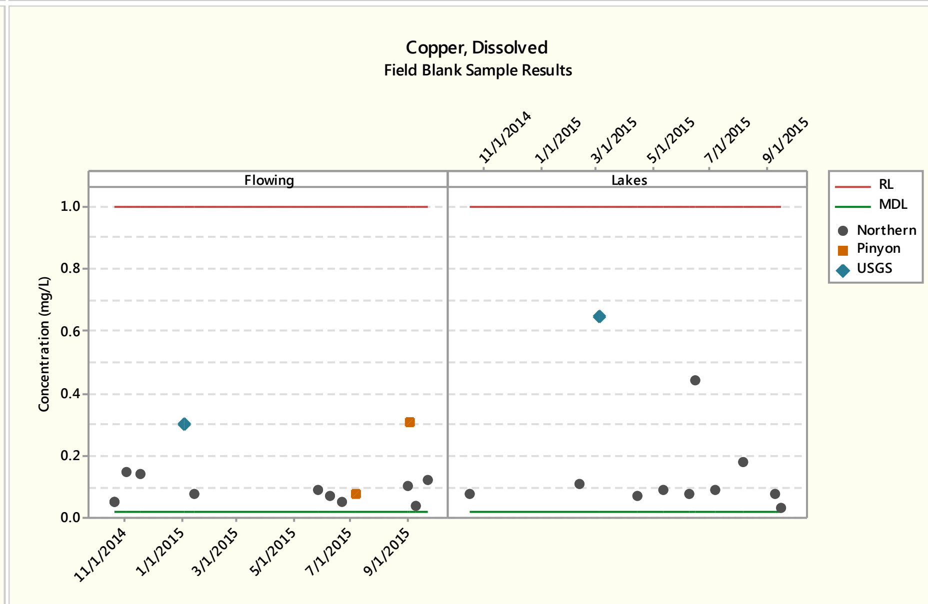

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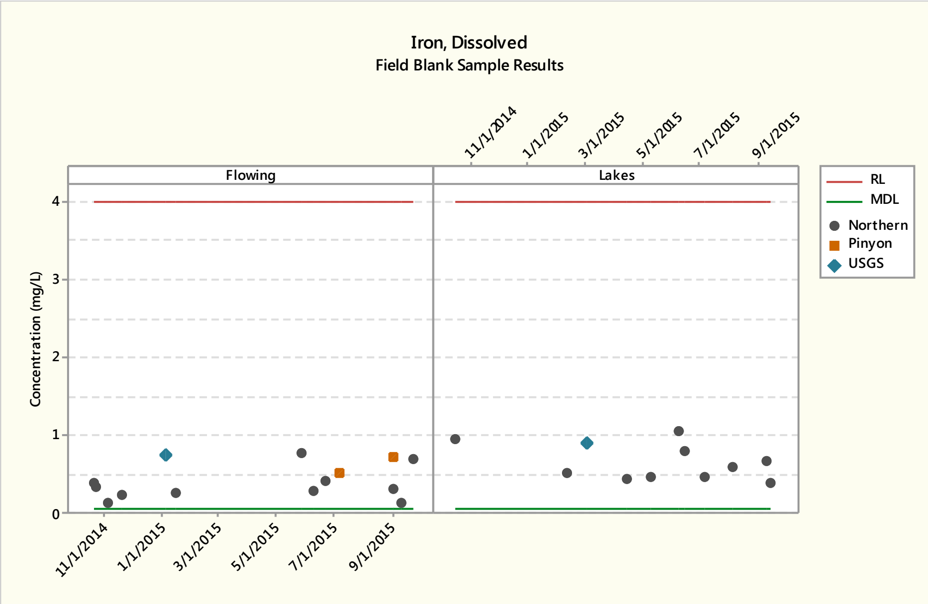

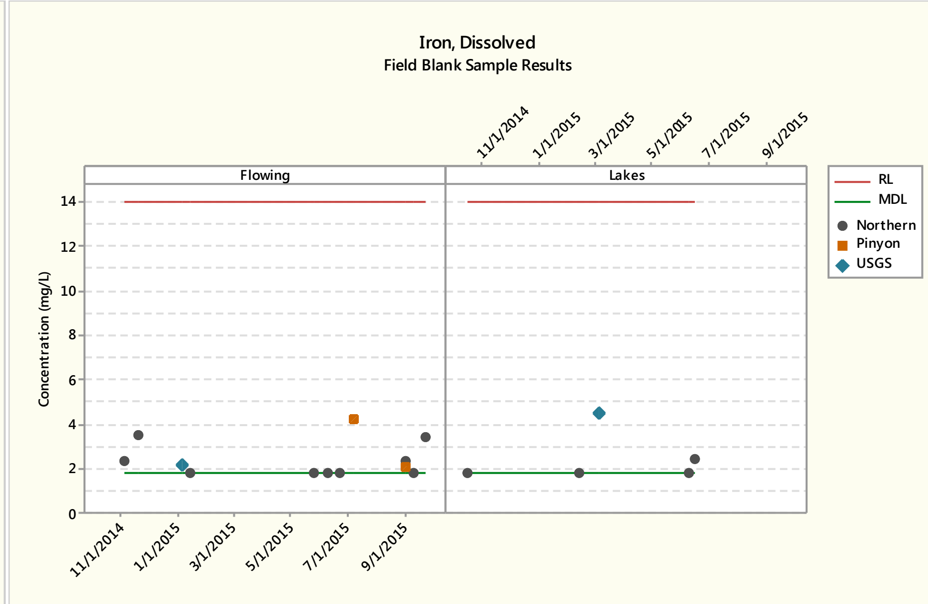

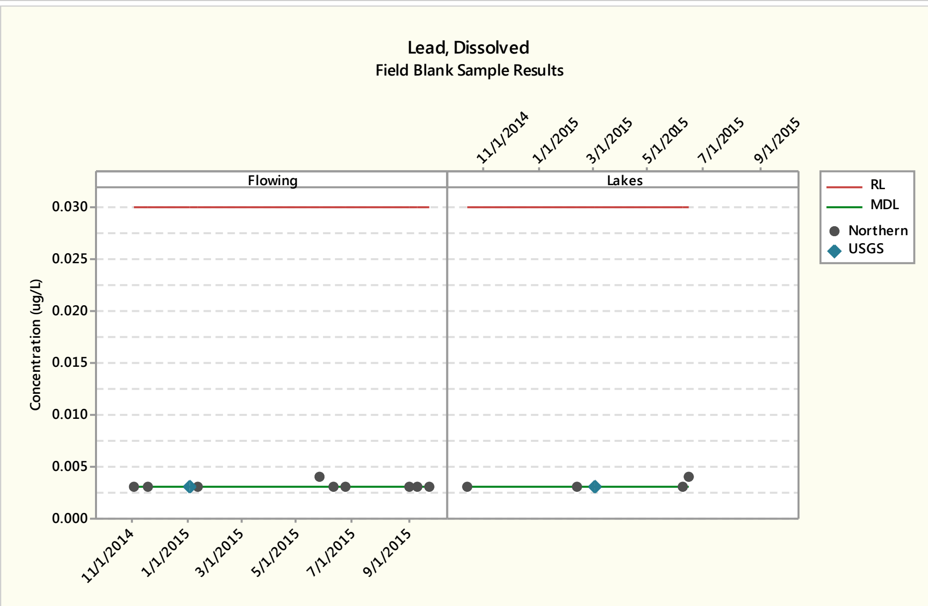

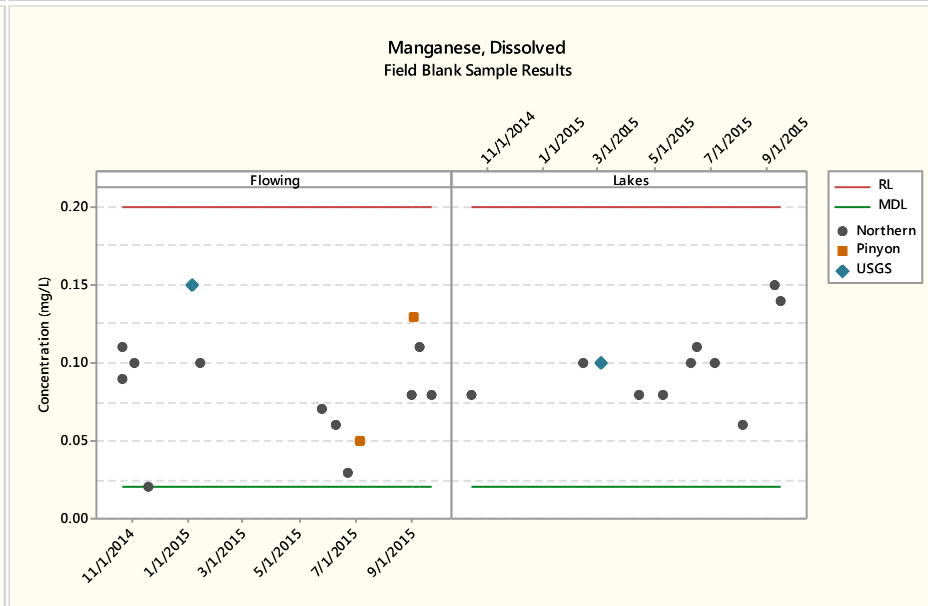

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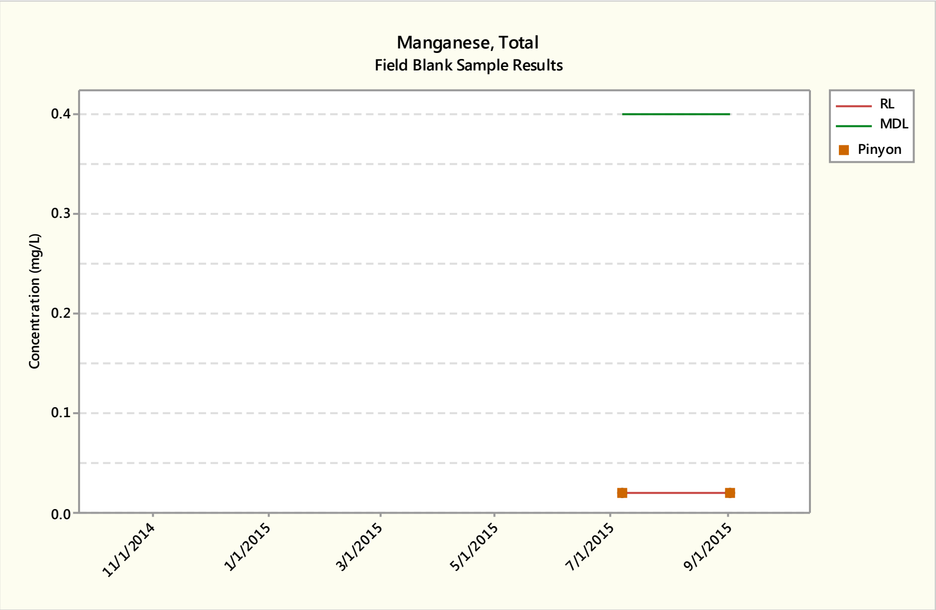

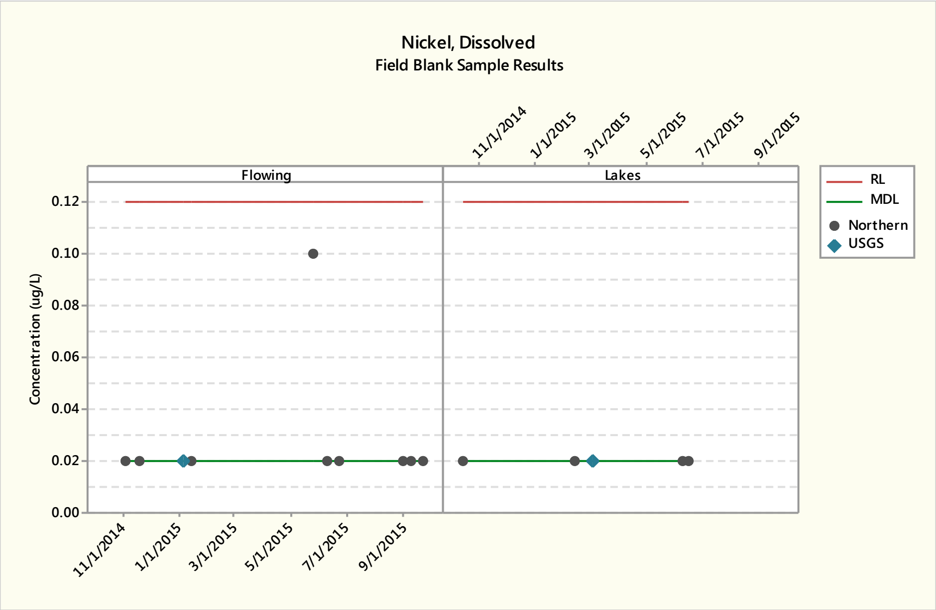

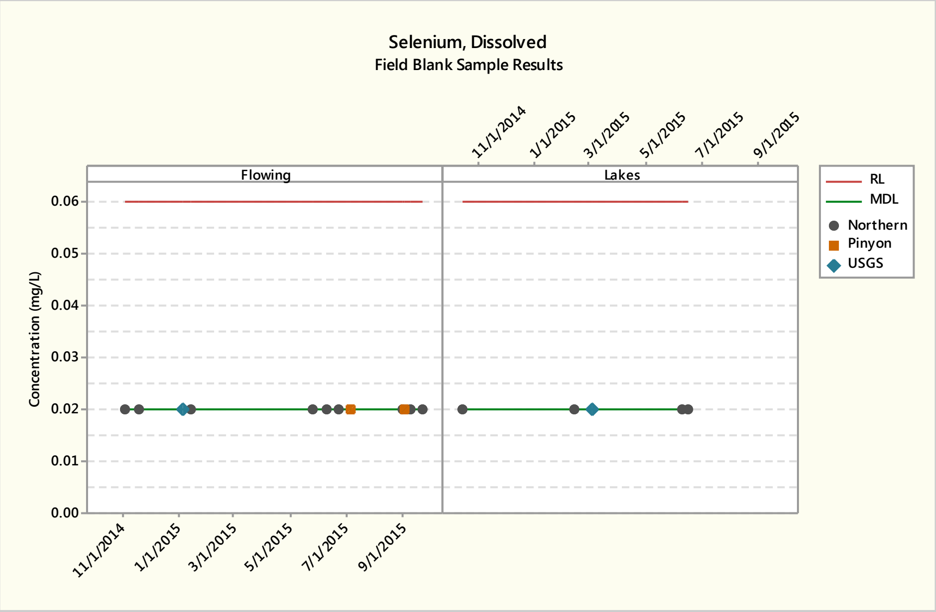

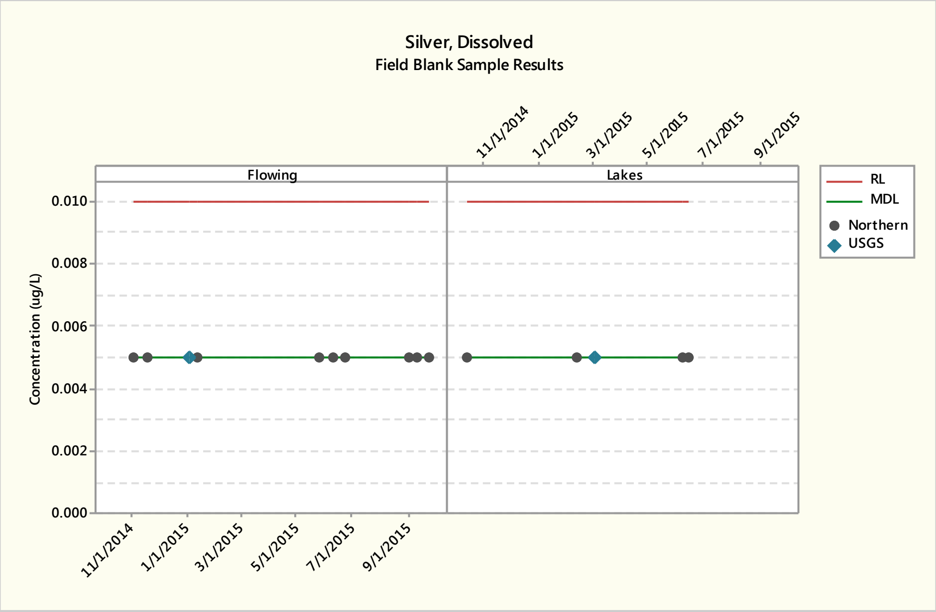

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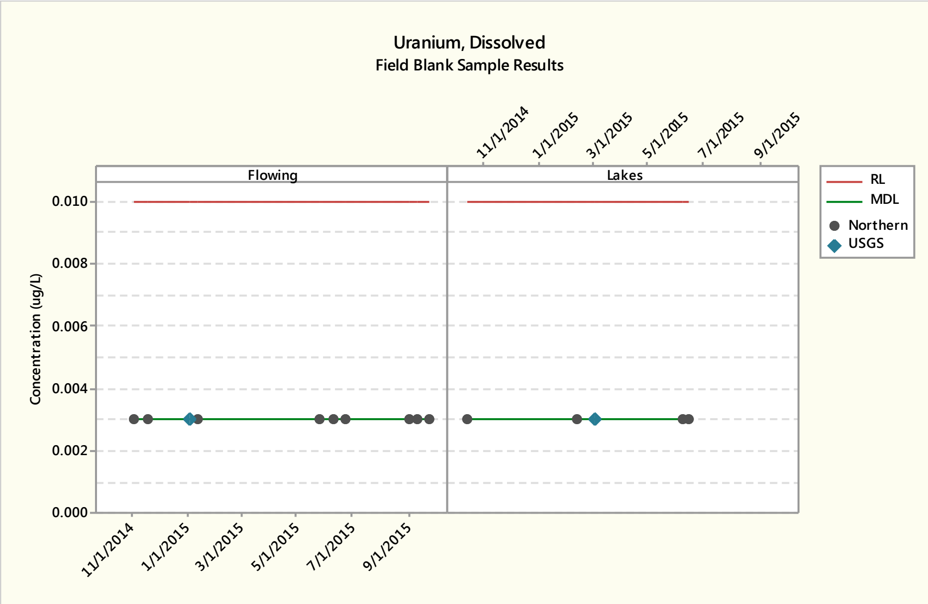

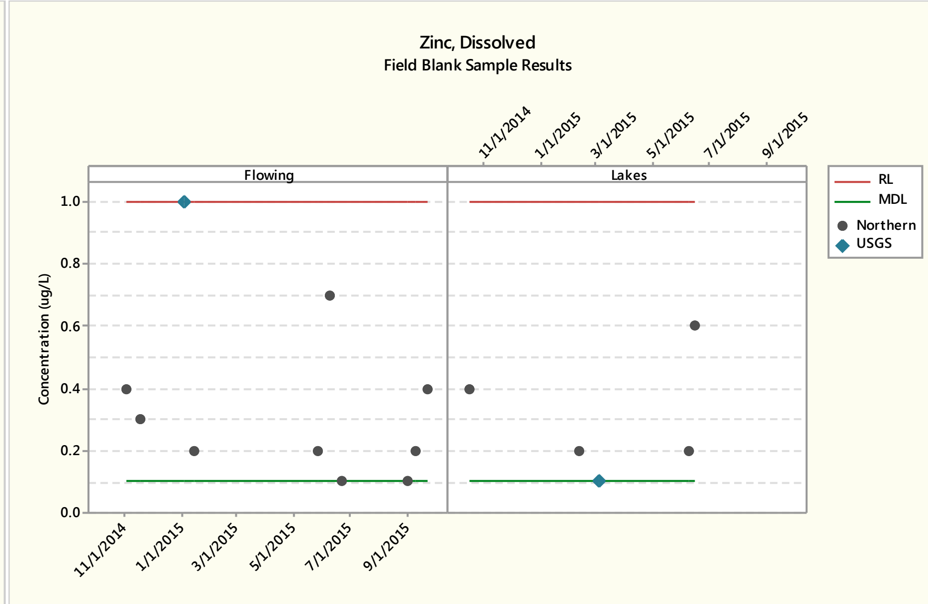

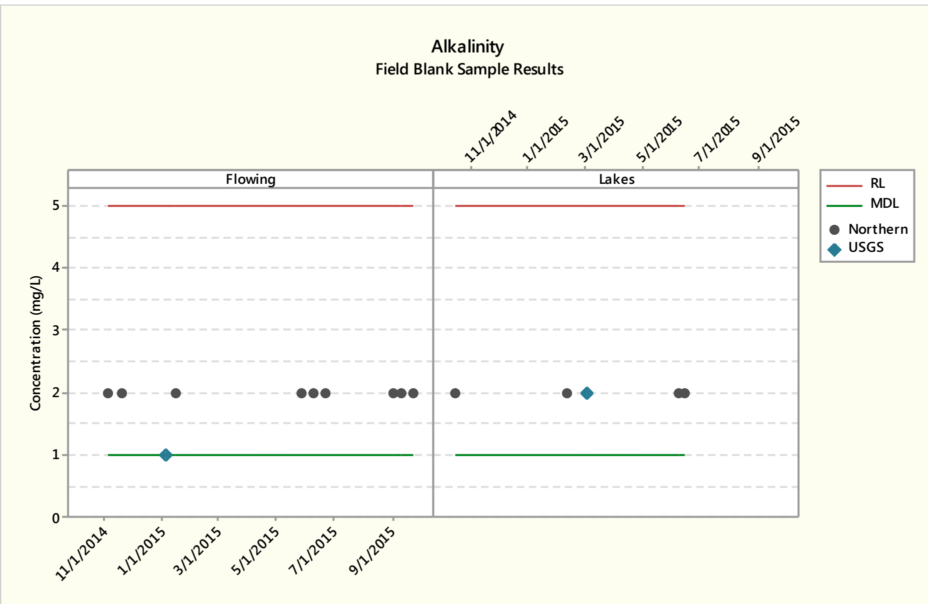

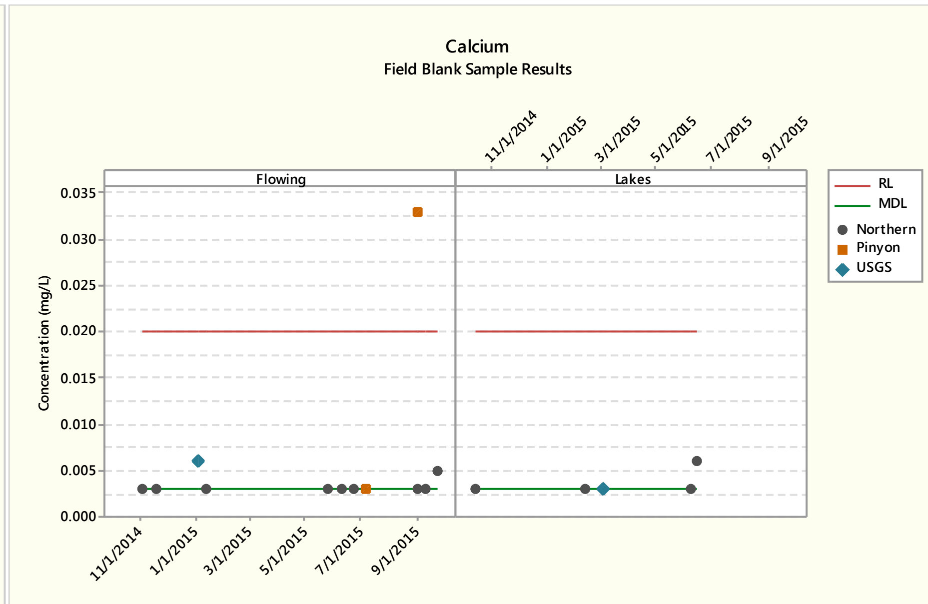

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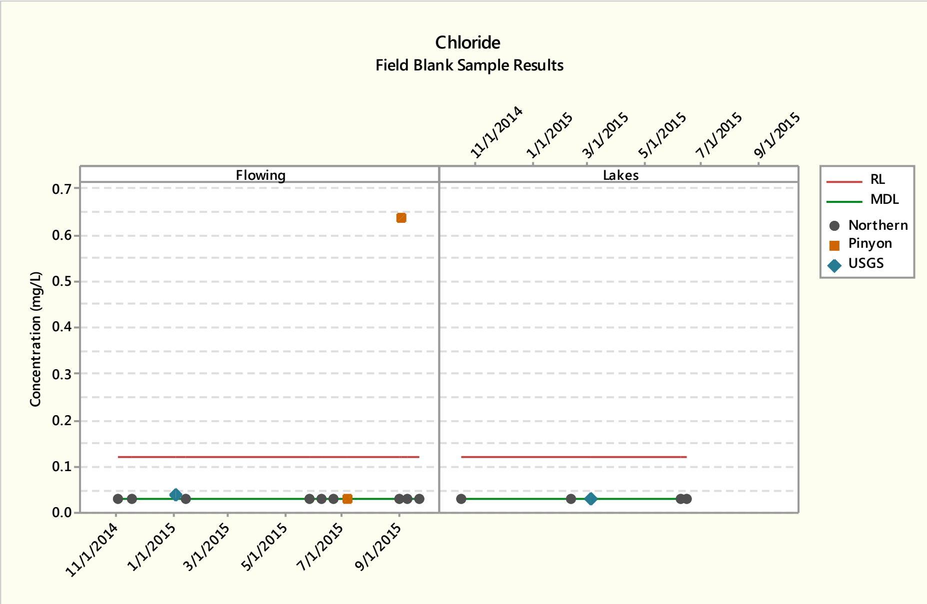

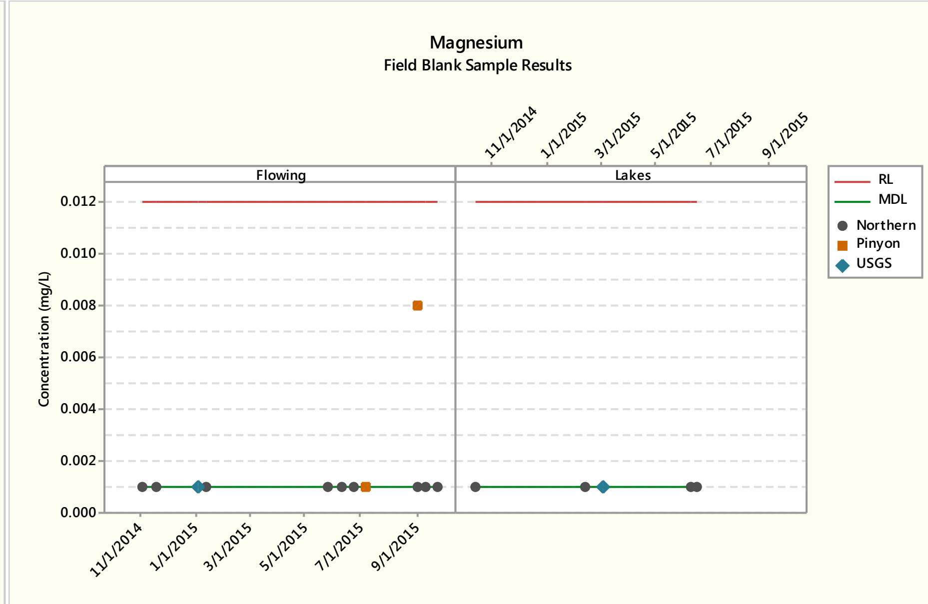

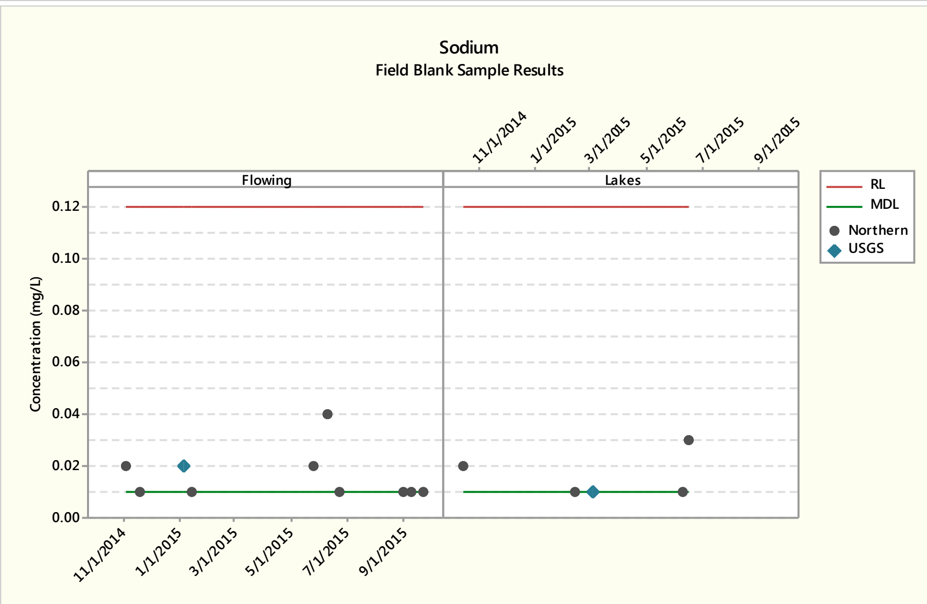

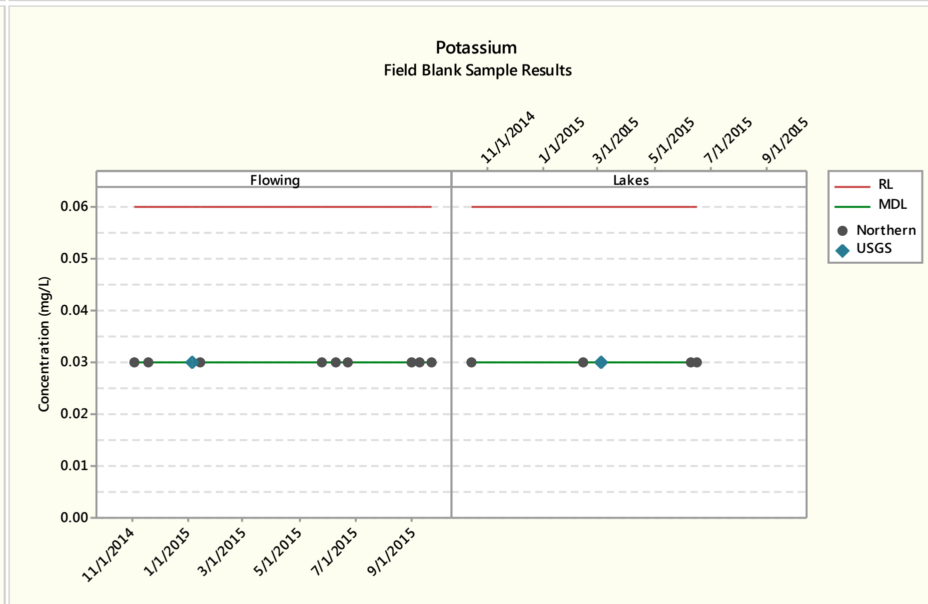

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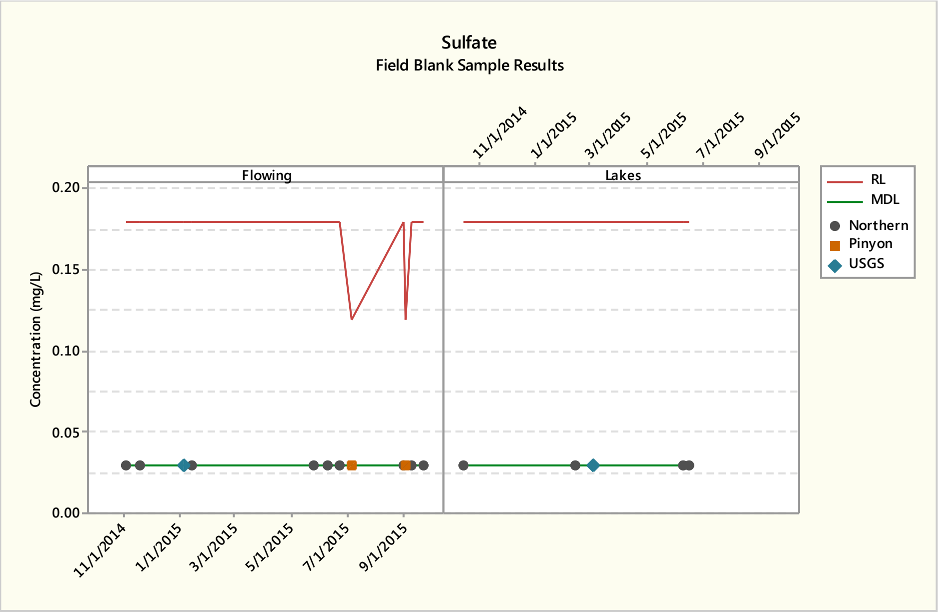

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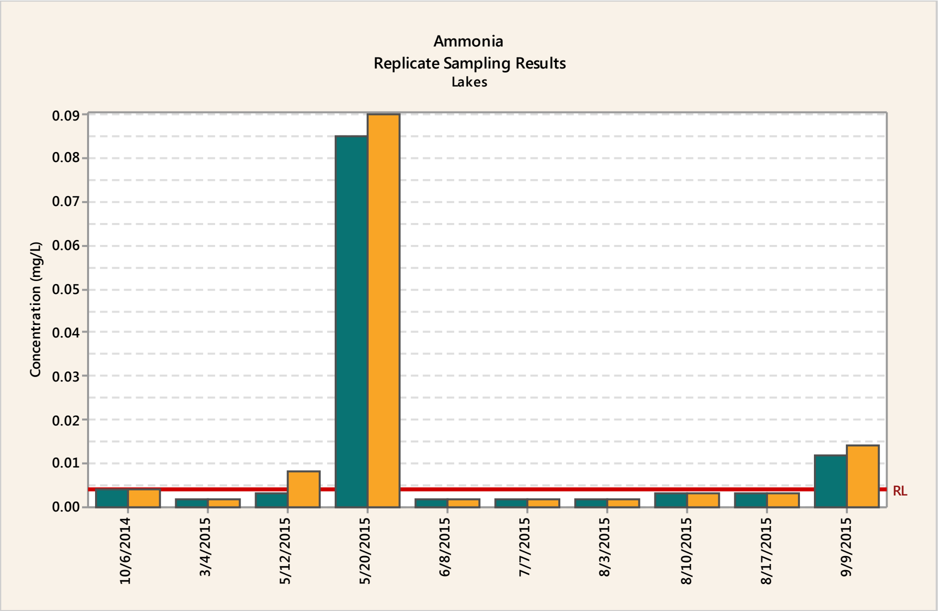

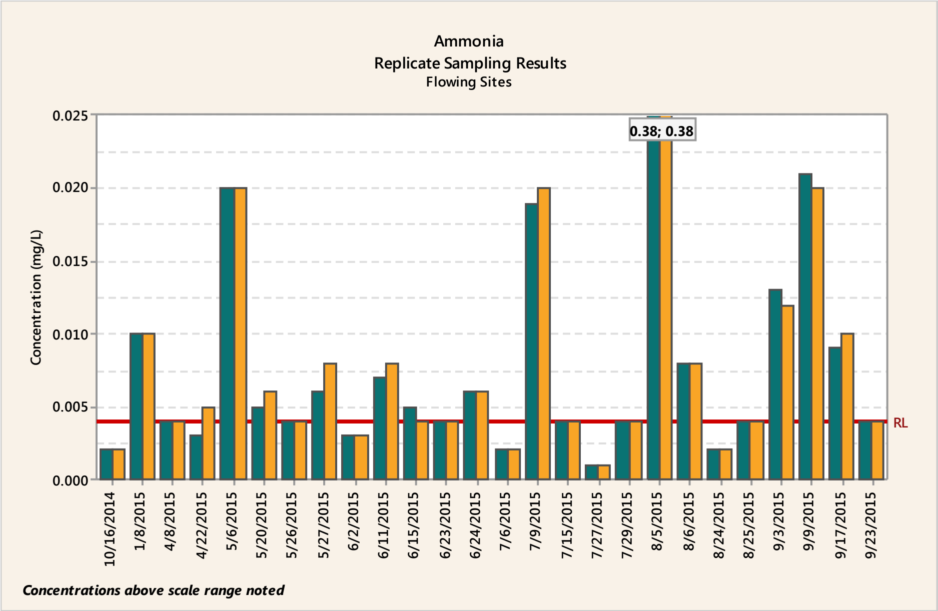

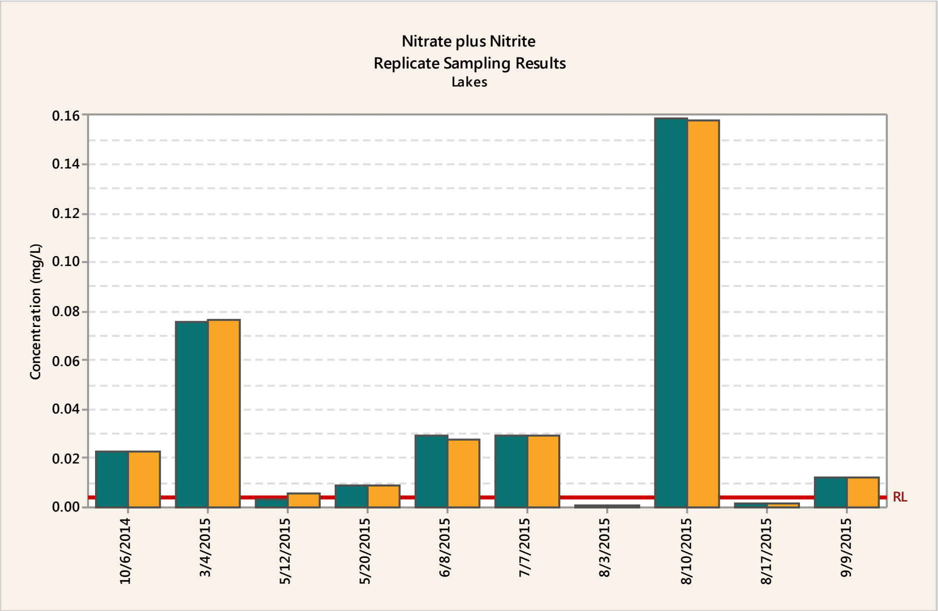

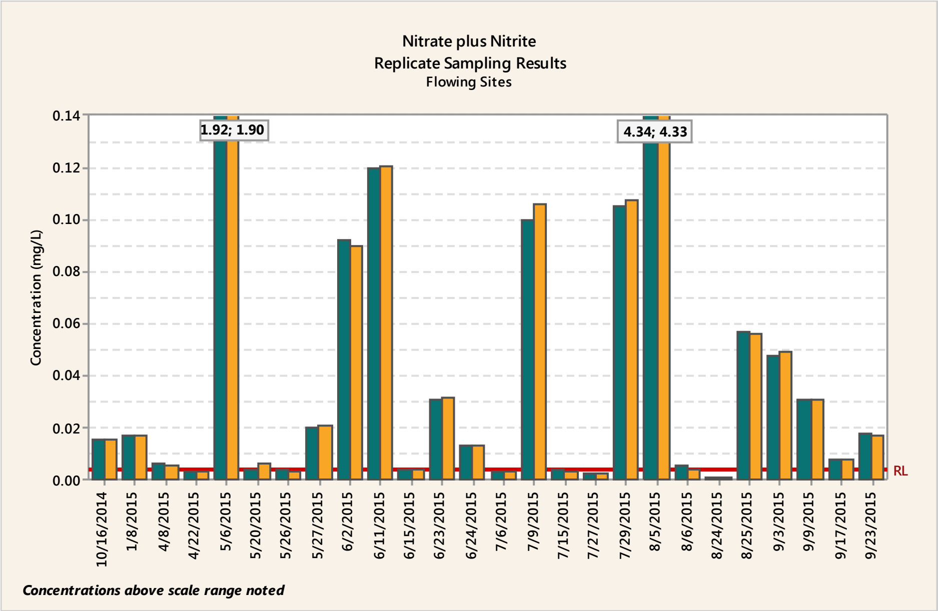

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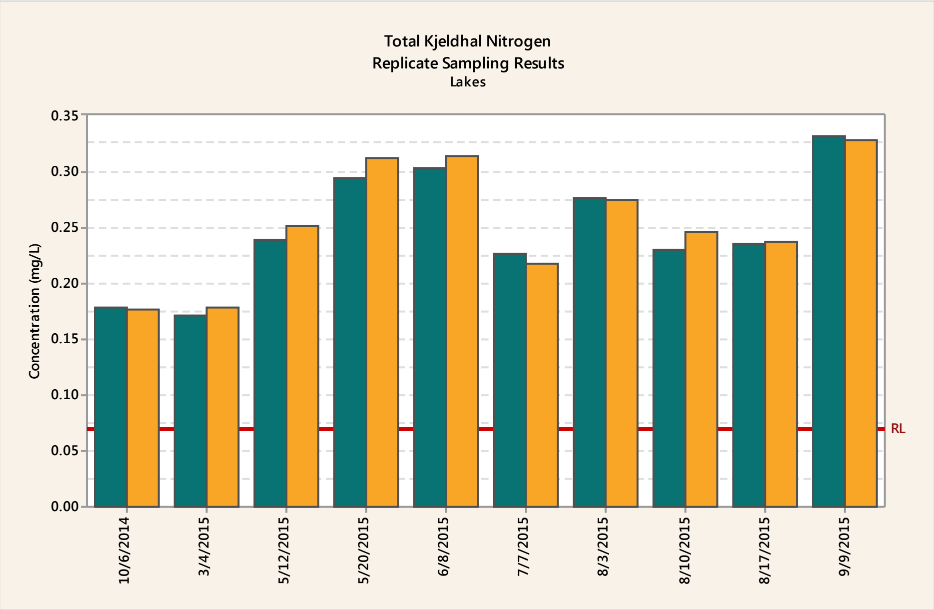
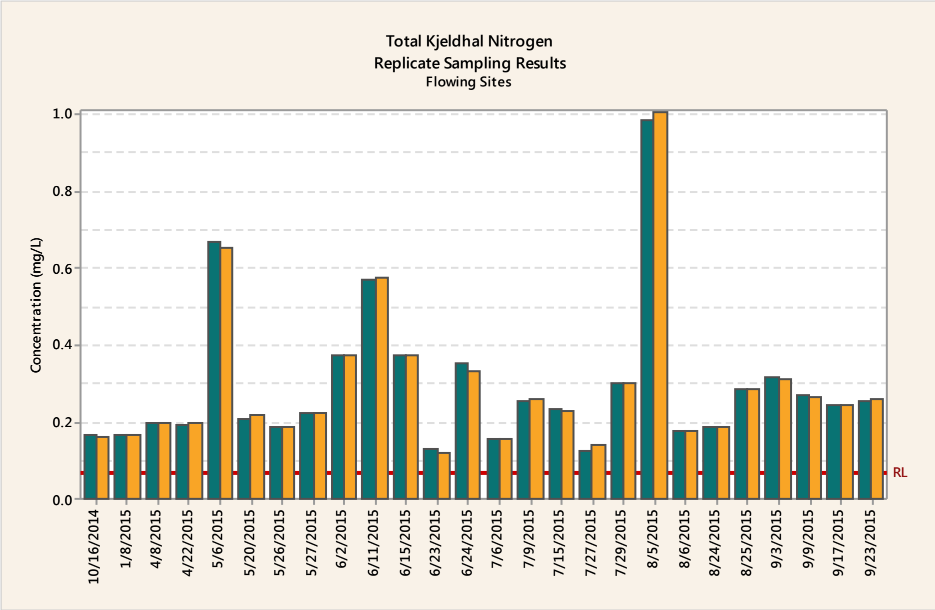
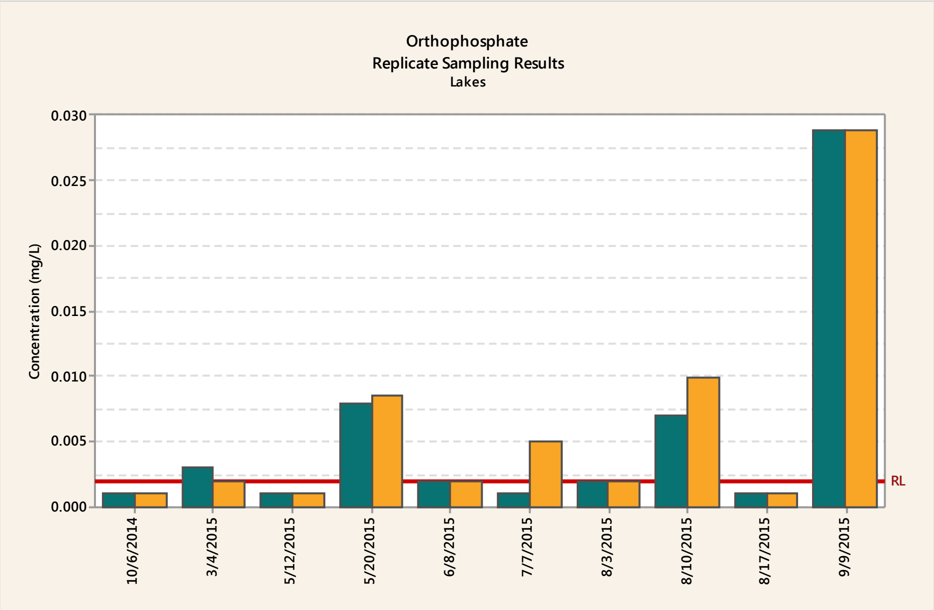
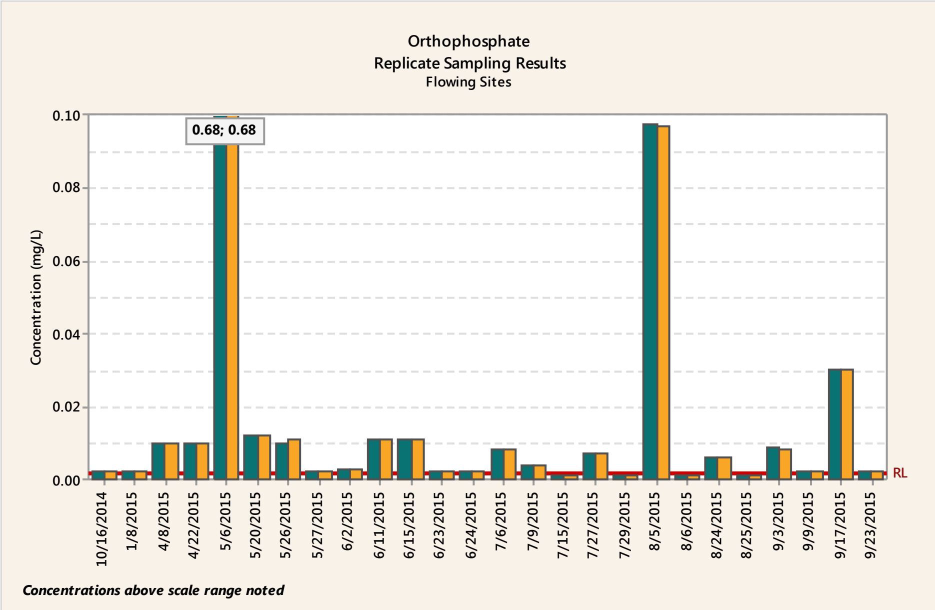
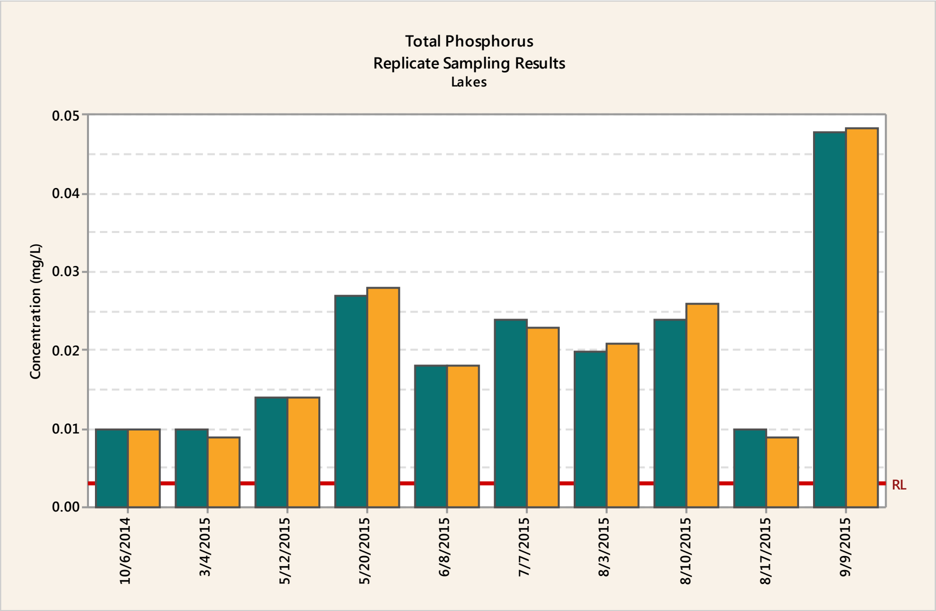


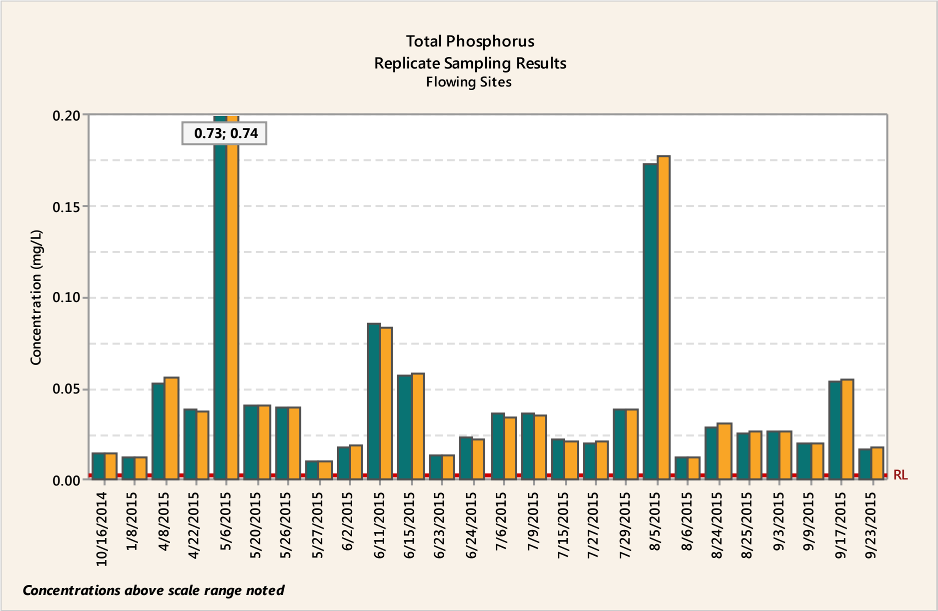


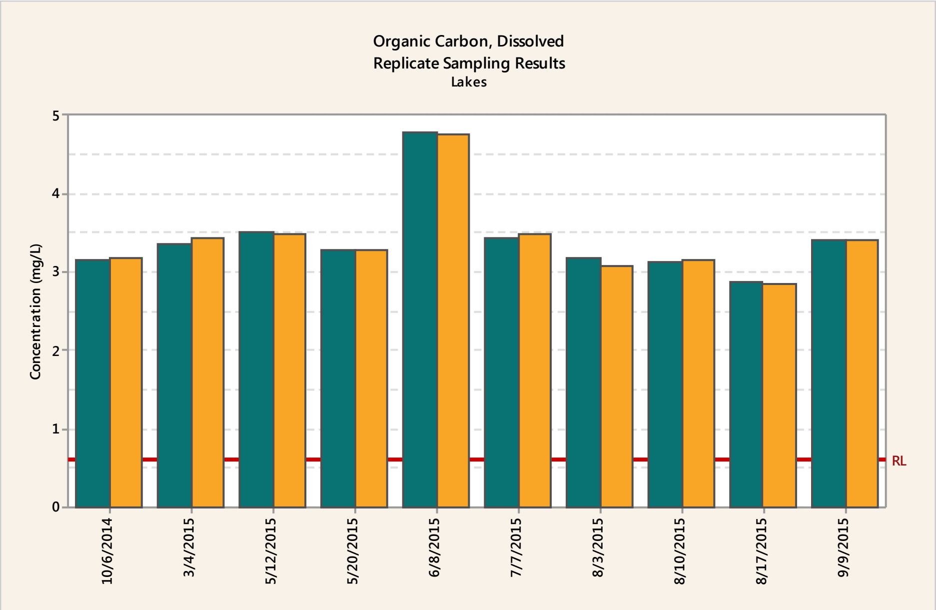


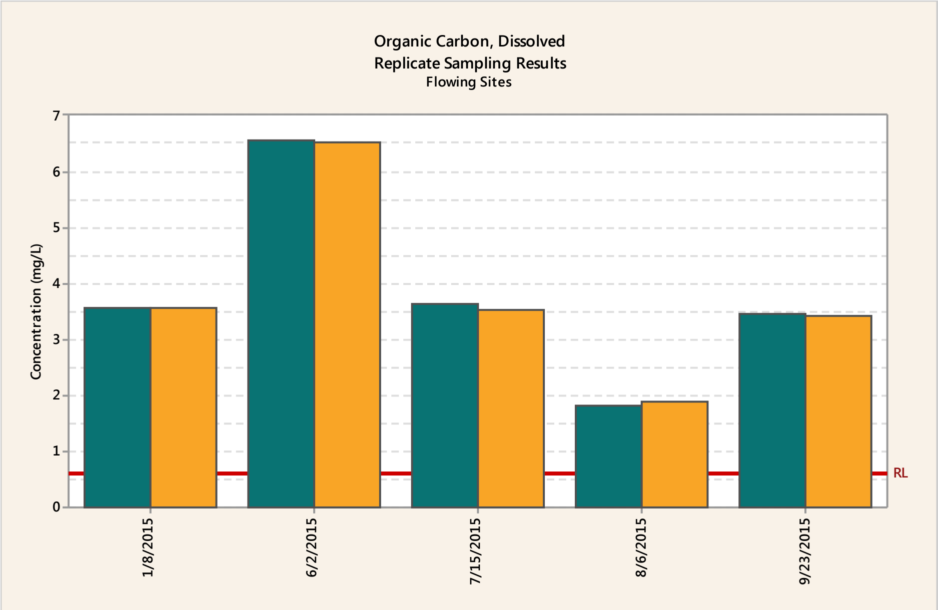


Appendix 2 – Field Replicate Results









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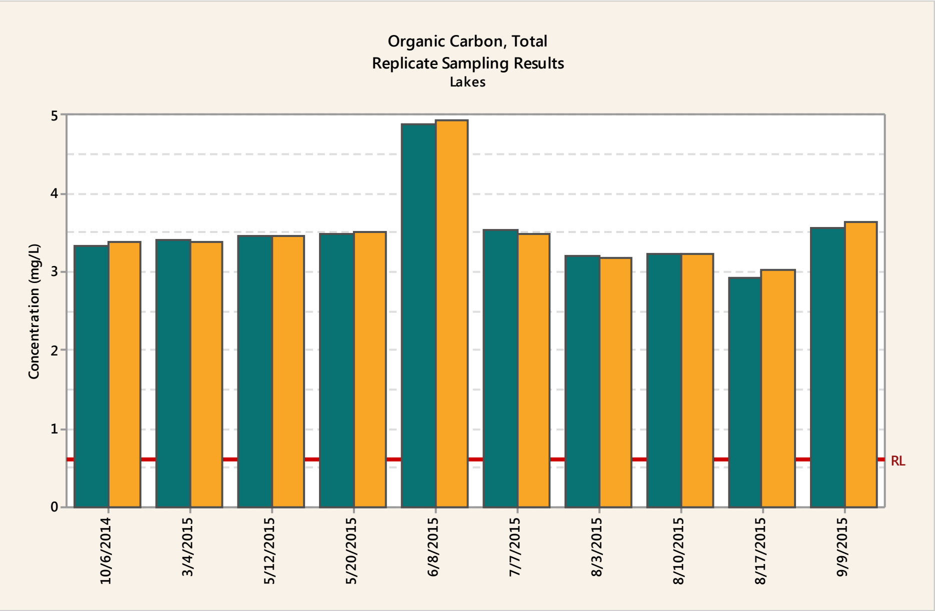

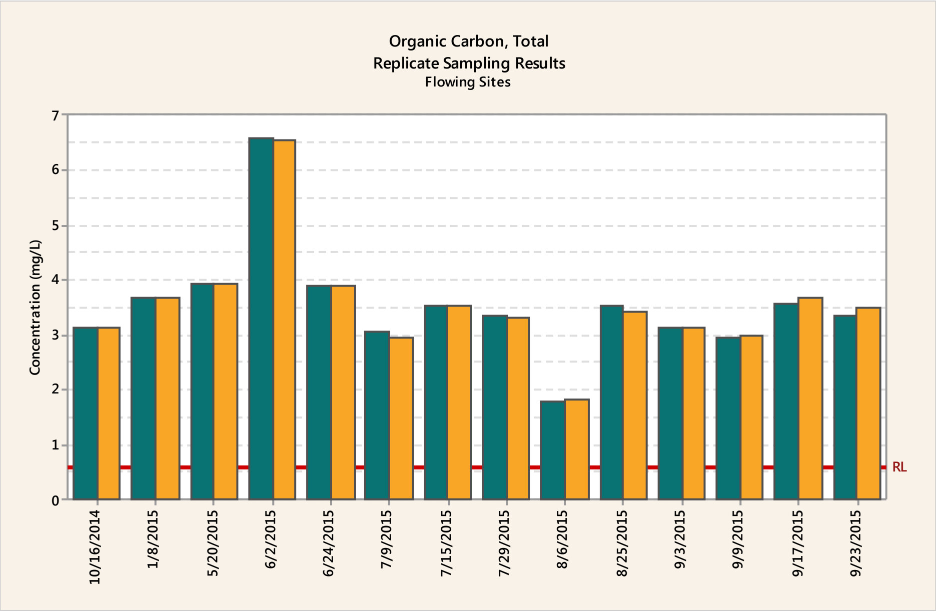

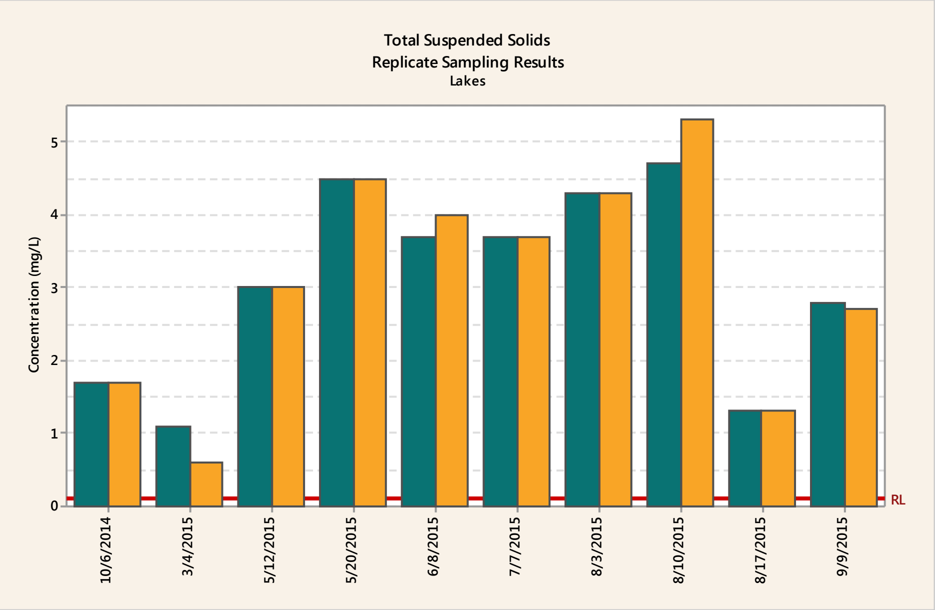

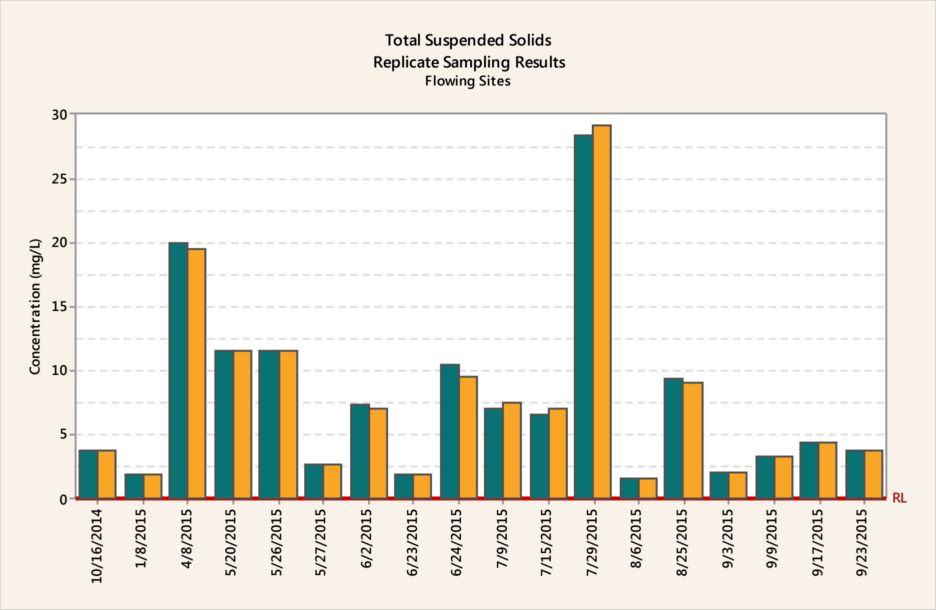

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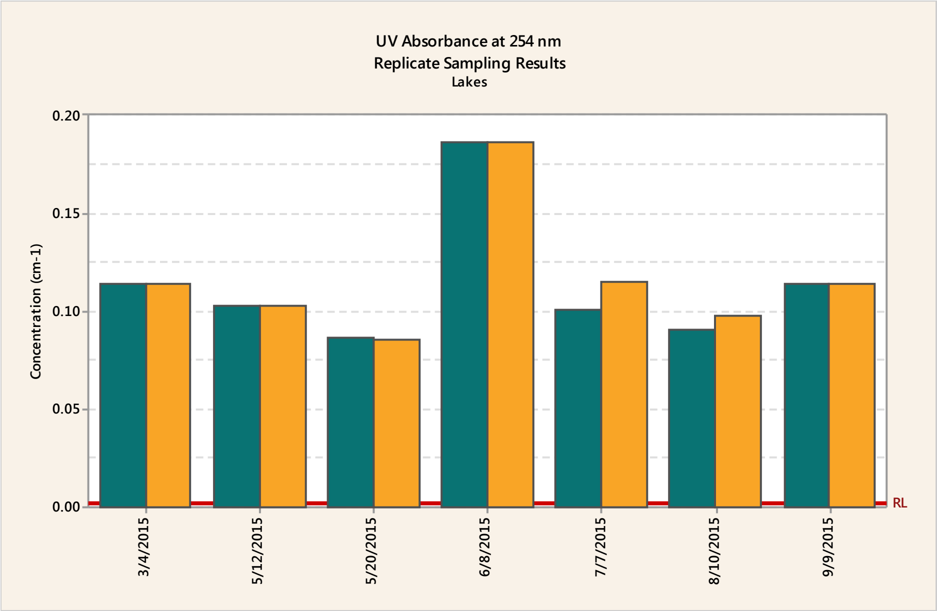

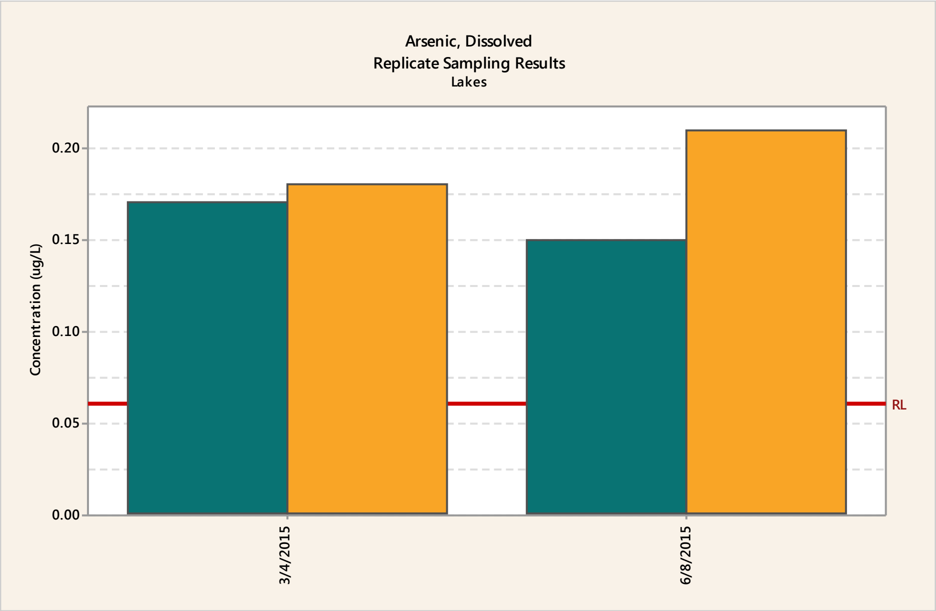

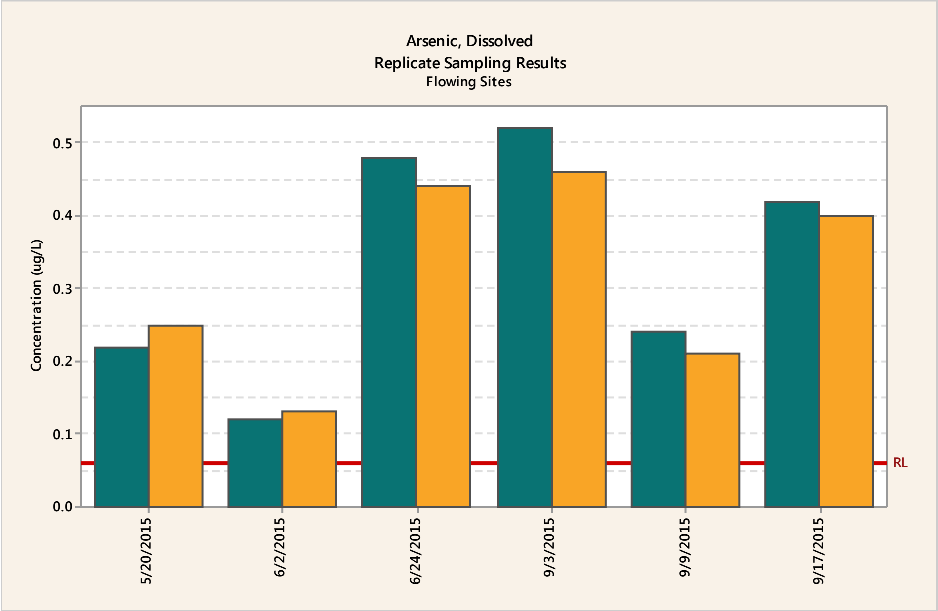

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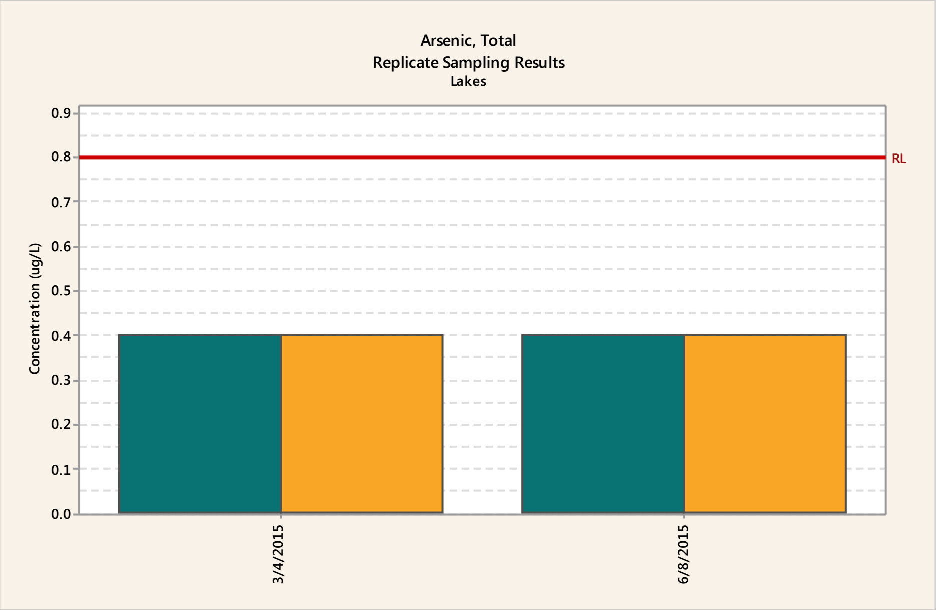

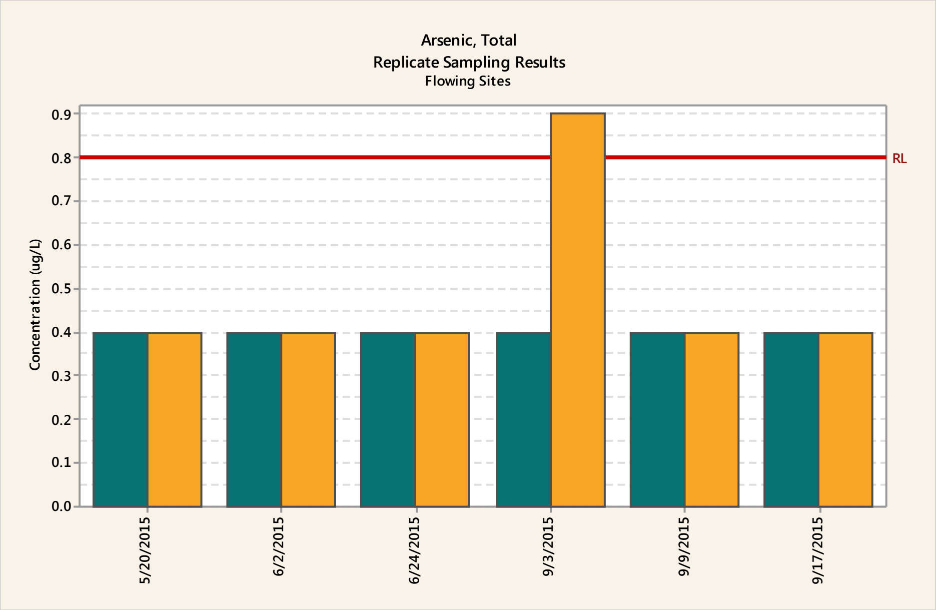

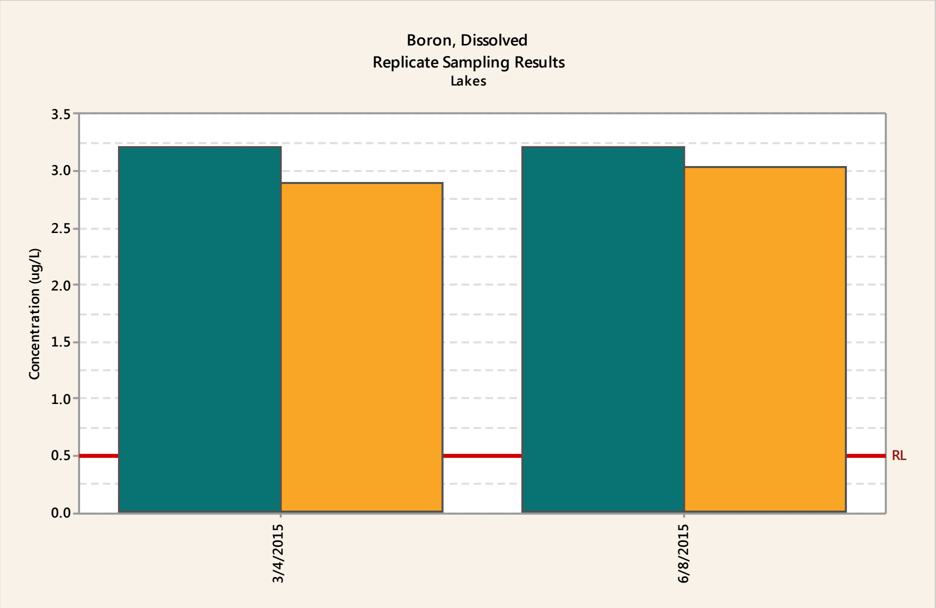

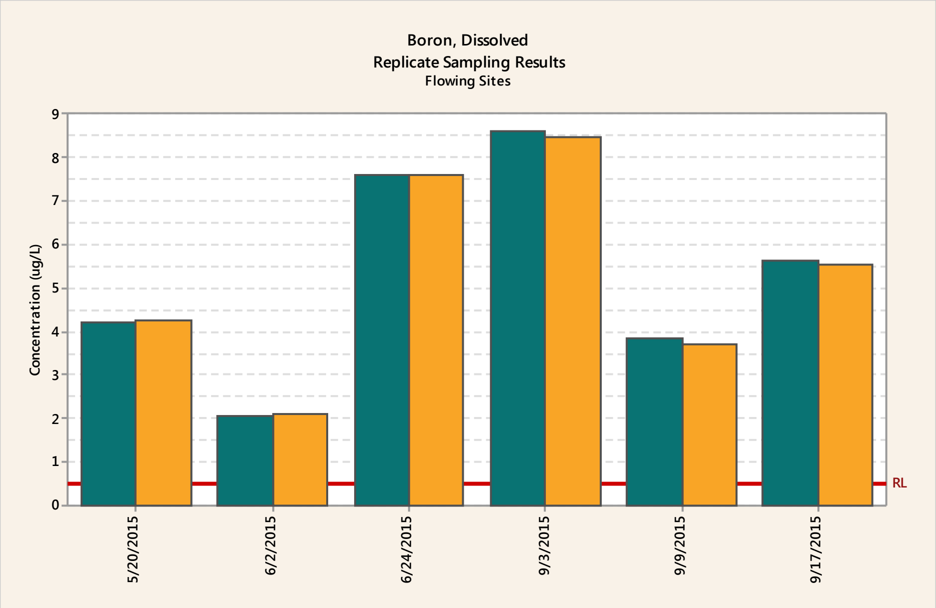

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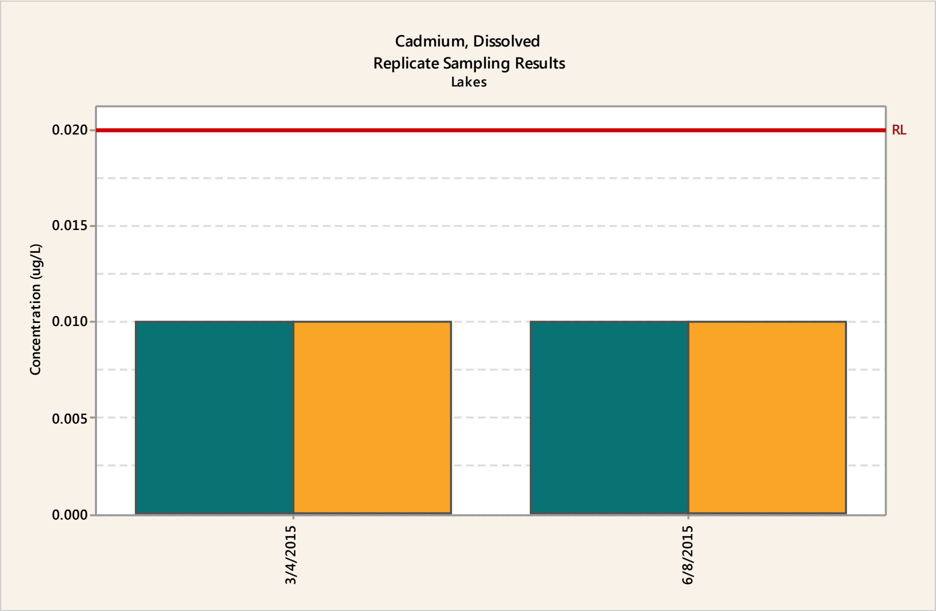

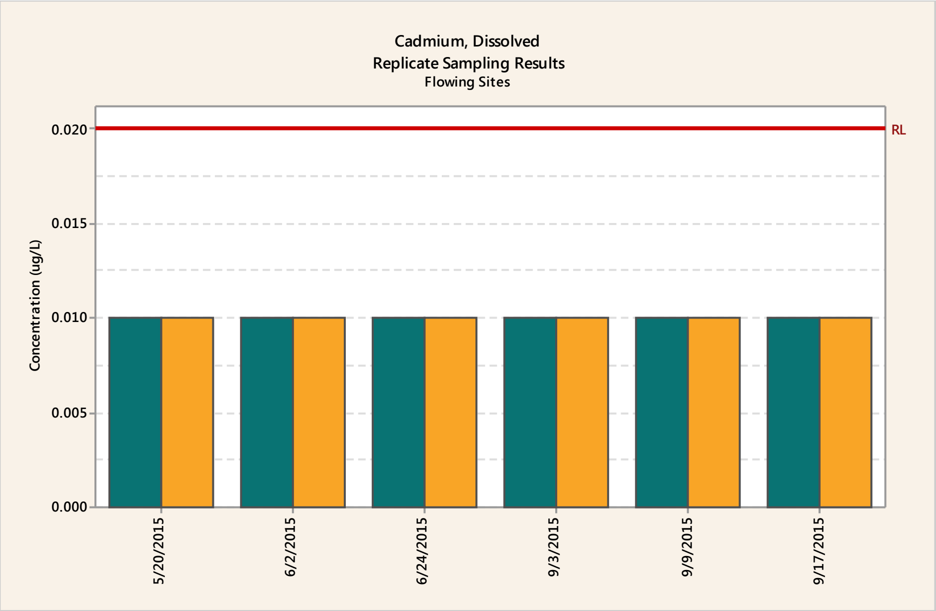

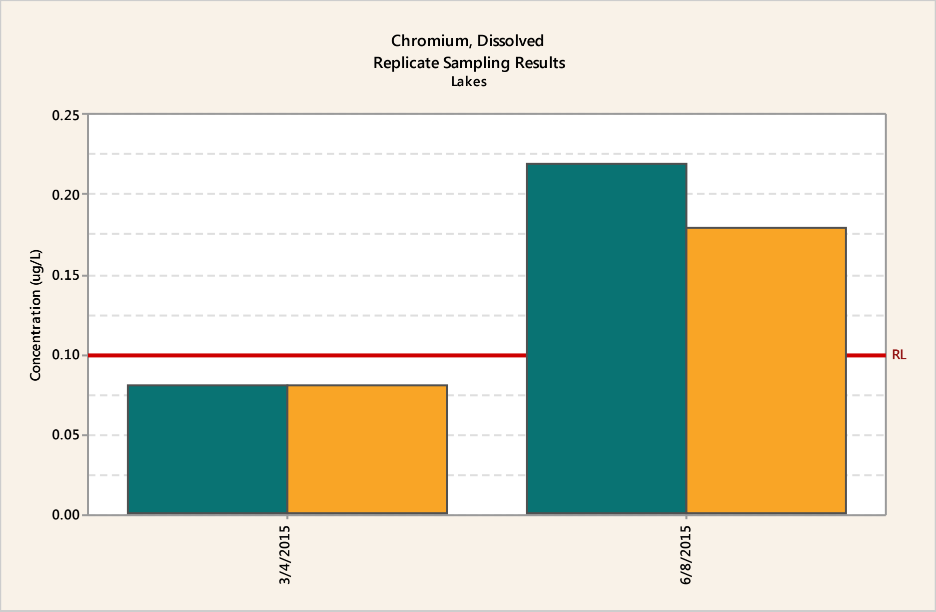

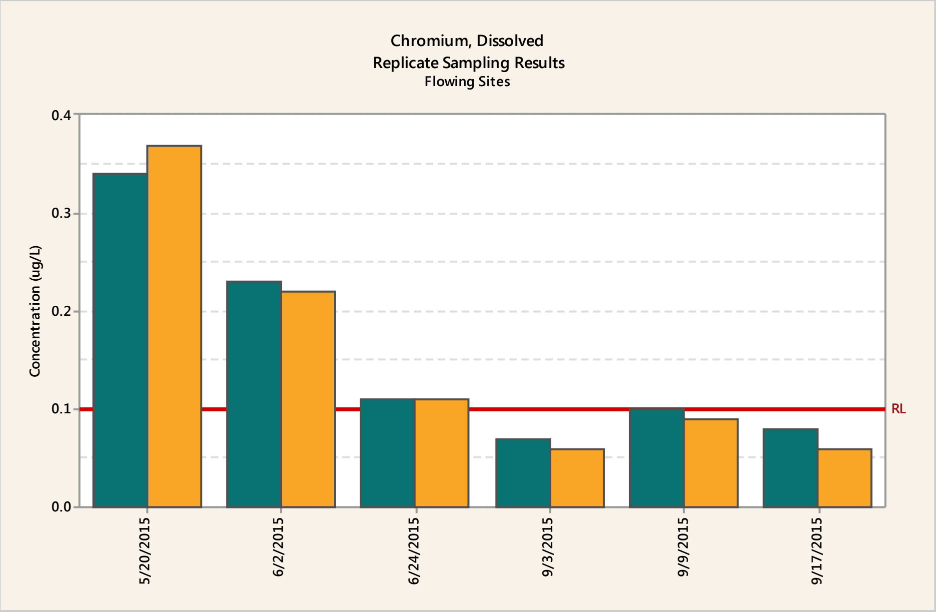

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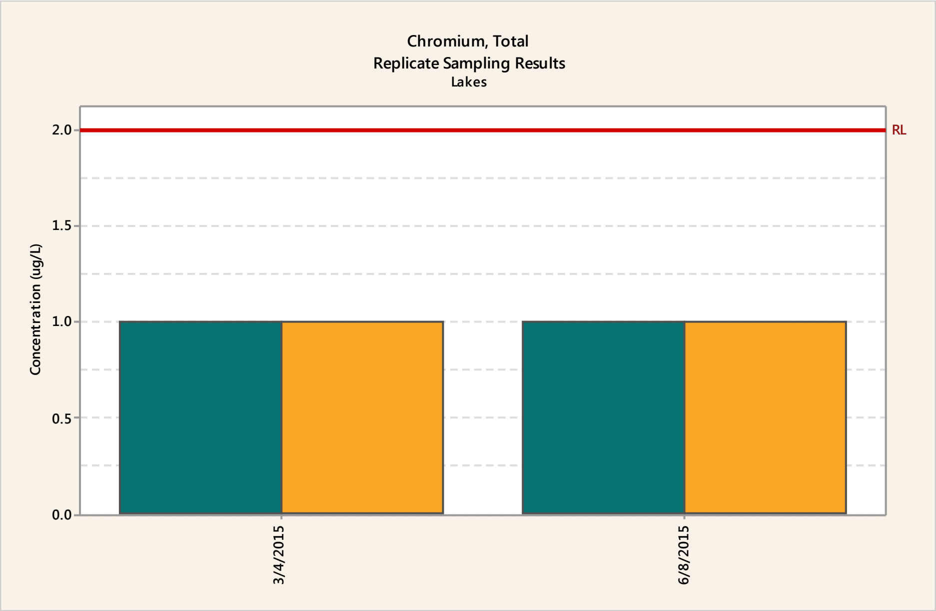

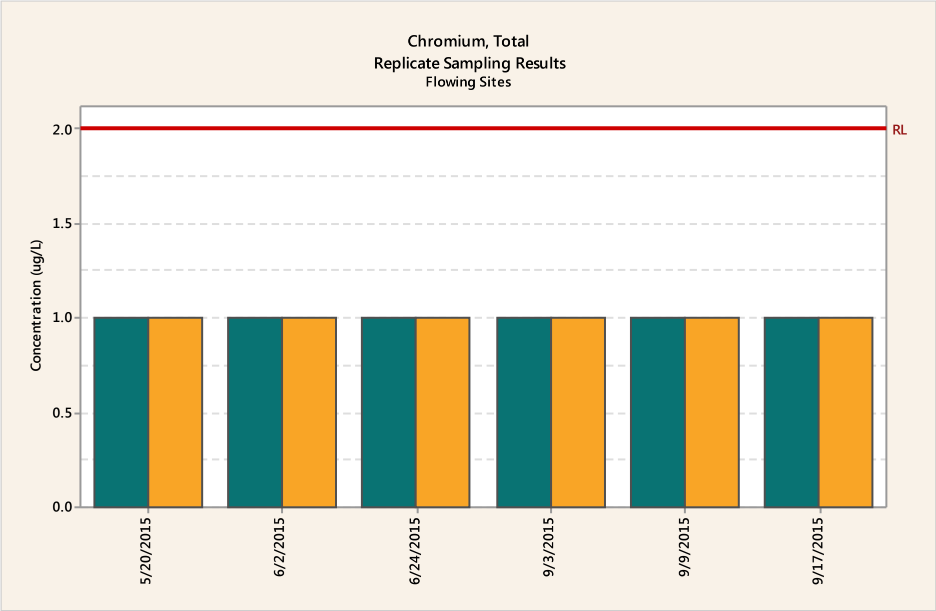

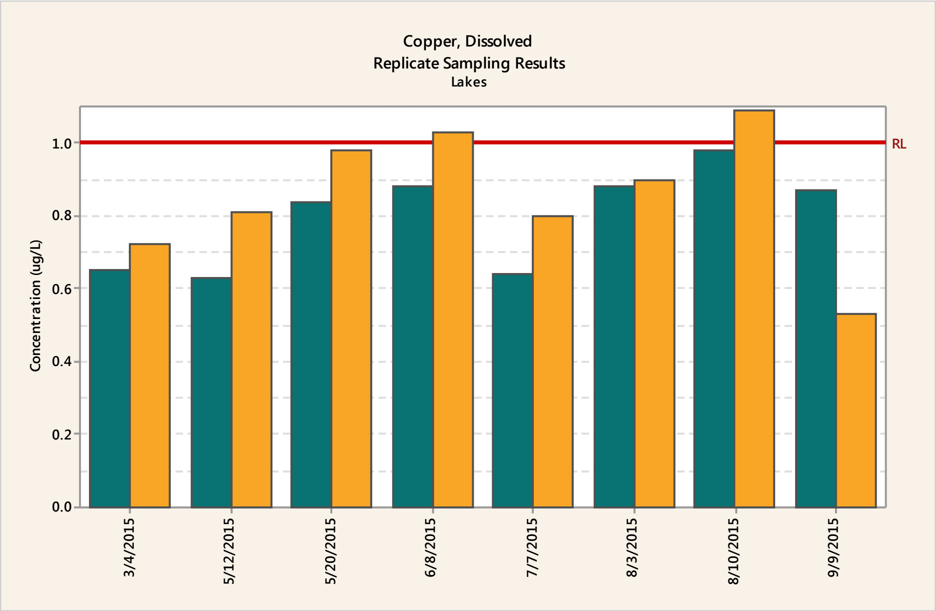

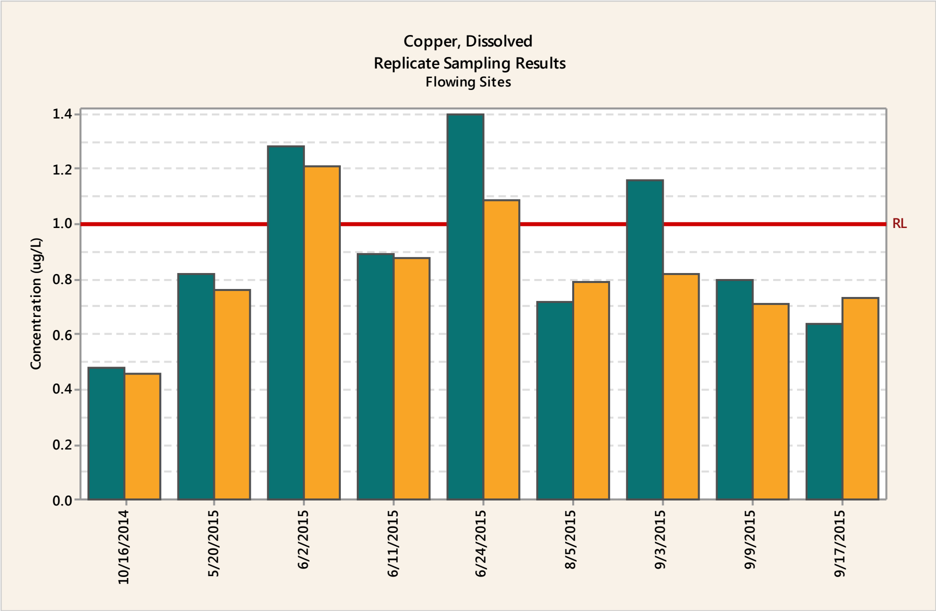

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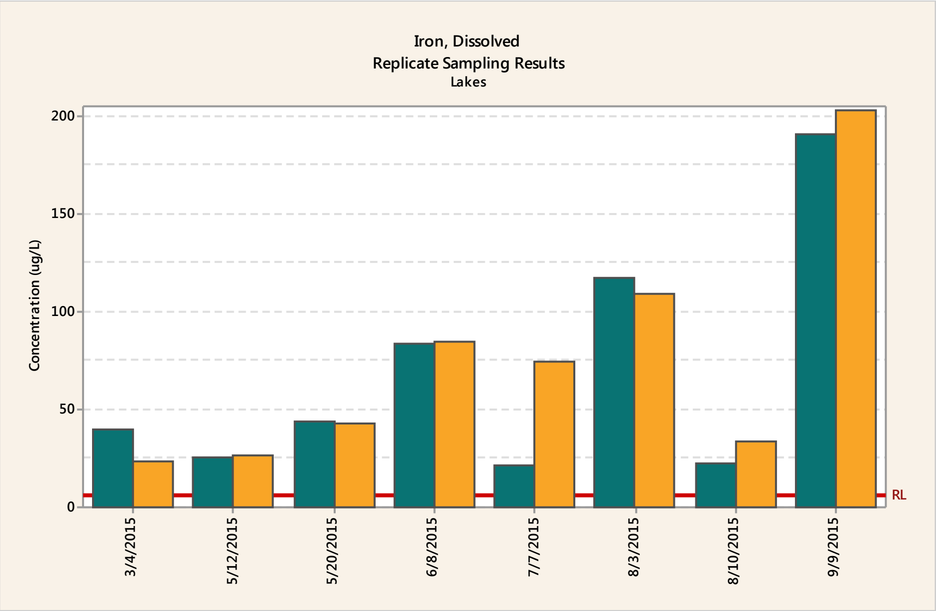

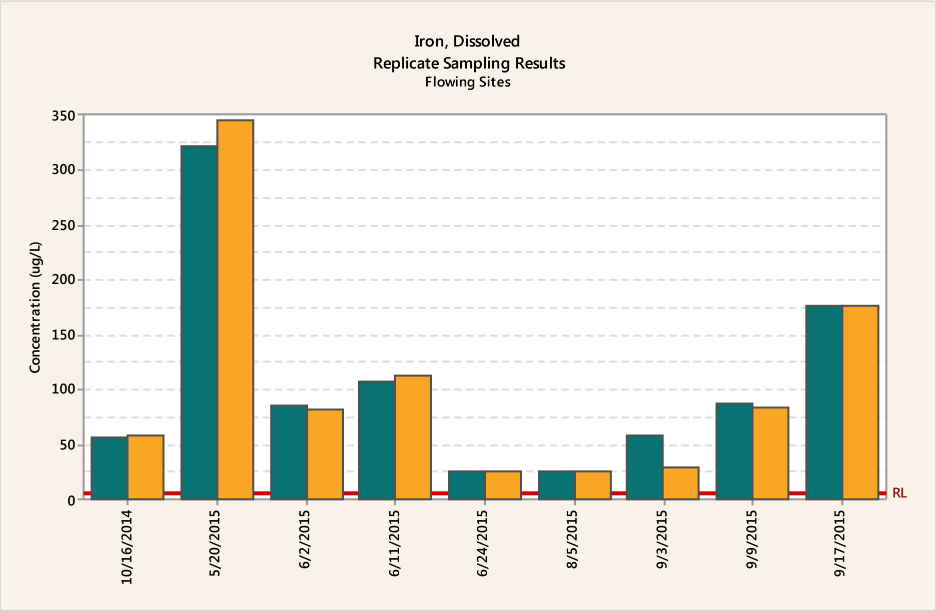

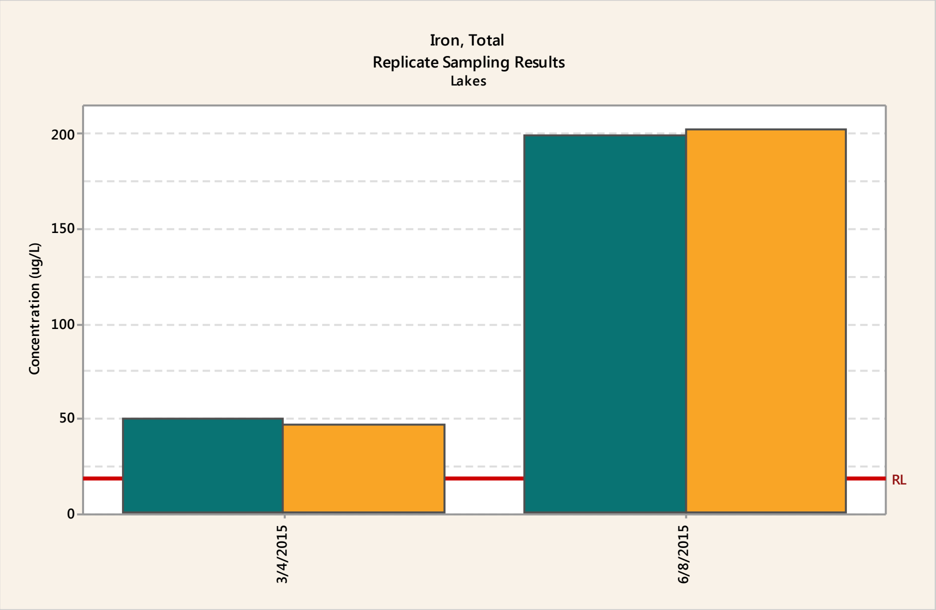

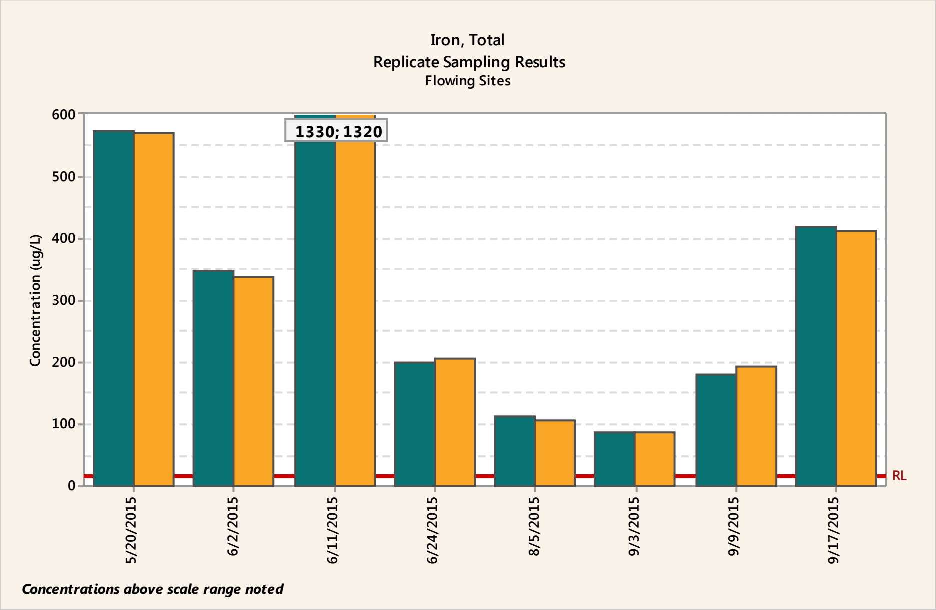

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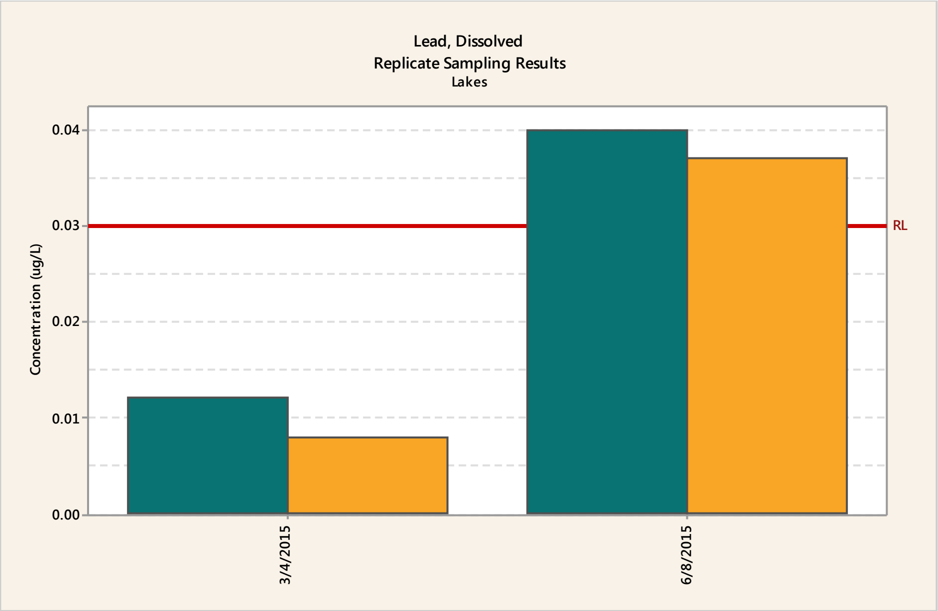

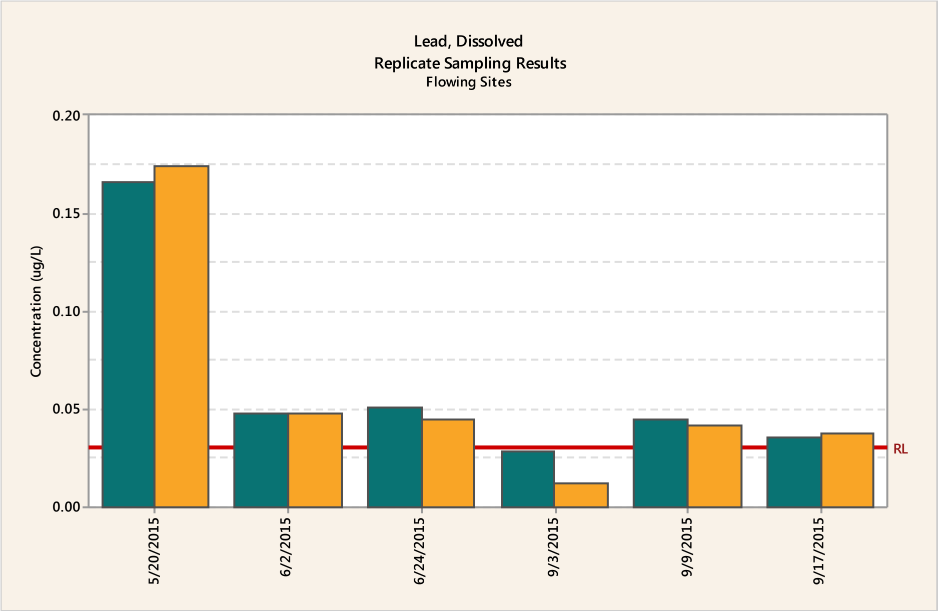

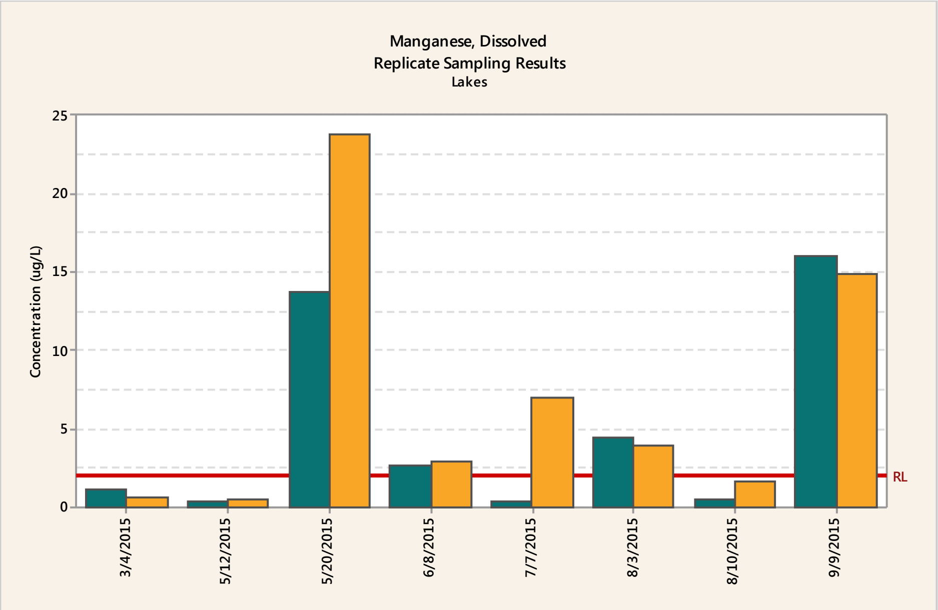

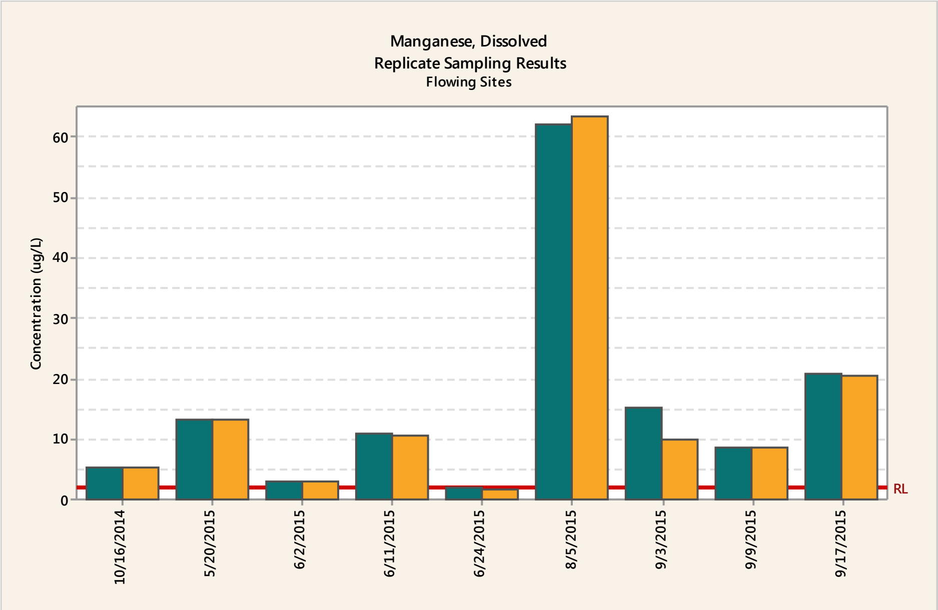

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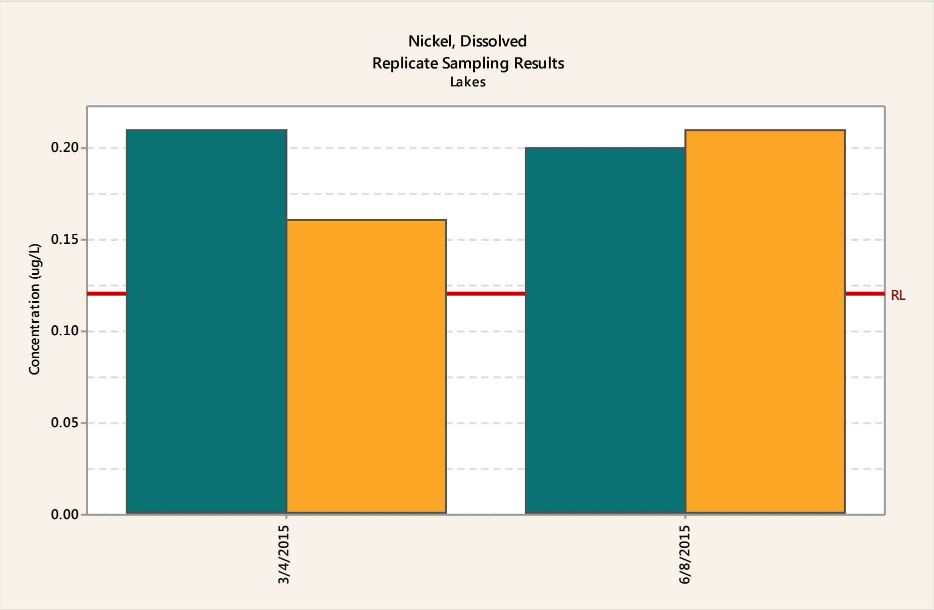

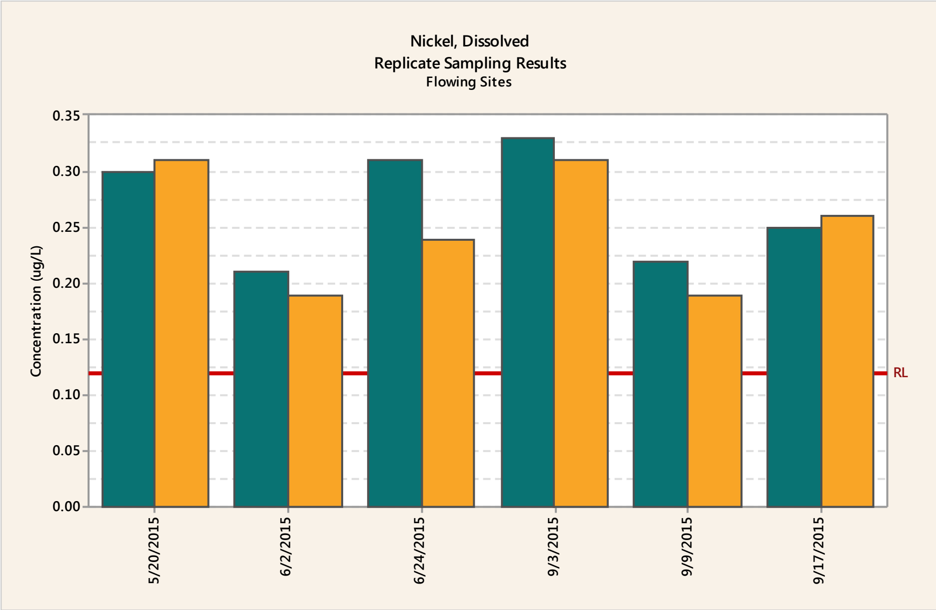

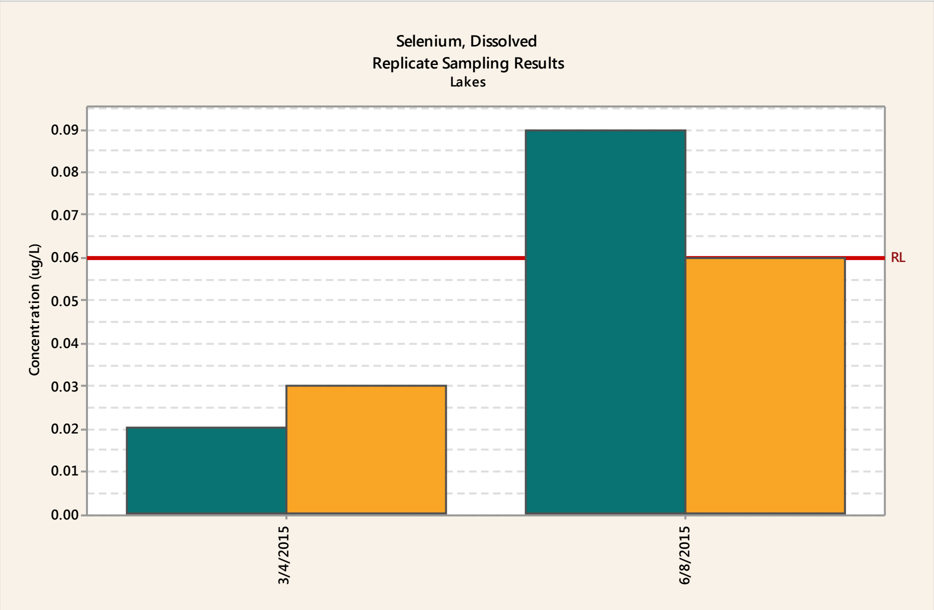

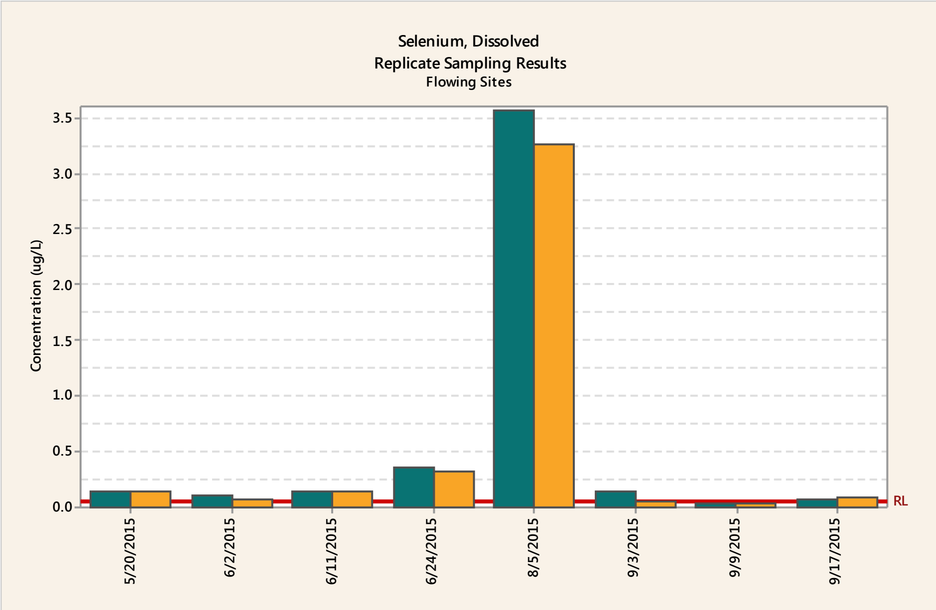

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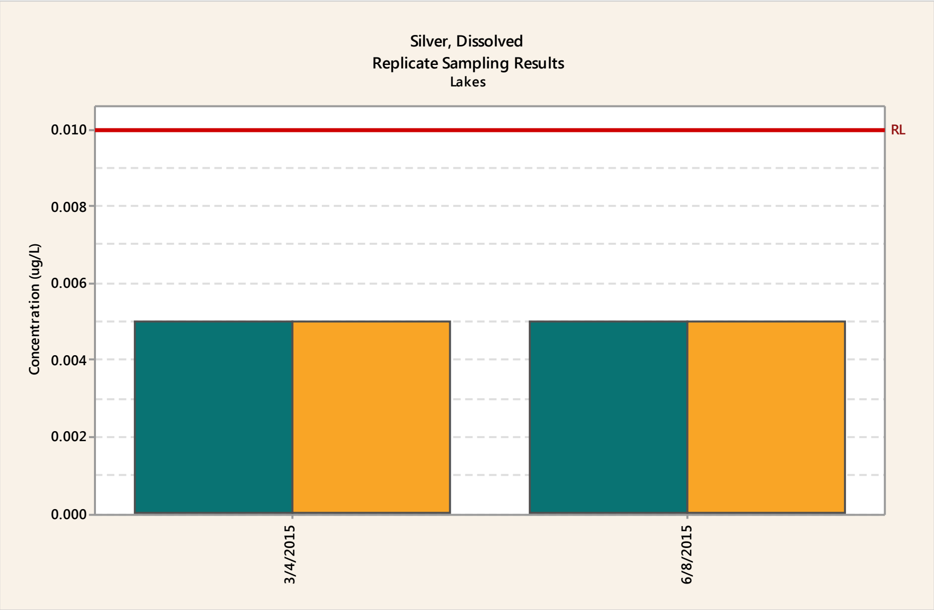

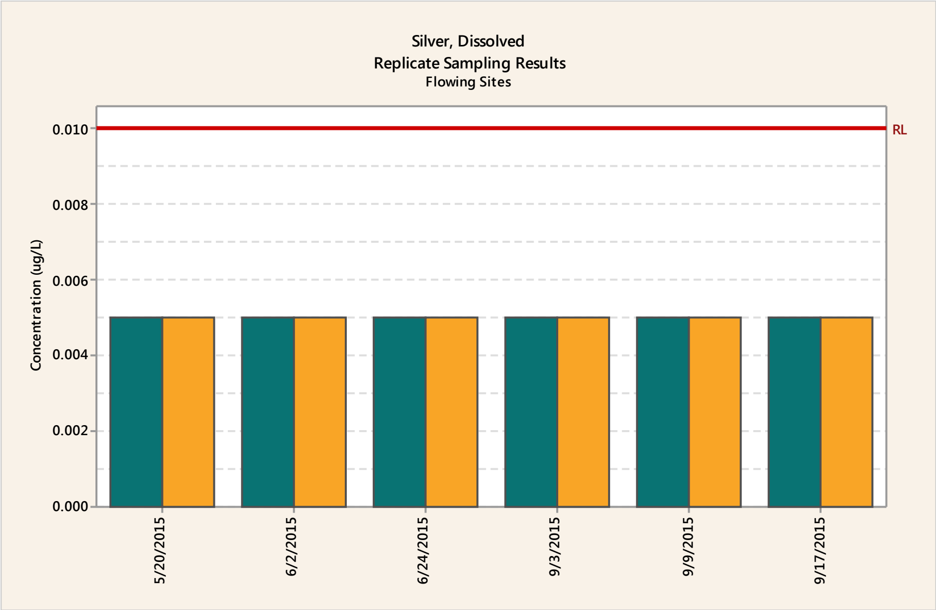

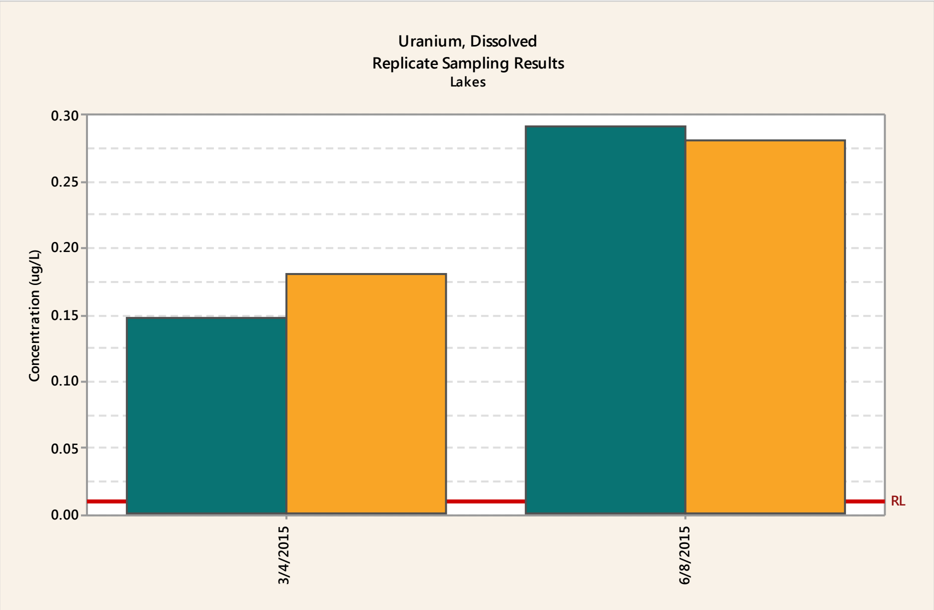

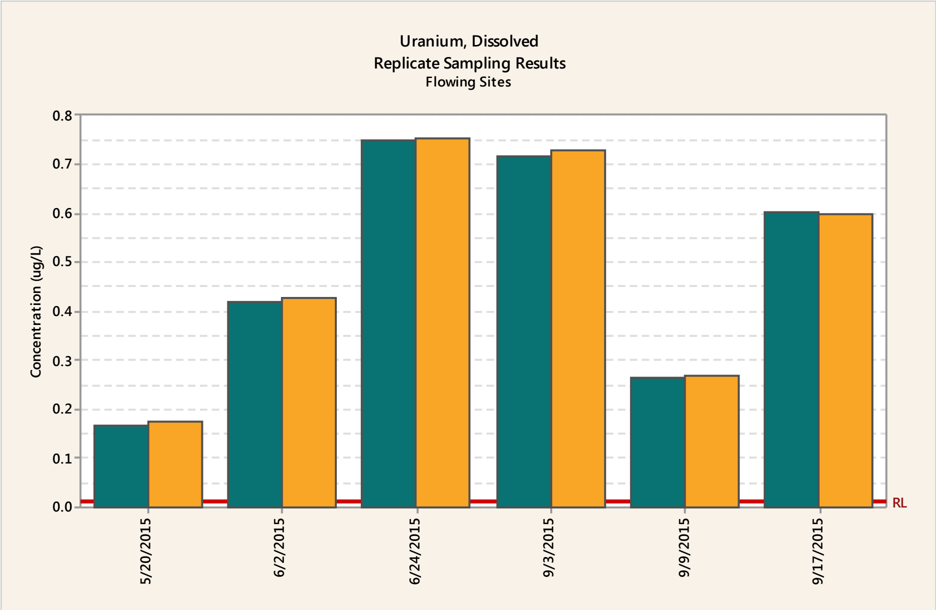

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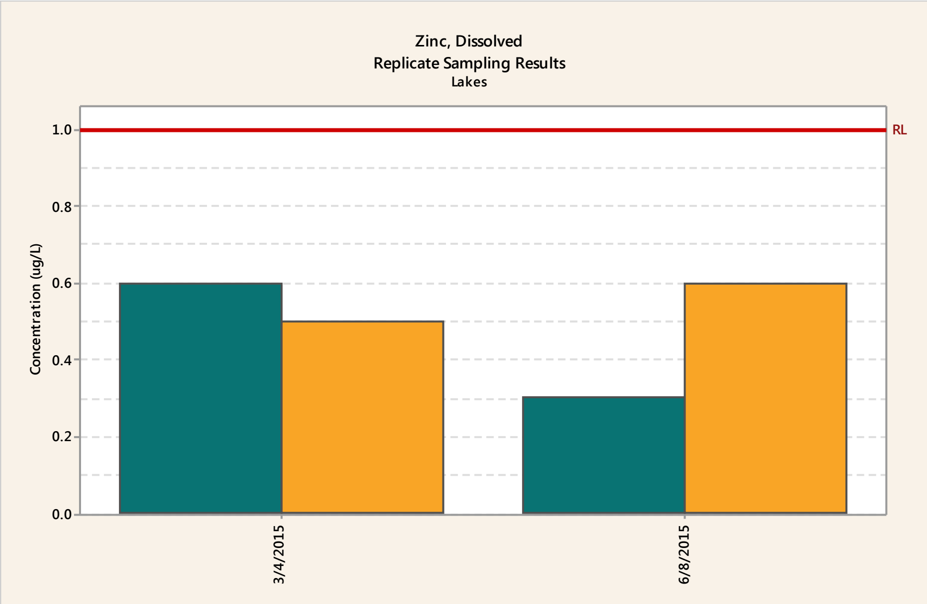

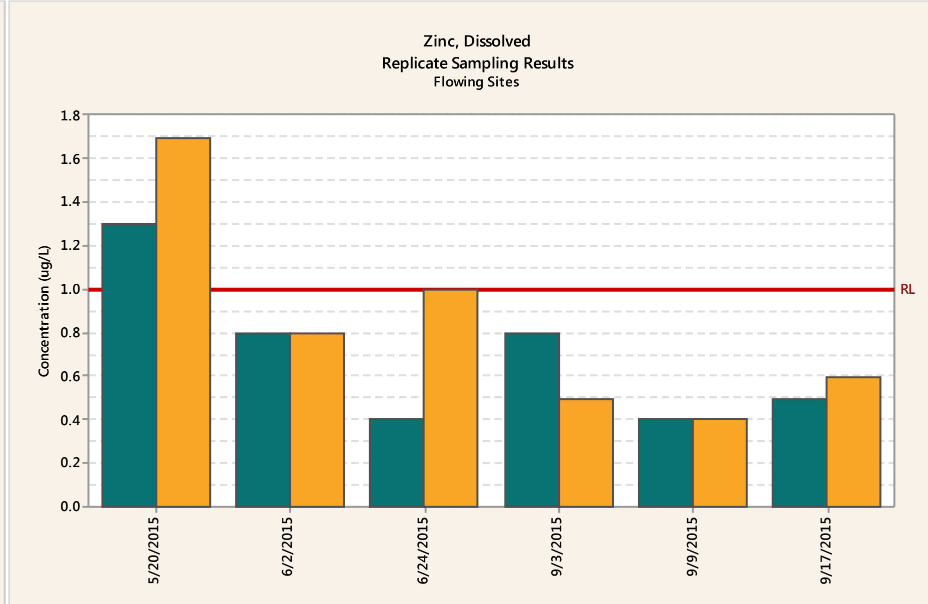

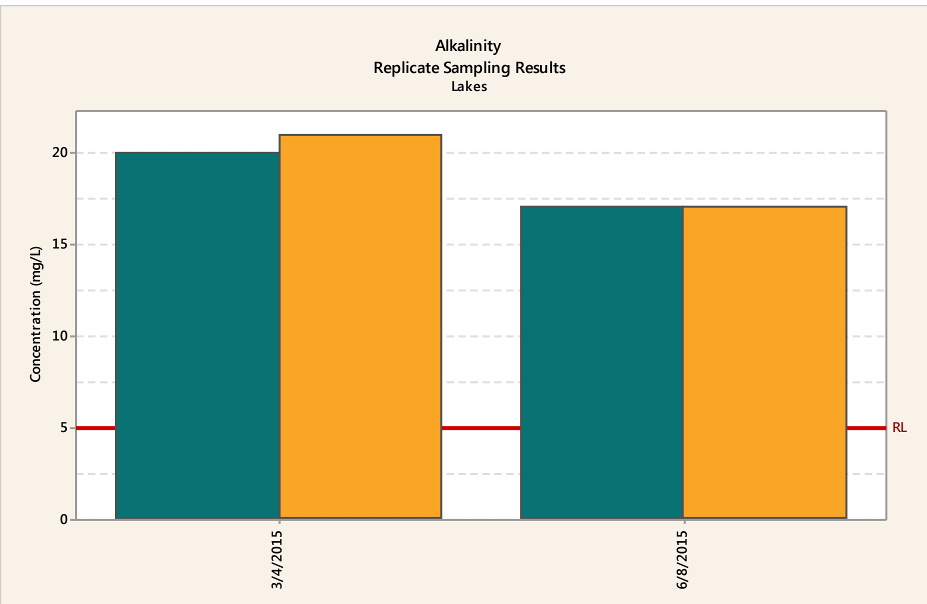

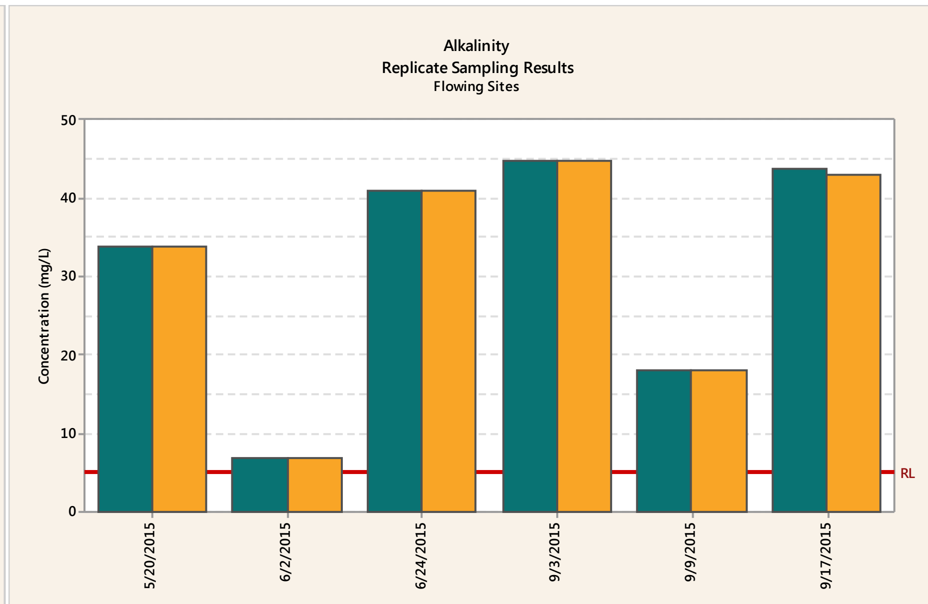

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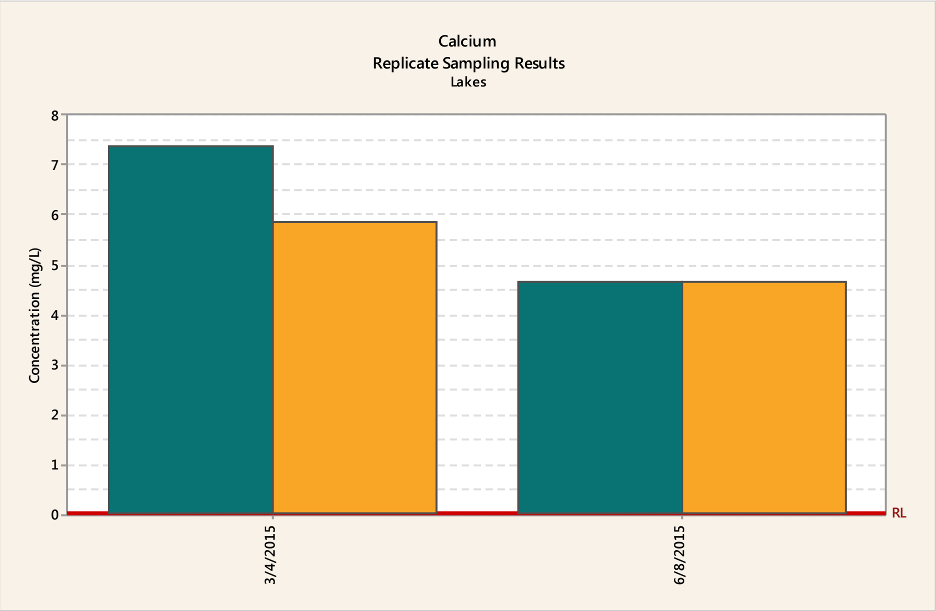

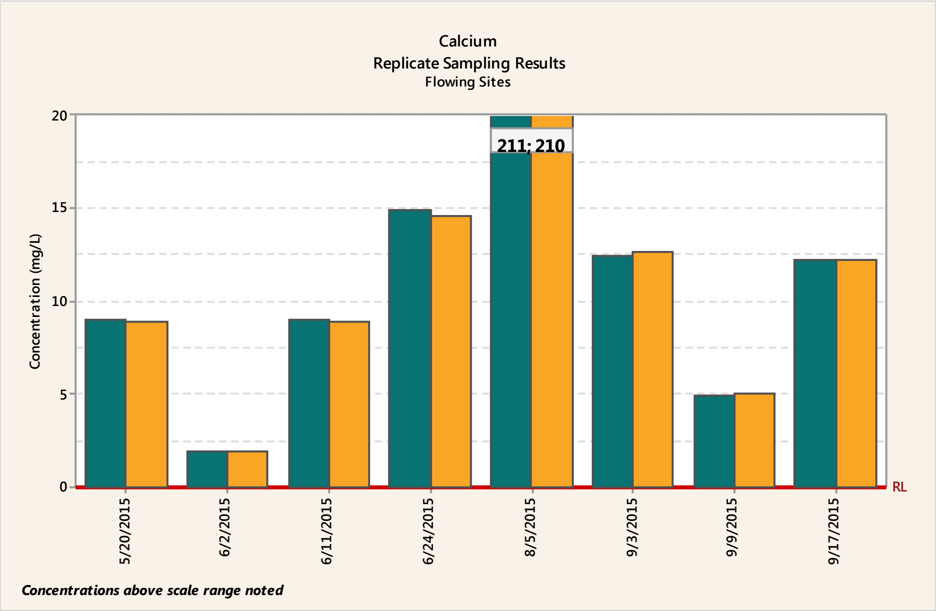

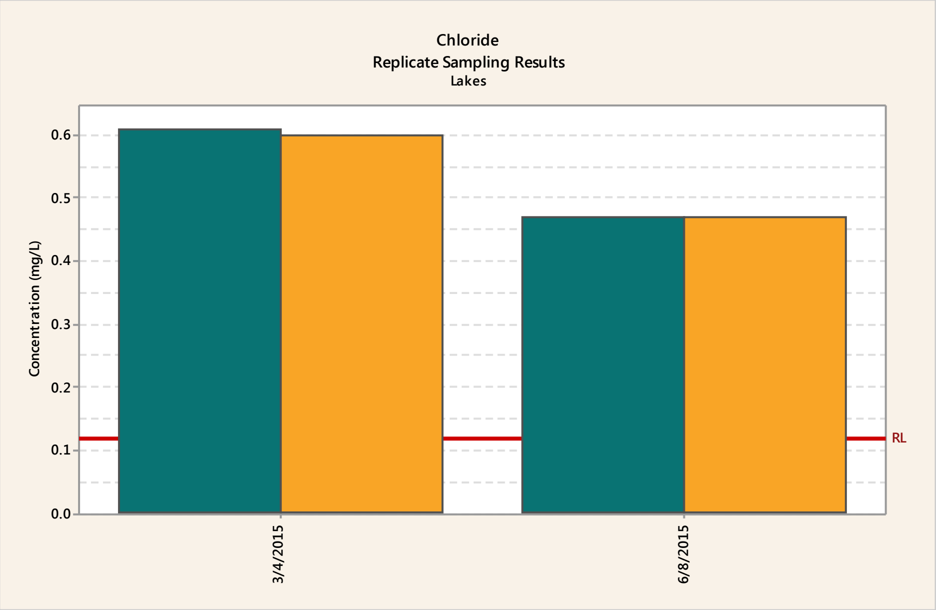

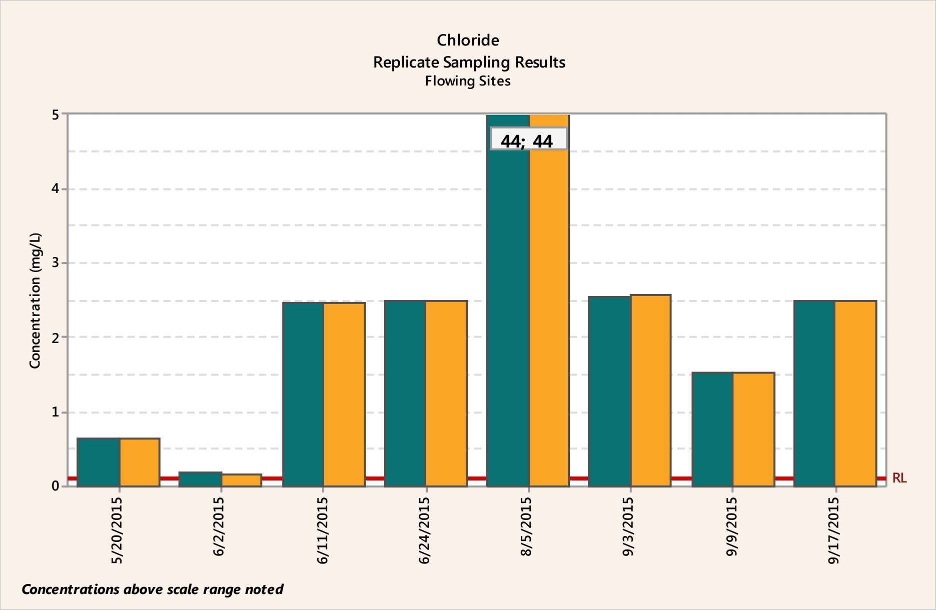

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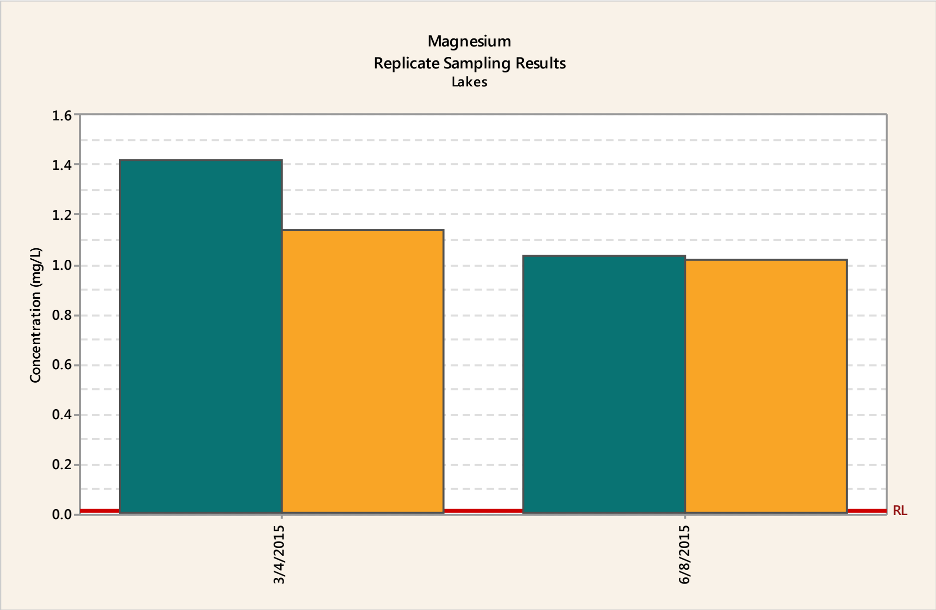

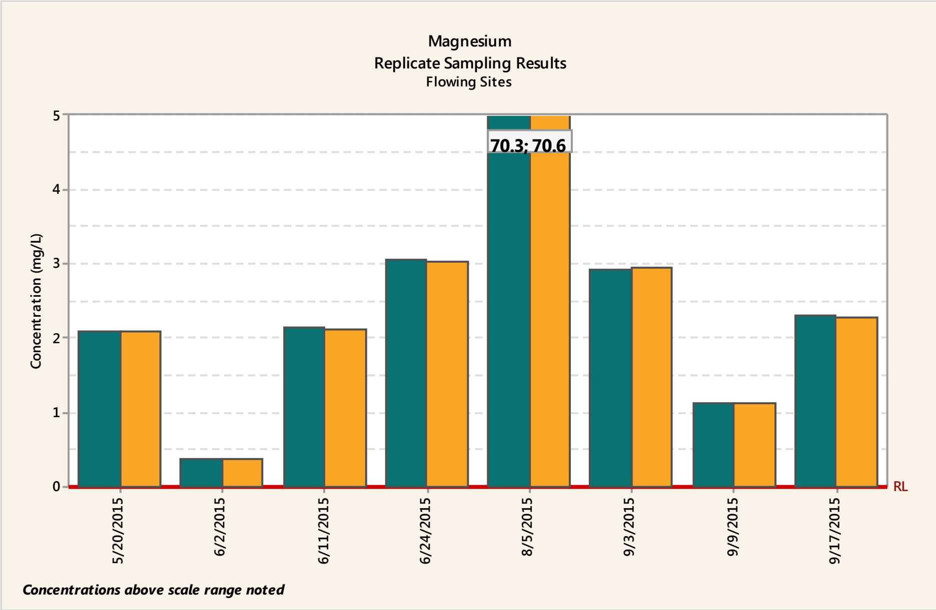

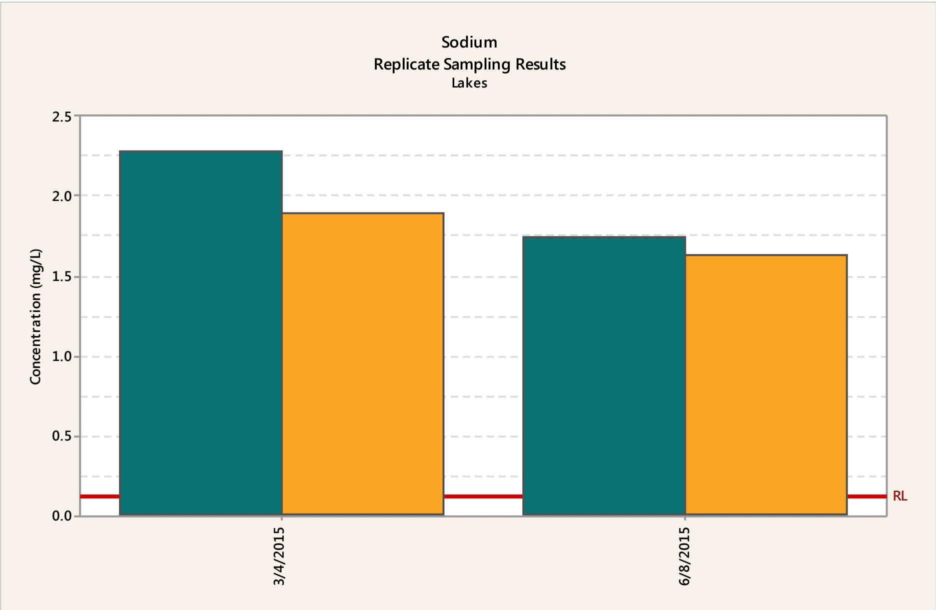

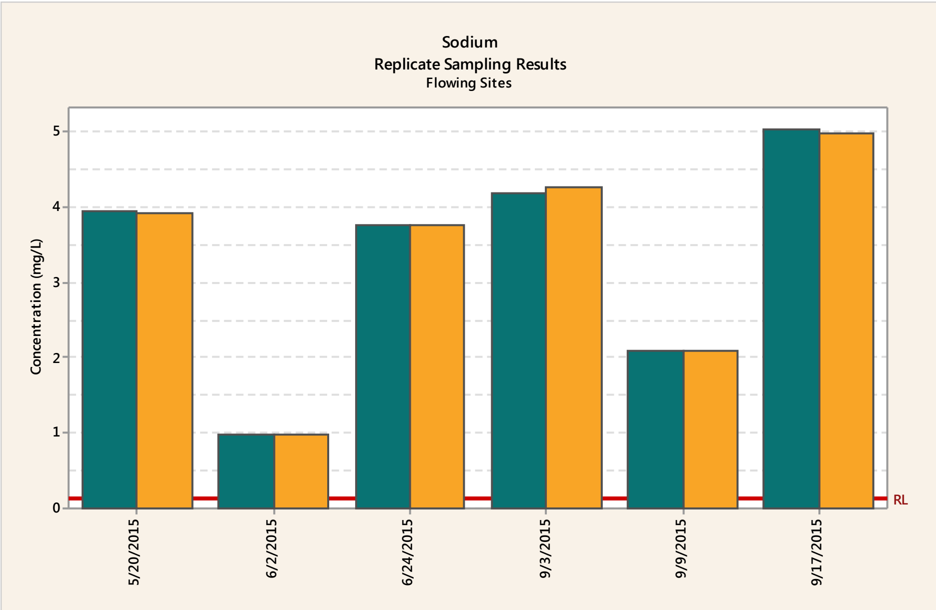

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