Northern Water's Baseline Monitoring Program Quality Assurance and Quality Control Report: Water Year 2013

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1. Introduction

Quality assurance and quality control measures form an important, integral component of Northern Water's Baseline 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, 2014) 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 (Northern) Baseline Water Quality Monitoring Program in water year 2013 (October 2012 – September 2013).

2. Sampling Summary

In water year 2013, samples for the baseline program were collected by two entities: Northern and the U.S. Geological Survey (USGS). Northern collected the majority of the samples at the flowing sites (canals, rivers and streams) and on the reservoirs on the east slope. The USGS collected samples on the lakes and reservoirs on the west slope, at two canal sites on the east slope and one winter sampling event on the reservoirs on the east slope. 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's important data quality objectives is to collect data that are comparable to that collected by the USGS (and other sampling entities).

The data for all samples collected by the USGS as part of the baseline program are shared between Northern and the USGS. All samples collected are sent to USGS-certified private laboratories for analysis. Northern 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 and the USGS process and flag the data in the same manner to ensure that there is consistency between the two datasets. These data are available on Northern's website and on the USGS's National Water Information System (NWIS) website.

In water year 2013, samples were collected by Pinyon Environmental (Pinyon) at supplemental sites outside of the baseline program to support mitigation efforts for the Windy Gap Firming Project. Pinyon has been trained by Northern and utilizes sampling protocols outlined in Northern's SOP

(Northern Water, 2014). In addition, Northern Field Services staff shadowed Pinyon for two sampling events during the 2013 sampling season to verify that they are following Northern's SOP. During shadowing events, concurrent replicate samples are collected (one sample collected by Northern and one by Pinyon) and the data are compared. Although the sampling by Pinyon is not part of the baseline program, these data are included in this report for comparison of QC results with the rest of the samples collected in 2013.

Field QC samples are collected by Northern, the USGS and Pinyon. In general, 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; these 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 2013 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	224	7	7	3.1%	3.1%	6.2%
West Slope	600	31	30	5.2%	5.0%	10.2%

There are various groups of analytes 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 this document 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 lab, 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's Program include lab 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 criterion for blank QC samples is 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 Criteria	Corrective Action
Lab 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.
Lab 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 2013 FIELD EQUIPMENT 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 (Figure 1) including filtration and sample preservation. 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 - COLLECTING FIELD BLANK SAMPLE

Table 3 provides a summary of the field equipment blank samples collected for each analyte in water year 2013. 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, USGS and Pinyon). 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 EQUIPMENT 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	Environmental				Median	Max
Ammonia as N	mg/L	37	824	4.5%	0.004	--	--	--
Nitrate plus Nitrite as N	mg/L	37	824	4.5%	0.004	1	--	0.005
Total Kjeldhal Nitrogen	mg/L	38	824	4.6%	0.07	--	--	--
Ortho Phosphate as P	mg/L	37	824	4.5%	0.002	--	--	--
Phosphorus, Total	mg/L	38	824	4.6%	0.003	1	--	0.019
Organic Carbon, Dissolved	mg/L	18	353	5.1%	0.6	--	--	--
Organic Carbon, Total	mg/L	29	592	4.9%	0.6	--	--	--
Dissolved Solids, Total	mg/L	34	689	4.9%	10	--	--	--
Suspended Solids, Non-Volatile	mg/L	3	55	5.5%	10	--	--	--
Suspended Solids, Total	mg/L	36	689	5.2%	10	--	--	--
UV Absorbance	cm^{-1}	12	257	4.7%	0.002	2	--	0.003
Alkalinity, Total	mg/L	21	389	5.4%	5	--	--	--
Calcium	mg/L	28	564	5.0%	0.02	--	--	--
Magnesium	mg/L	29	568	5.1%	0.012	--	--	--
Arsenic, Dissolved	ug/L	13	163	8.0%	0.06	--	--	--
Arsenic, Total	ug/L	13	162	8.0%	0.2	1	--	0.3
Cadmium, Dissolved	ug/L	13	163	8.0%	0.02	--	--	--
Copper, Dissolved	ug/L	22	389	5.7%	1	1	--	1.06
Iron, Dissolved	ug/L	29	568	5.1%	4	--	--	--
Iron, Total	ug/L	22	389	5.7%	14	--	--	--
Lead, Dissolved	ug/L	13	163	8.0%	0.06	--	--	--
Manganese, Dissolved	ug/L	29	568	5.1%	0.2	3	0.26	0.47
Mercury, Total	ng/L	6	81	7.4%	0.5	--	--	--
Nickel, Dissolved	ug/L	13	163	8.0%	0.12	--	--	--
Selenium, Dissolved	ug/L	13	163	8.0%	0.06	--	--	--
Silver, Dissolved	ug/L	13	163	8.0%	0.008	--	--	--
Zinc, Total	ug/L	13	163	8.0%	2	--	--	--

There were 27 compounds analyzed with the field equipment blanks. There were a total of nine occurrences for six analytes where values were reported at a concentration above the RL. Four of the six analytes (nitrate plus nitrite, UV absorbance, total arsenic, and dissolved copper) had reported values just slightly above the RL and do not warrant discussion, although the copper value will be discussed in the Data Quality section of this report. Total phosphorus and dissolved manganese, the remaining two analytes with detected values above the RL, are discussed below.

- Total Phosphorus – There was one occurrence where total phosphorus from a field blank sample was reported with a concentration of 0.019 mg/L, one order of magnitude higher than the 0.003 mg/L RL. This sample was submitted by the USGS in July 2013. Correspondence with the USGS determined that the cause of this occurrence was source water contamination, likely from an improperly prepared container that was used to transport the D.I. water. Although not included in this report, the USGS submitted a source water blank (a D.I. water sample that is brought into the field but not processed in any way) along with the field equipment blank for this sampling event. The source water blank also had an elevated concentration, 0.16 mg/L, which was similar to the reported value of the field equipment blank. This lead to the conclusion that the D.I. water was the source of contamination, not the field processing. These data are included in Northern's database with the remark 'source water contamination'.

- Dissolved Manganese – There were three occurrences where dissolved manganese was reported with a value above the 0.2 ug/L RL. The reported values were 0.25, 0.26 and 0.47 ug/L. All of the samples were submitted by Northern. The reported 0.25 and 0.26 ug/L values were just above the RL and not concerning. The 0.47 ug/L value was verified by the laboratory.

  There have been documented issues with dissolved manganese in the past. Manganese is susceptible to filter contamination, and this may be more apparent if filter preparation (rinsed with D.I. water) occurs some time before the sampling event. Northern and the USGS use different brands of disposable capsule filters; Geotech and Pall respectively. The USGS preps filters directly in the field. Northern preps filters the week of the sampling event, generally filter prep is done on Monday for all samples collected that week. Since that data for the blank samples that fall outside the acceptable criteria are only for samples submitted by Northern, the filter used and/or filter prep may be a contributing factor. Another factor that could contribute to the elevated blank results is that the filters used are certified for a 0.5 ug/L limit of detection, which is higher than the 0.2 ug/L RL. Dissolved manganese QC data will be closely monitored in the future to see if the data continue to fall outside of the acceptable criteria.

3.2 2013 Lab Blank Samples

Lab 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. Lab water blanks are collected approximately once per quarter.

There were not any lab water blank samples submitted in water year 2013. Northern's SOP was being revised and finalized during this time; the previous SOP did not specify quarterly submittal of lab water blanks in the QC sampling criterion.

Equipment blanks are collected to determine if the sampling equipment is being thoroughly cleaned and decontaminated before it leaves the lab. Equipment blanks are collected in the same manner as the

lab water blanks except that the analyte-free D.I. water is poured into the sampling equipment prior to pouring into the sample bottle. One round of equipment blanks is collected each spring.

There was not an equipment blank submitted in water year 2013. Northern's SOP was being revised and finalized during this time; the previous SOP did not specify a yearly submittal of an equipment blank in the QC sampling criterion.

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 lab measurements are. The consistent adherence to the protocols presented in this document 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's Program include:

- **Split replicates** 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** 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** 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 on Table 4.

TABLE 4 – CRITERION FOR REPLICATE SAMPLES

Field QC Sample Type	Collection Frequency	Acceptance Criteria	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, lab 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, lab error; request re-analysis of sample; flag suspect data.

4.1 2013 FIELD REPLICATE SAMPLES

Table 5 provides a summary of the field replicate samples collected for each analyte in water year 2013. 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, USGS and Pinyon). 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 5 - SUMMARY OF FIELD REPLICATE SAMPLES BY ANALYTE

Analyte	Unit	Number of Samples		Percent Replicate Samples	Reporting Limit (RL)	Number of Replicate Samples > RL	Relative Percent Difference for Replicate Samples above RL		Difference in Concentration between Field and Replicate Samples above RL	
		Replicate	Environmental				Median	Maximum	Median	Maximum
Ammonia as N	mg/L	36	824	4.4%	0.004	14	3%	11%	0.001	0.043
Nitrate plus Nitrite as N	mg/L	36	824	4.4%	0.004	28	1%	45%	0.001	0.0085
Total Kjeldhal Nitrogen	mg/L	37	824	4.5%	0.07	36	2%	24%	0.004	0.136
Ortho Phosphate as P	mg/L	36	824	4.4%	0.002	25	0%	22%	0	0.0055
Phosphorus, Total	mg/L	37	824	4.5%	0.003	37	2%	38%	0.001	0.039
Organic Carbon, Dissolved	mg/L	14	353	4.0%	0.6	14	2%	9%	0.065	0.27
Organic Carbon, Total	mg/L	26	592	4.4%	0.6	26	1%	4%	0.04	0.14
Dissolved Solids, Total	mg/L	31	689	4.5%	10	31	4%	23%	2	16
Suspended Solids, Total	mg/L	31	689	4.5%	10	5	2%	9%	1	6
Chlorophyll a	mg/m^3	14	507	2.8%	0.1	14	12%	116%	0.34	0.9
UV Absorbance	cm^{-1}	10	257	3.9%	0.002	10	1%	55%	0.0015	0.087
Alkalinity, Total	mg/L	17	389	4.4%	5	17	0%	4%	0	2
Calcium	mg/L	24	564	4.3%	0.02	24	1%	5%	0.1	0.9
Magnesium	mg/L	24	568	4.2%	0.012	24	1%	5%	0.015	0.19
Arsenic, Dissolved	ug/L	9	163	5.5%	0.06	9	11%	24%	0.02	0.3125
Arsenic, Total	ug/L	9	162	5.6%	0.2	7	0%	32%	0	0.6
Cadmium, Dissolved	ug/L	9	163	5.5%	0.02	1	--	0%	--	0
Copper, Dissolved	ug/L	17	389	4.4%	1	6	6%	15%	0.07	0.2
Iron, Dissolved	ug/L	24	568	4.2%	4	24	2%	24%	1.6	160
Iron, Total	ug/L	17	389	4.4%	14	17	2%	28%	10	560
Lead, Dissolved	ug/L	8	163	4.9%	0.06	4	10%	12%	0.0175	0.024
Manganese, Dissolved	ug/L	24	568	4.2%	0.2	24	4%	57%	0.425	70
Mercury, Total	ng/L	3	81	3.7%	0.5	3	4%	14%	0.1	0.1
Nickel, Dissolved	ug/L	9	163	5.5%	0.12	9	10%	22%	0.02	0.09
Selenium, Dissolved	ug/L	9	163	5.5%	0.06	6	0%	12%	0	0.01
Silver, Dissolved	ug/L	9	163	5.5%	0.008	0	--	--	--	--
Zinc, Total	ug/L	9	163	5.5%	2	1	--	8%	--	0.2

There were 27 compounds analyzed with replicate samples. There were a total of 13 occurrences for 7 different analytes where the acceptance criteria were not met. The data for these occurrences are shown in Table 6. The highlighted rows group occurrences that will be discussed further. All of these occurrences are indicated in Northern's database with a remark that states there is a significant difference between environmental and replicate samples.

TABLE 6 - REPLICATE SAMPLE DATA OUTSIDE OF ACCEPTANCE CRITERIA

Date	Sampler	Analyte	Unit	RL	Reported Value			RPD
					Environ-mental	Replicate	Difference	
1/3/2013	Northern	Chlorophyll a	mg/m^3	0.1	0.19	0.71	0.52	116%
1/22/2013	Northern	Manganese, Dissolved	ug/L	0.2	1.24	0.69	0.55	57%
1/31/2013	USGS	Arsenic, Total	ug/L	0.2	1.6	2.2	0.6	32%
1/31/2013	USGS	Iron, Total	ug/L	14	1710	2270	560	28%
1/31/2013	USGS	Nitrate plus Nitrite as N	mg/L	0.004	0.023	0.0145	0.0085	45%
1/31/2013	USGS	Phosphorus, Total	mg/L	0.003	0.083	0.122	0.039	38%
3/28/2013	USGS	UV Absorbance	cm-1	0.002	0.202	0.115	0.087	55%
4/29/2013	Northern	Manganese, Dissolved	ug/L	0.2	2.55	3.63	1.08	35%
5/22/2013	USGS	Phosphorus, Total	mg/L	0.003	0.033	0.043	0.01	26%
6/4/2013	Northern	Chlorophyll a	mg/m^3	0.1	0.7	1.5	0.8	73%
6/4/2013	Northern	Manganese, Dissolved	ug/L	0.2	1.5	2.37	0.87	45%
7/30/2013	Northern	Chlorophyll a	mg/m^3	0.1	0.91	1.28	0.37	34%
8/27/2013	USGS	Phosphorus, Total	mg/L	0.003	0.023	0.031	0.008	30%

- Chlorophyll a – All of the replicate samples submitted for chlorophyll analysis were collected by Northern; the USGS do not submit replicates for chlorophyll. All of the instances where there were RPD's outside of the acceptance criterion, the concentration was fairly low (≤ 1.5 mg/m^3). The standard method for chlorophyll analysis does not allow for data verification by means of duplicate analysis by the laboratory as all the sample is used in the initial analysis. Therefore these data are accepted as valid without verification.

- Dissolved Manganese – There were three replicate samples for dissolved manganese that were above the acceptable RPD of 25%. All of these samples were submitted by Northern. One out of the three, the sample with the 57% RPD, was verified. As discussed in section *3.1 2013 Field Equipment Blank Samples*, there have been issues with dissolved manganese in the past. Dissolved manganese QC data will be closely monitored in the future to see if the data continue to fall outside of the acceptable criteria.

- January 2013 Sampling Event – The January 31, 2013 samples were collected from the bottom of Willow Creek Reservoir. These were sequential replicates; one sample collected right after the other, which is most likely the major factor in high RPD's. When sequential replicates are collected at the bottom of a reservoir site, sediment can be disturbed and/or the samples can be collected at slightly different depths which can result in big differences in the water quality (especially under anoxic conditions, which was the case during this sampling event). In addition to the four analytes in Table 6, there were several other analytes where the concentration for

the replicate was significantly elevated compared to the environmental sample, but all had RPD's under the acceptance range of 25%. The data were verified by the laboratory.

- UV Absorbance – This sample was a sequential replicate collected at the bottom of Willow Creek Reservoir. There were other differences in reported concentrations between the environmental and replicate samples but all had RPD's below 25%. The value was not verified.

- Total Phosphorus – Both of these were sequential replicates collected during lake sampling. These replicate samples had fairly low total phosphorus concentrations. The values were not verified outside of laboratory duplicate analyses that are part of the standard procedure for this particular lab (High Sierra Water Lab).

4.2 2013 Northern and Pinyon Concurrent Sampling Events

Northern's staff shadowed Pinyon for two sampling events during the sampling season to ensure they are following proper procedures. In 2013, these sampling events occurred in May and September. During these events, concurrent replicate samples are collected (one sample collected by Northern and one by Pinyon) and the data are compared.

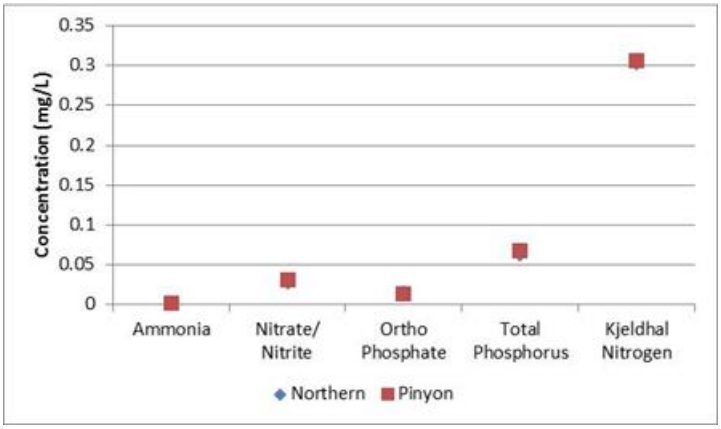

FIGURE 2 - LAB RESULTS FOR CONCURRENT SAMPLING, MAY 2013

Laboratory data for this sampling is limited to nutrients. In 2013, the laboratory data compared well and are shown in Figure 2 and Figure 3. This indicates that Pinyon is preparing the sampling equipment and collecting and processing samples properly according to Northern's SOP.

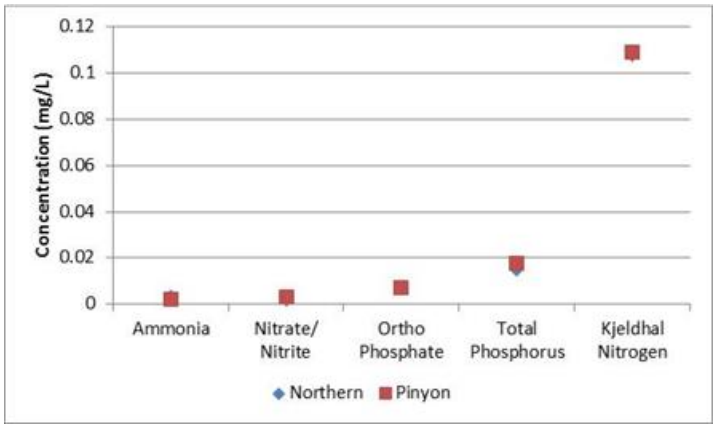

FIGURE 3 - LAB RESULTS FOR CONCURRENT SAMPLING, SEPTEMBER 2013

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 uses one of Northern's YSI 6820 multi-parameter probes to collect this data. In 2013, this comparison shows that there were data quality issues with the field data that Pinyon collected (Table 7). The values highlighted in yellow are those that did not compare well.

Parameter	May 2013		September 2013	
	Northern	Pinyon	Northern	Pinyon
Flow (cfs)	201.29	253.85	15.8	15.8
Dissolved Oxygen (mg/L)	10.03	10.76	7.87	6.24
pH	7.67	7.59	7.16	8.02
Specific Conductivity (uS/cm)	88	77	123	571
Temperature (Deg C)	3.2	2.94	12.13	12.5
Turbidity (NTU)	20.4	22.3	1.5	1.2

TABLE 7 - FIELD DATA FOR CONCURRENT SAMPLING EVENTS

As a result, Northern requested and reviewed all of Pinyon's equipment calibration logs. The logs indicated that on several occasions the equipment was not being properly calibrated and/or there was a large drift between pre- and post-calibration values, which were outside of the acceptable calibration criterion defined in Northern's SOP. In these instances, the data were flagged as rejected or disqualified in Northern's database. The rejected data totaled 196 records: 41values for dissolved oxygen, 26 values for pH, 89 values for specific conductivity, and 40 values for turbidity.

To remediate the issue, Northern met with Pinyon and reviewed the errors from the calibration logs. The calibration protocol was reviewed in detail. Pinyon agreed to do a post calibration check after sampling the first site in addition to the standard post calibration check after all sites were sampled. Pinyon also began sending calibration logs for Northern to review monthly. These actions began in 2014.

5. DATA QUALITY

All data collected in the field and received from the laboratories are subject to thorough data QA/QC review and validation by Northern prior to being uploaded to Northern's databases. Data validation and review of the field data is conducted by both Field Services staff and Water Quality Department staff, while data validation and review of the laboratory data is conducted by Water Quality Department staff. Also note that data validation and review is 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's SOP (Northern Water, 2014).

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'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'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.

In water year 2013, in addition to the Pinyon data discussed previously, there were three other instances where a significant amount of data were rejected or disqualified from Northern's databases. There was one instance when a large number of records were marked as suspect. These were:

- Northern YSI 6600 Turbidity Data – Beginning in 2011, turbidity values collected by Northern with the YSI 6600 probe began to show increased values when compared to historic data. In 2012 and 2013 the turbidity values were unusually high compared to historic values and turbidity data collected by other entities (USGS and Fort Collins). Figure 4 shows how the values increased from 2009 to 2013 at a site on Horsetooth Reservoir.

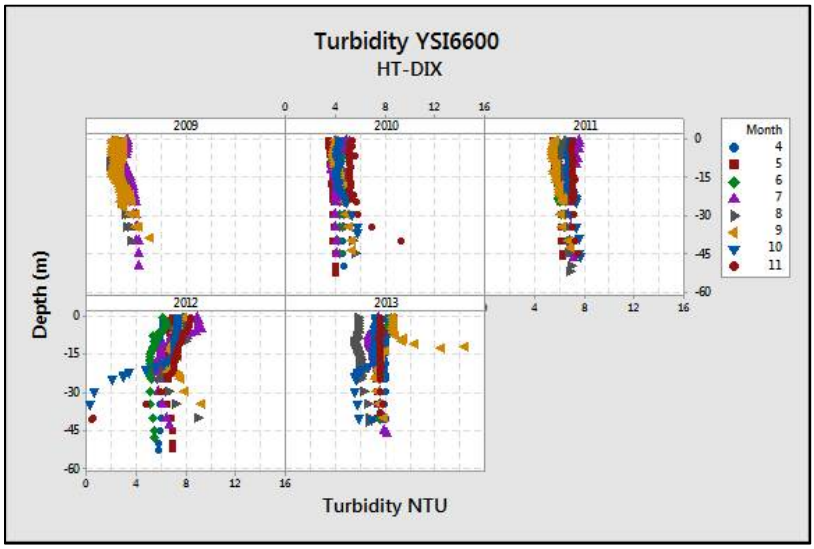

FIGURE 4 - YSI 660 TURBIDITY FROM 2009 - 2013

Northern's Field Service staff investigated the cause of the increase, paying especially close attention to calibration protocol and the calibration standard that was used. This review showed that standard protocols were being followed and the cause for the increased concentrations was not known. The YSI 6600 was sent in to the manufacturer for routine maintenance in December 2013. During the maintenance, a part of the turbidity sensor was replaced. When the YSI 6600 was returned, the turbidity data no longer appeared to be suspect. The values were back in agreement with historic data. It was concluded that the sensor that was replaced was the cause of the elevated turbidity values.

As a result, all turbidity data collected with the YSI 6600 in water year 2013 (as well as 2011 and 2012) were disqualified from Northern's database. These data were primarily from the east slope reservoirs, some data from Shadow Mountain Reservoir, and limited data collected at the flowing sites. In total, for all three years, 2873 lakes and reservoirs records and 128 flowing sites records were disqualified. All disqualified records were flagged with the remark "sensor failure".

As an additional QAQC procedure to verify turbidity, beginning in 2014 Field Services began to do in-field QAQC checks with a portable turbidity meter (Hach 2100Q) to validate the YSI 6600 turbidity values.

- Dissolved Oxygen Data, West Slope Lakes and Reservoirs – In early September 2013, the barometer in the YSI probe used by the USGS failed; it stopped auto-compensating. The barometric pressure reported by YSI should have been checked against an independent barometer in the field, but was not. This resulted in an incorrect reading of barometric pressure, which resulted in incorrect dissolved oxygen values for this sampling event.

  As a result, all dissolved oxygen values were disqualified from Northern's database and from NWIS. This applied only to the first scheduled sampling event in September (Sept 10-12, 2013) on the west slope lakes and reservoirs. In total, 197 records were disqualified.

- USGS Dissolved Lead Data, West Slope Lakes and Reservoirs - Beginning in June 2011, suspect data were reported for dissolved lead for samples collected by the USGS on the lakes and reservoirs. The suspect data were extremely elevated compared to historical data and there were not consistent results from samples collected within the same water body or with the replicates. Suspect values were consistently verified at the laboratory (Huffman Laboratory).

  The USGS investigated these occurrences and discovered that the sampling vessel that was being used, the Kemmerer, was most likely introducing lead into the sample. The messenger, the part of the Kemmerer that closes the vessel at depth, had cracked and was leaching lead. This theory was validated by the variability of the data, the variability of replicates and the absence of lead in blank samples. This issue was isolated to when the USGS collected samples with the Kemmerer; the data from samples that Northern submitted during the same time period did not show elevated or inconsistent values.

  As a result, October 2012 data were disqualified from Northern's database and from NWIS. In addition, data from June 2011 to September 2012 were also disqualified from both data sources. The data were from samples collected on both east and west slope lakes and reservoirs. In total, 112 records were disqualified.

- Dissolved Copper and Dissolved Zinc, West Slope Lakes and Reservoirs – In January 2013, the results for dissolved copper and zinc were significantly elevated compared to historic data. In addition, the field blank that was submitted for this event had slightly elevated concentrations; copper 1.06 ug/L slightly above the 1 ug/L RL (as shown in Table 3) and zinc 1.3 ug/L which is below the RL of 2 ug/L. These samples were collected by the USGS.

All values were verified by the lab (Huffman Laboratory) and there was good agreement among duplicate laboratory analyses that were done as part of the labs internal QAQC protocols. The USGS investigated the data and found no obvious reason for the high detections. There was speculation that these could be wind-borne contamination.

As a result, all dissolved copper and dissolved zinc values from this sampling event were flagged as verified and suspect in Northern's database. All dissolved copper data have a remark referencing the blank detect for copper in both Northern's database and NWIS. In total, 36 records were marked as suspect.

6. 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 the data can be improved. In 2013, 899 samples were collected, 75 of which were QC samples. Given the magnitude of the sampling, 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 or were not found to compromise data quality in general. This indicates that Northern's data quality objectives are being met.

7. REFERENCES

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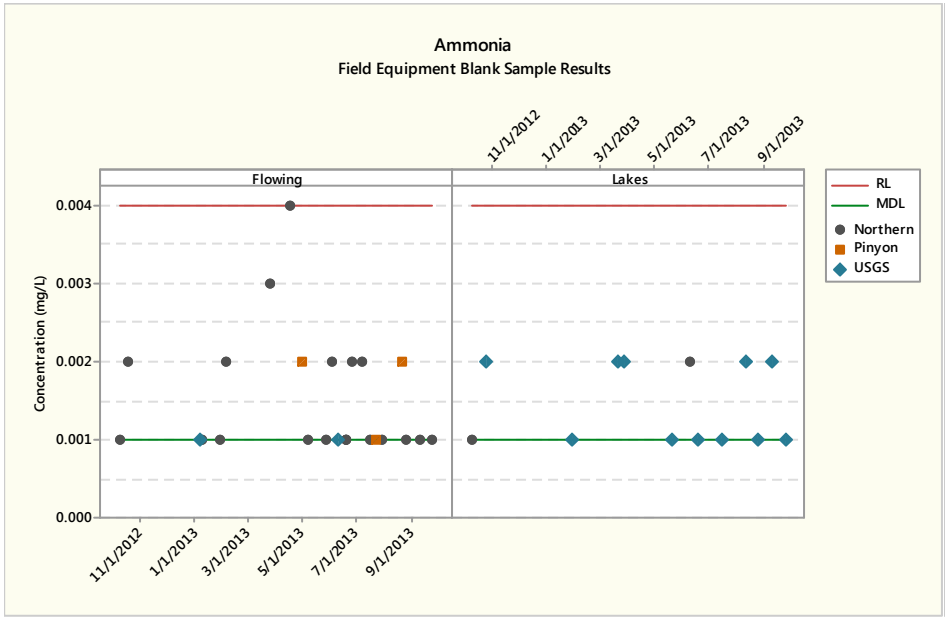
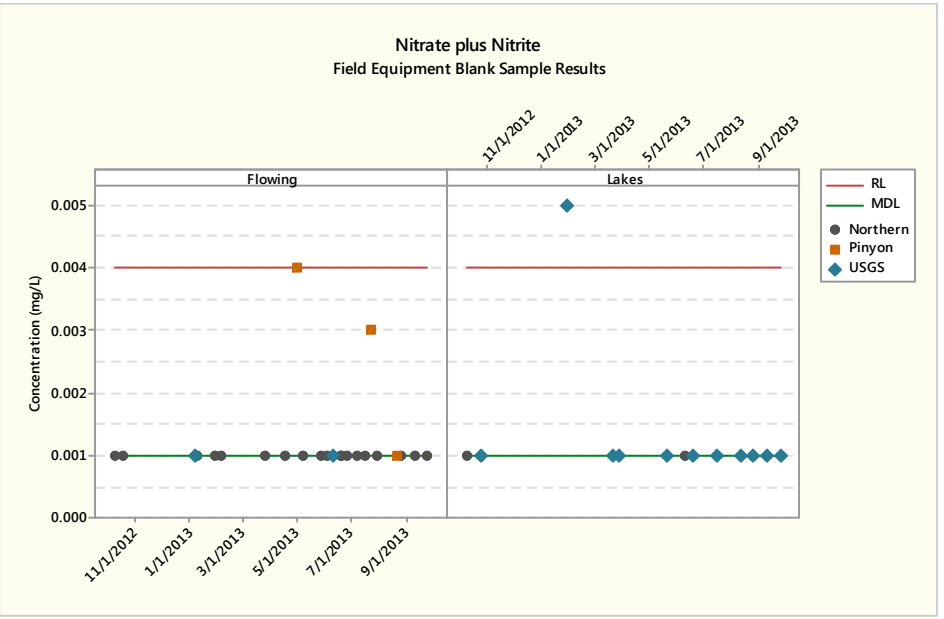
APPENDICES

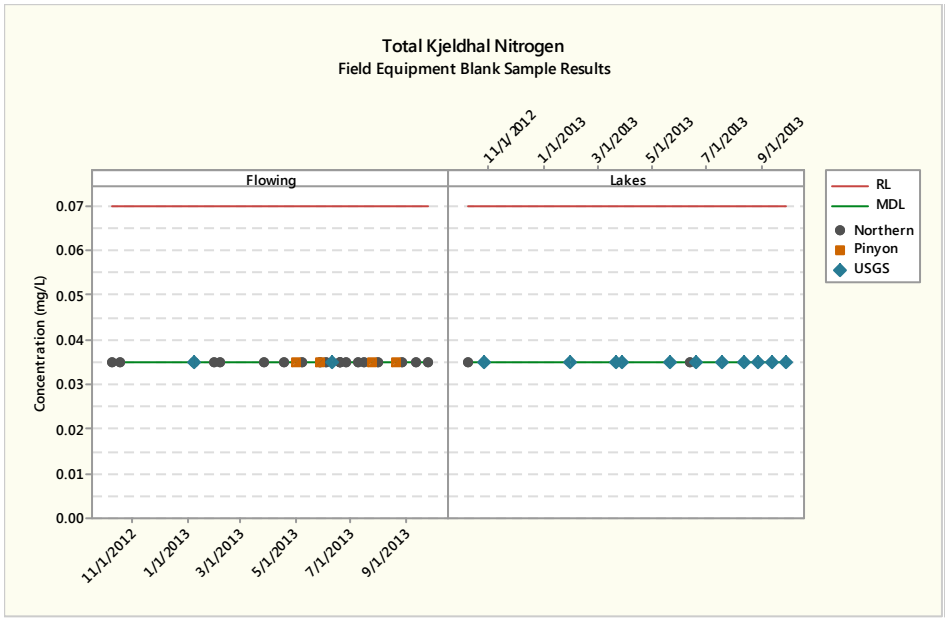
Appendix 1 – Field Blank Time Series Plots

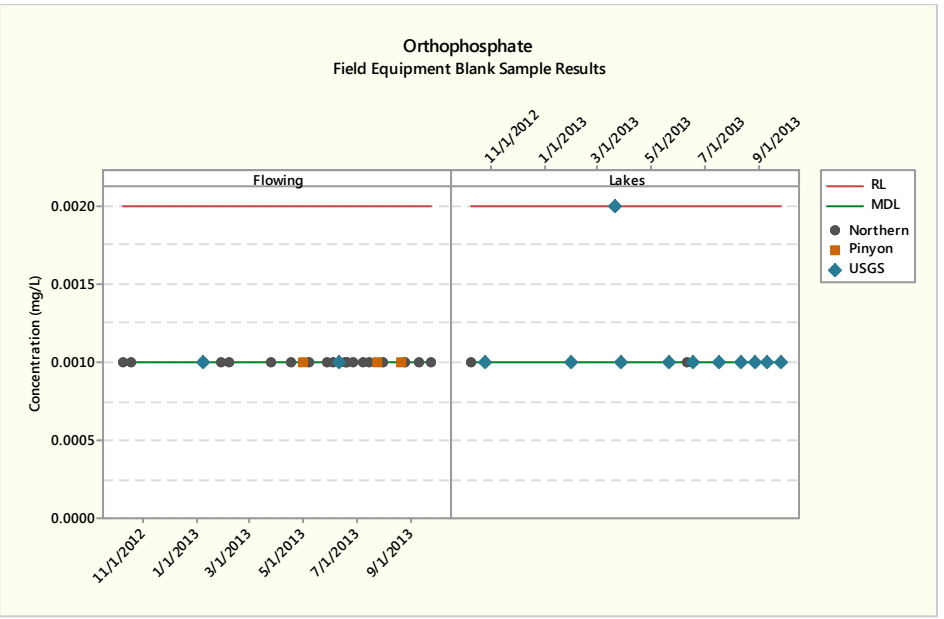
Appendix 2 – Field Replicate Results

Appendix I – Field Blank Time Series Plots









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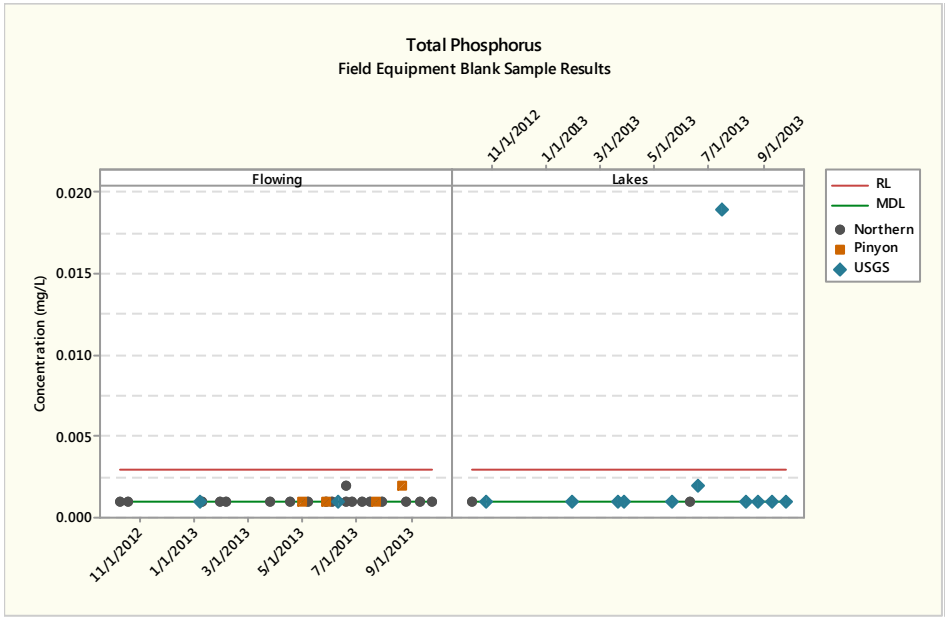

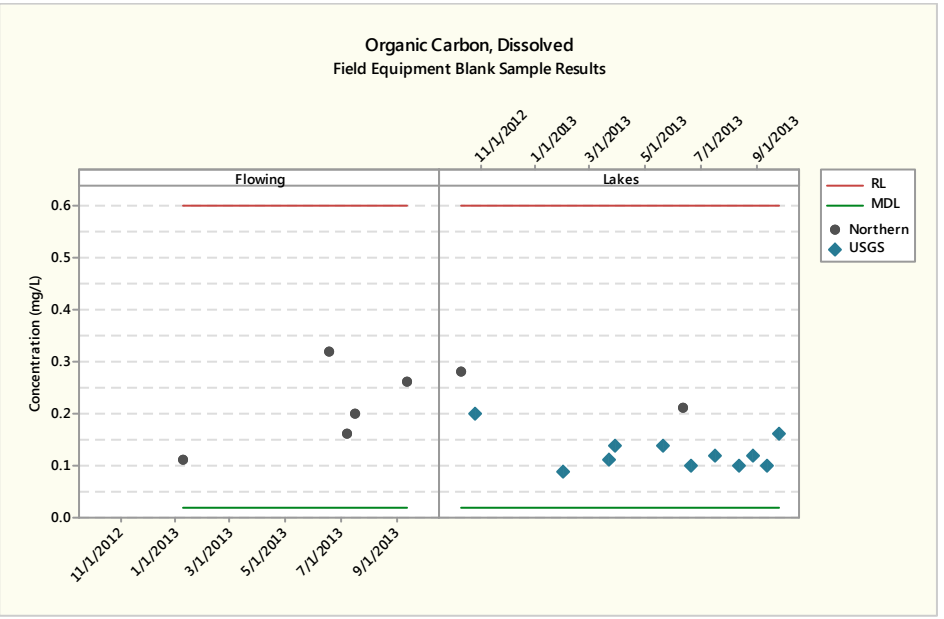

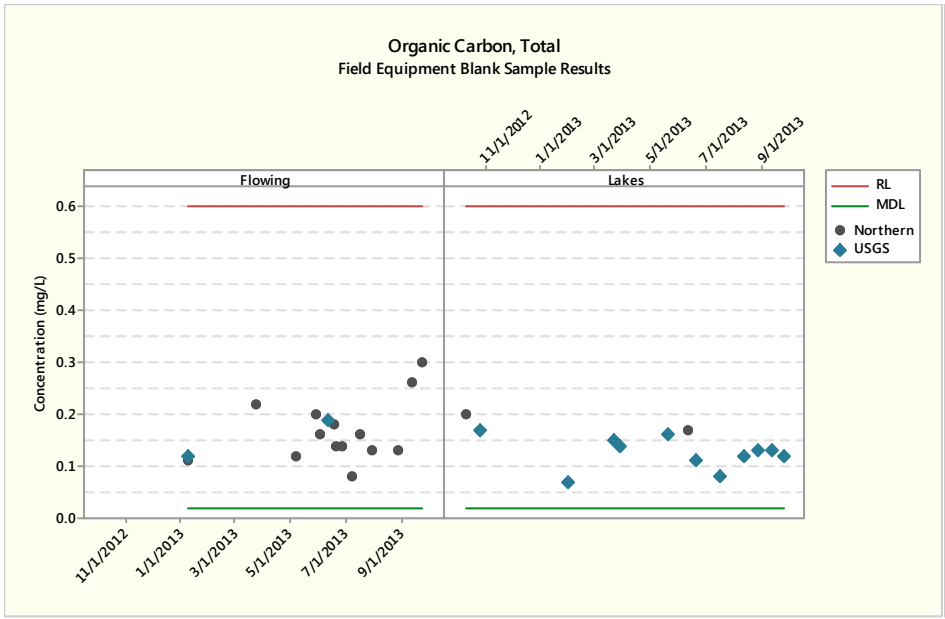

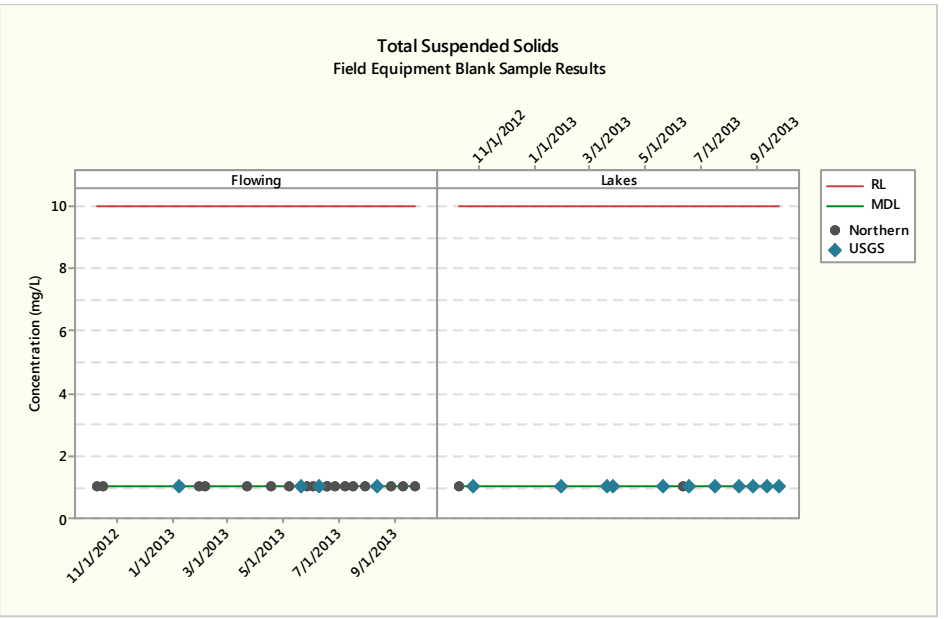

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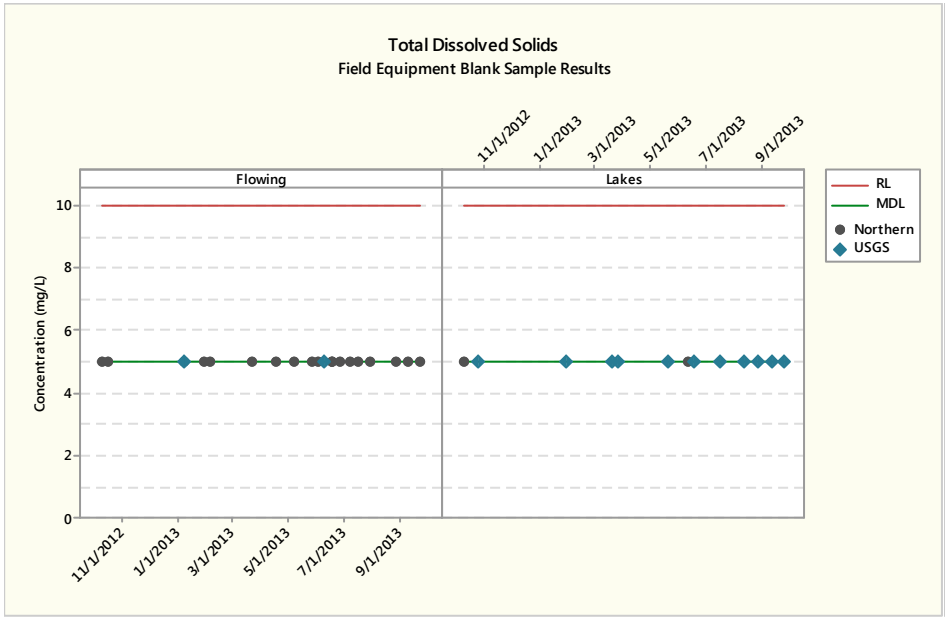

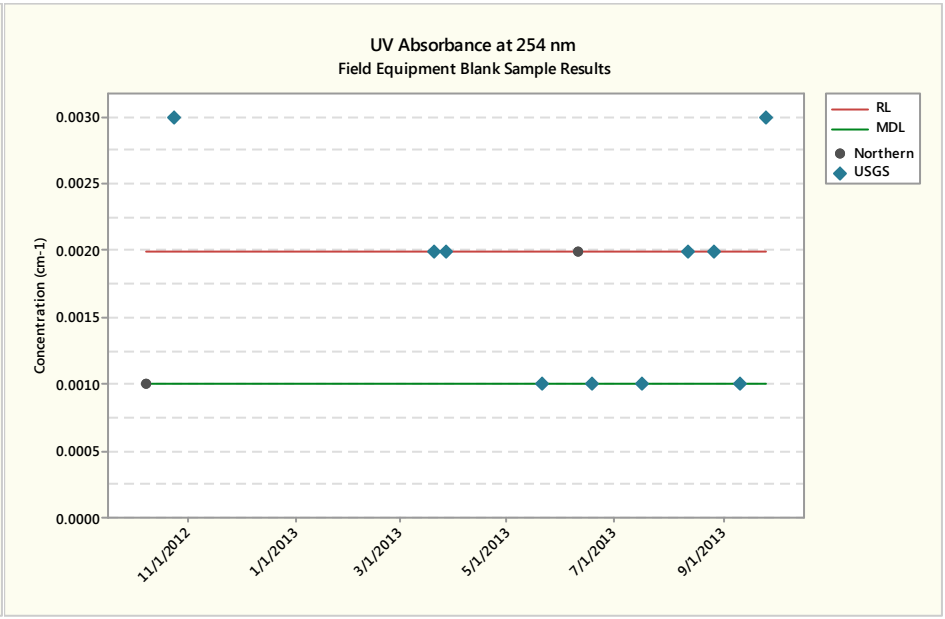

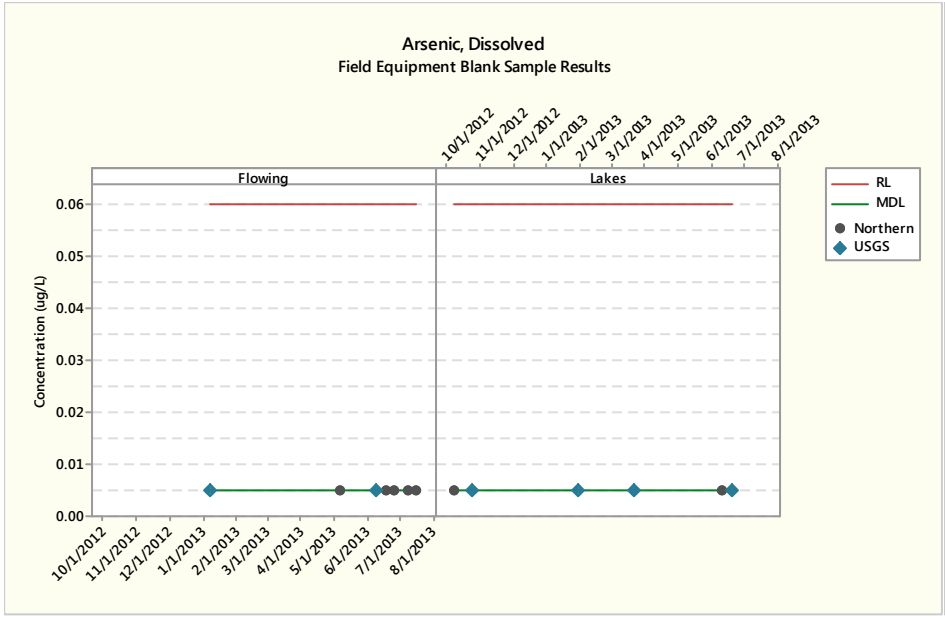

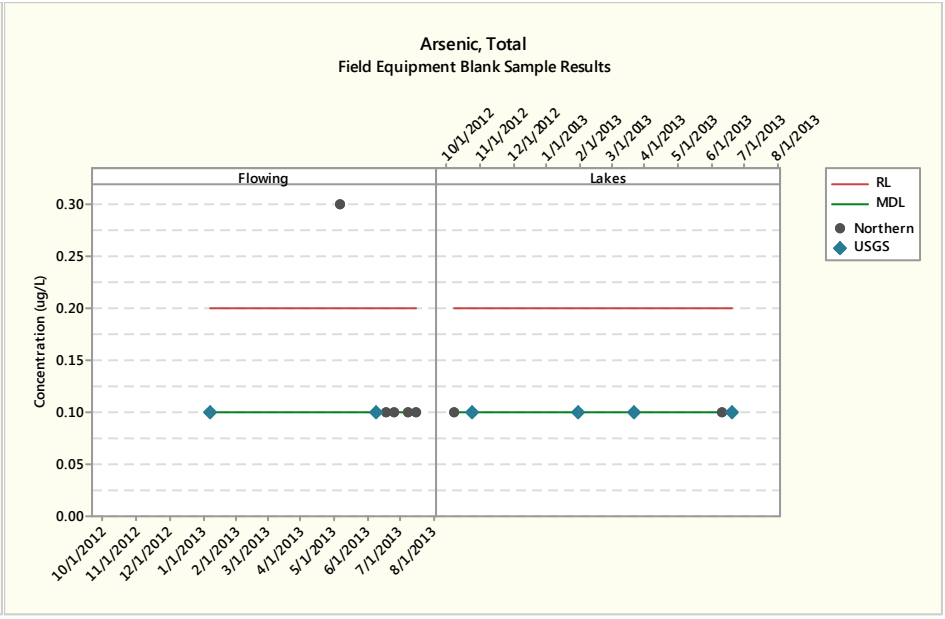

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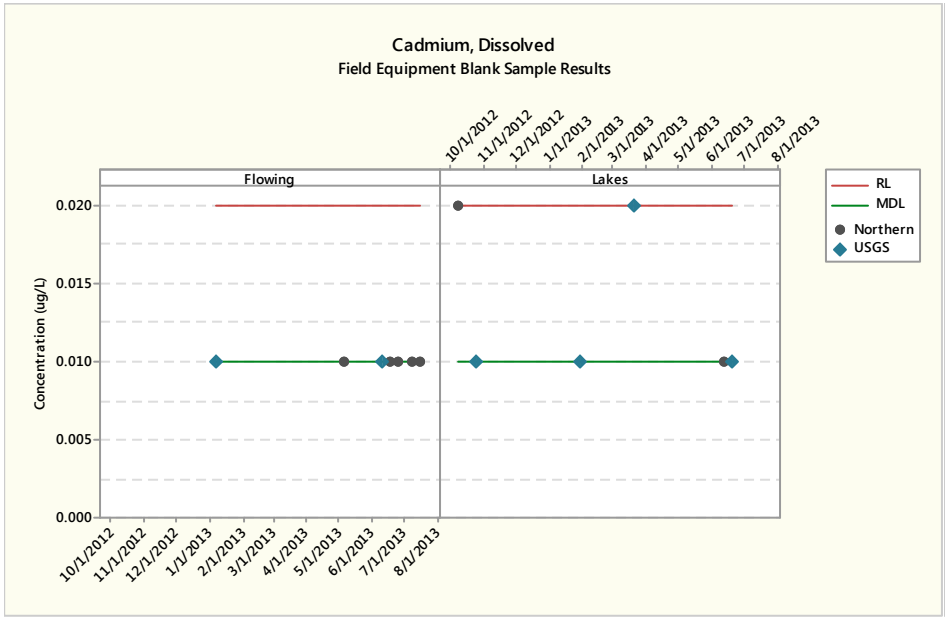

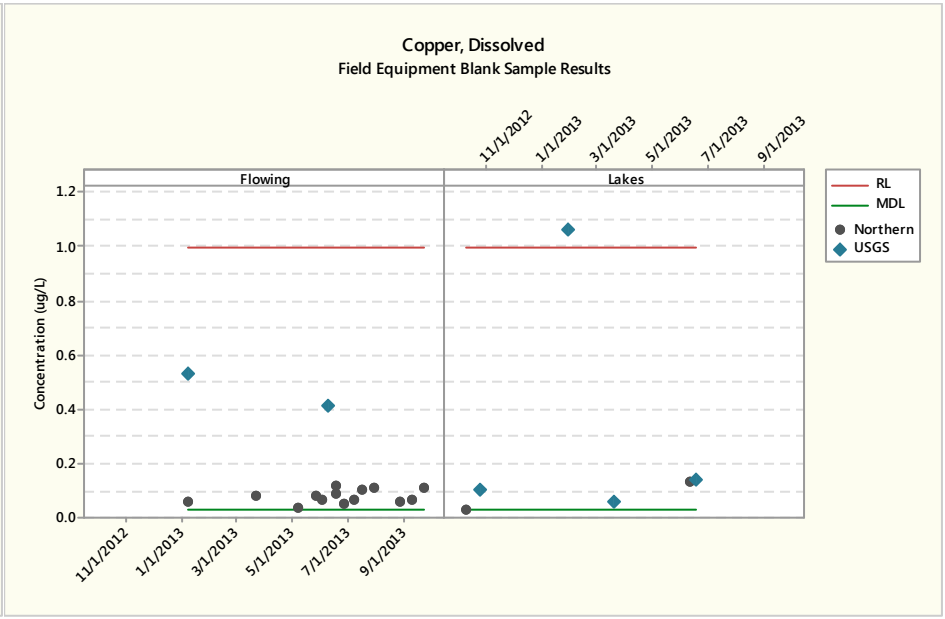

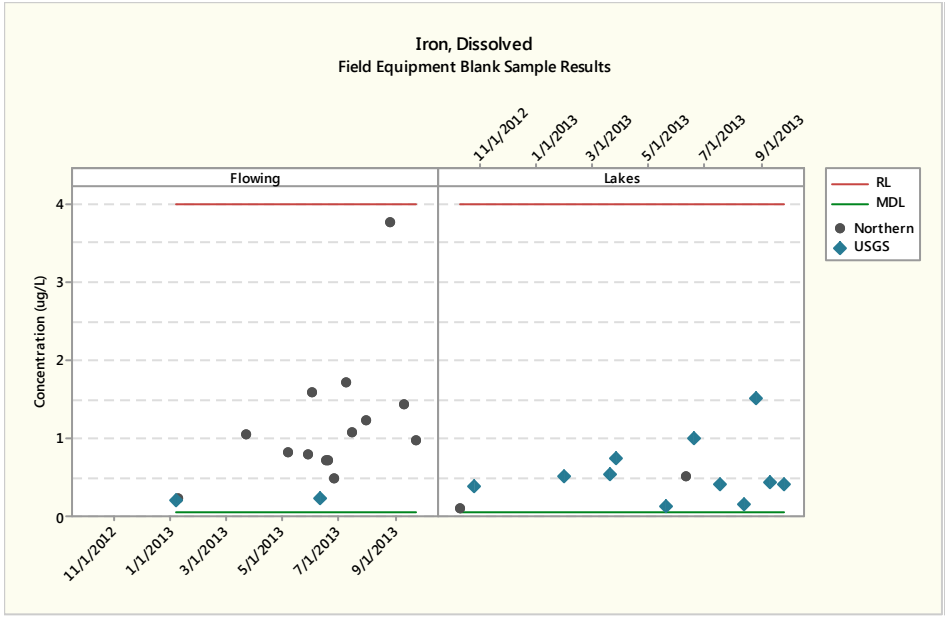

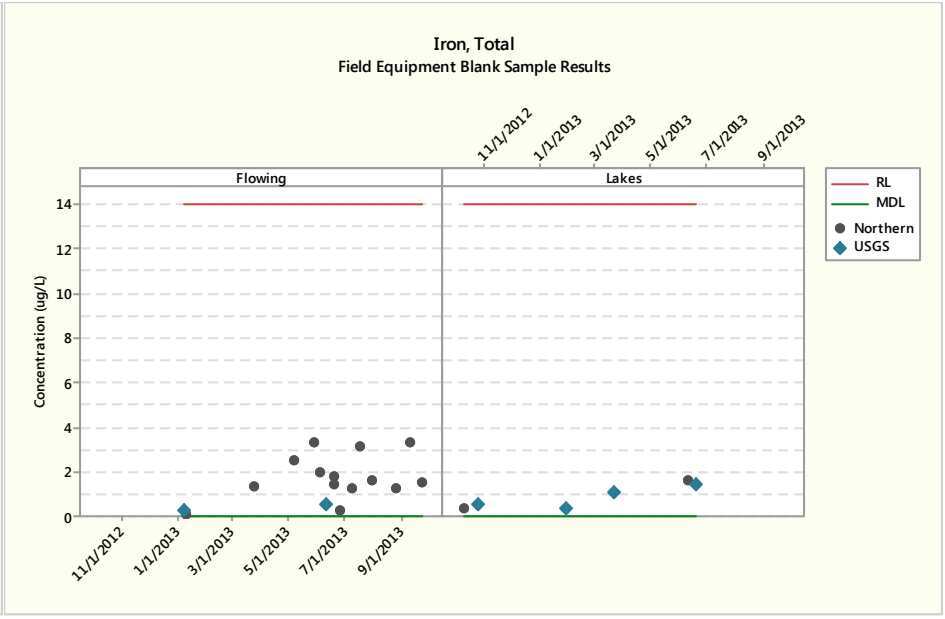

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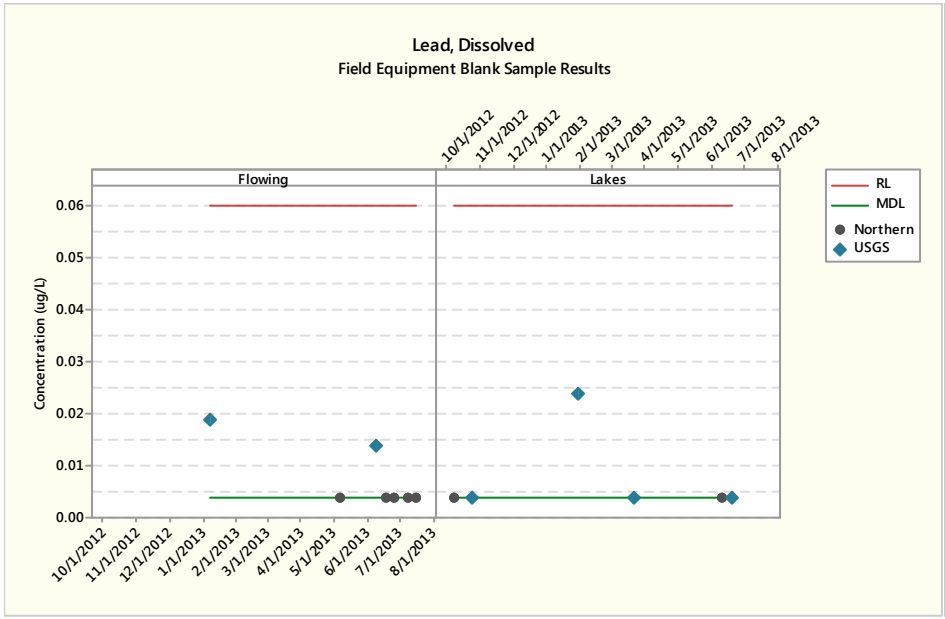

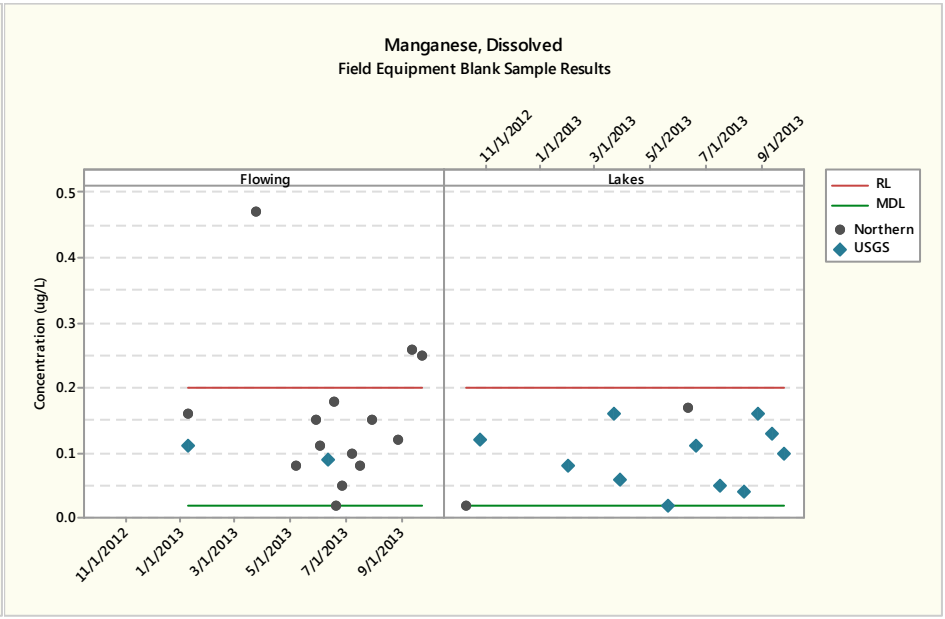

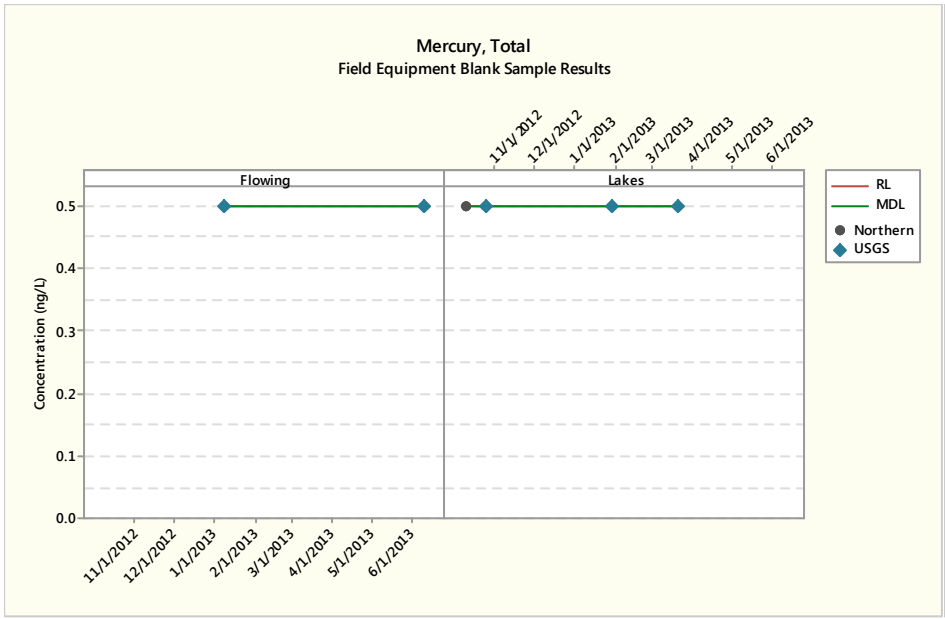

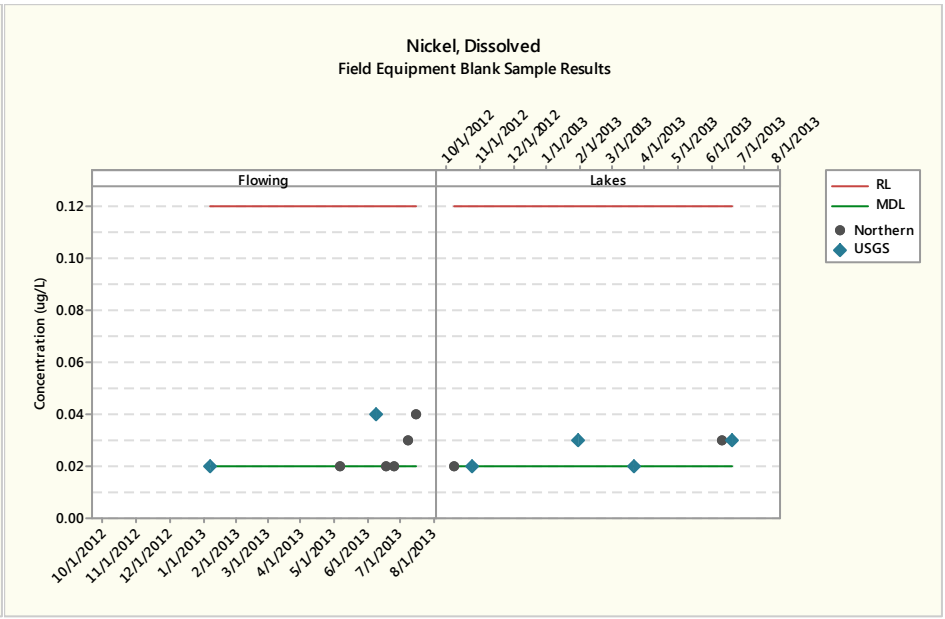

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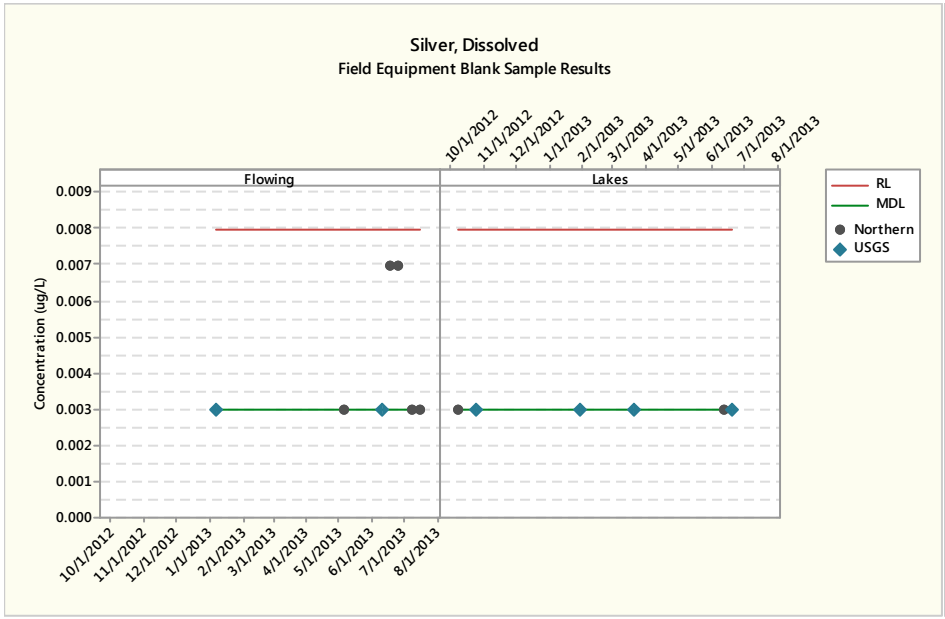

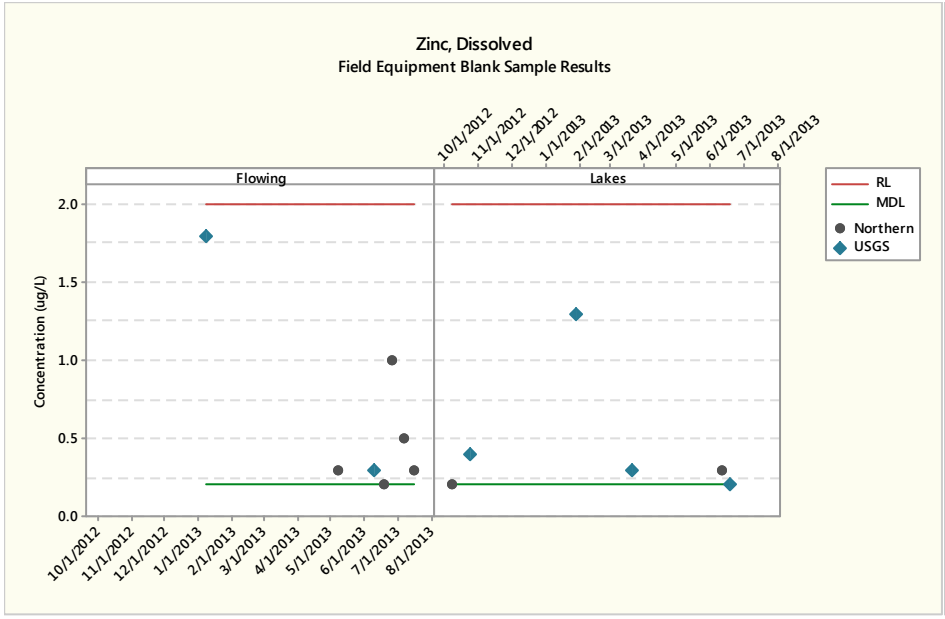

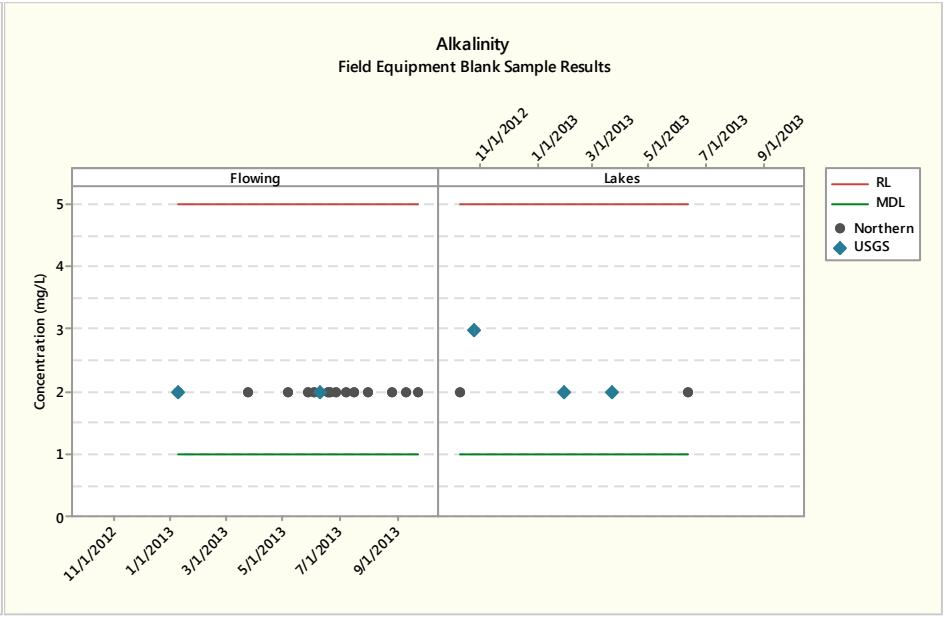

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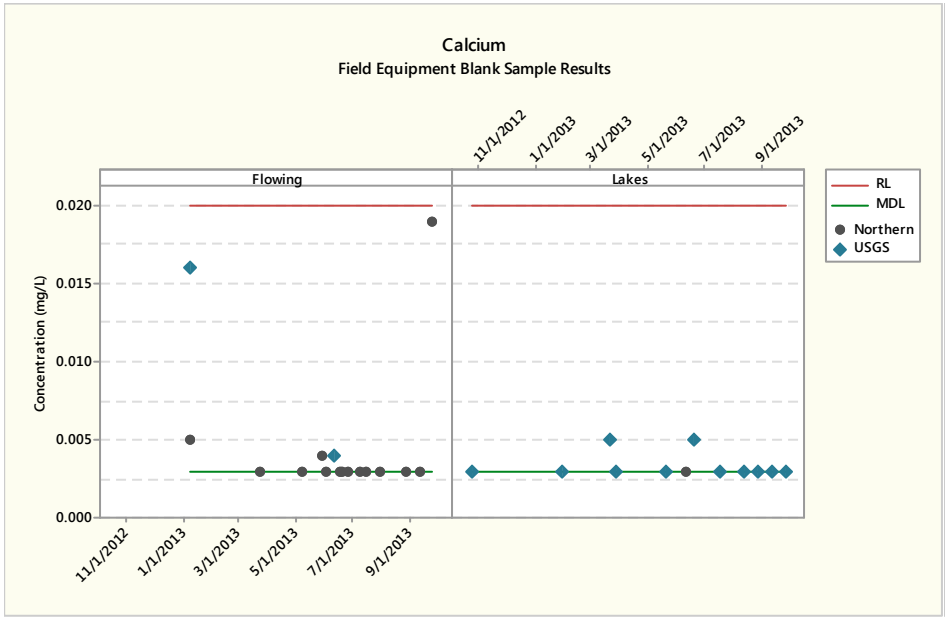

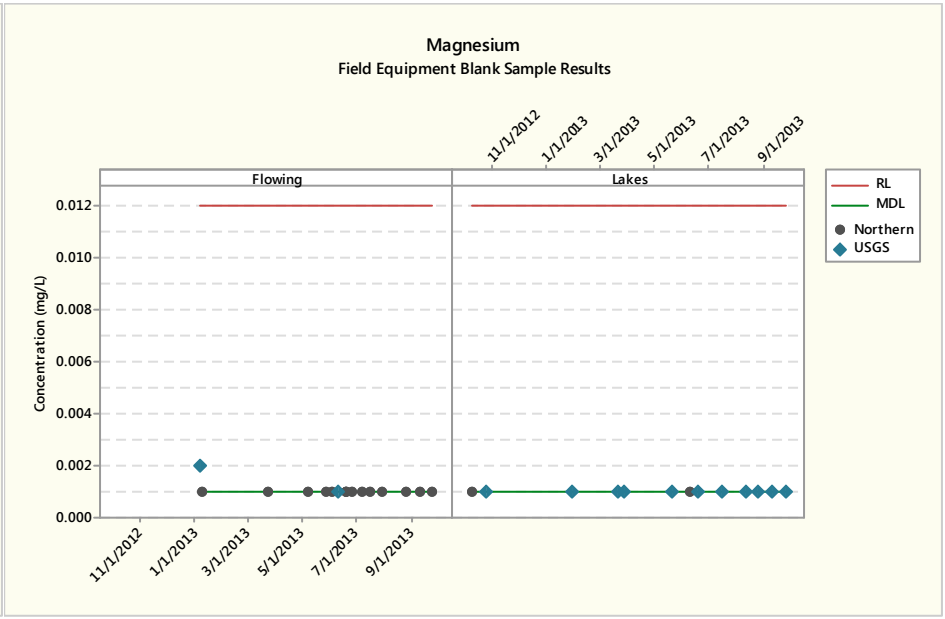

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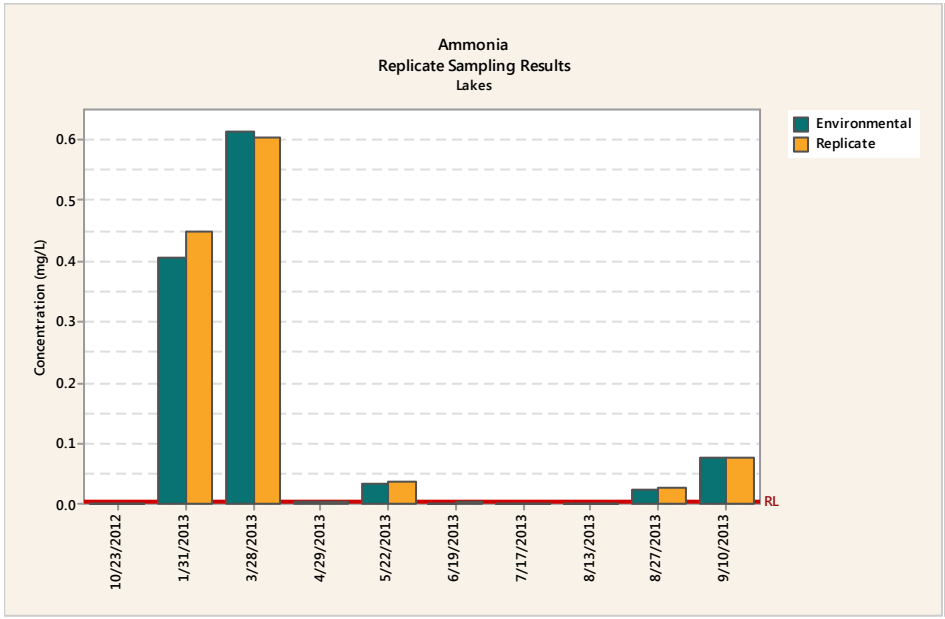

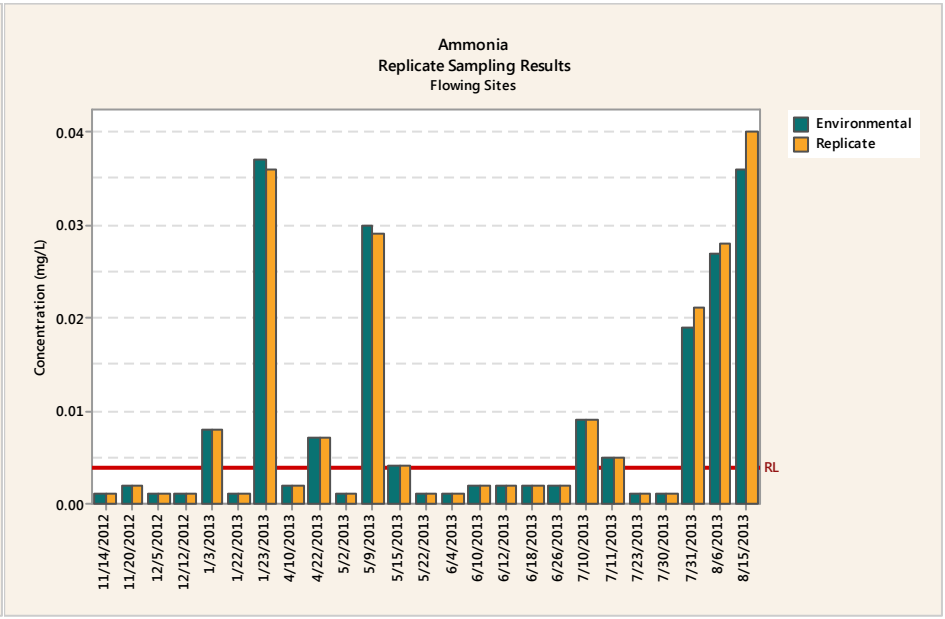

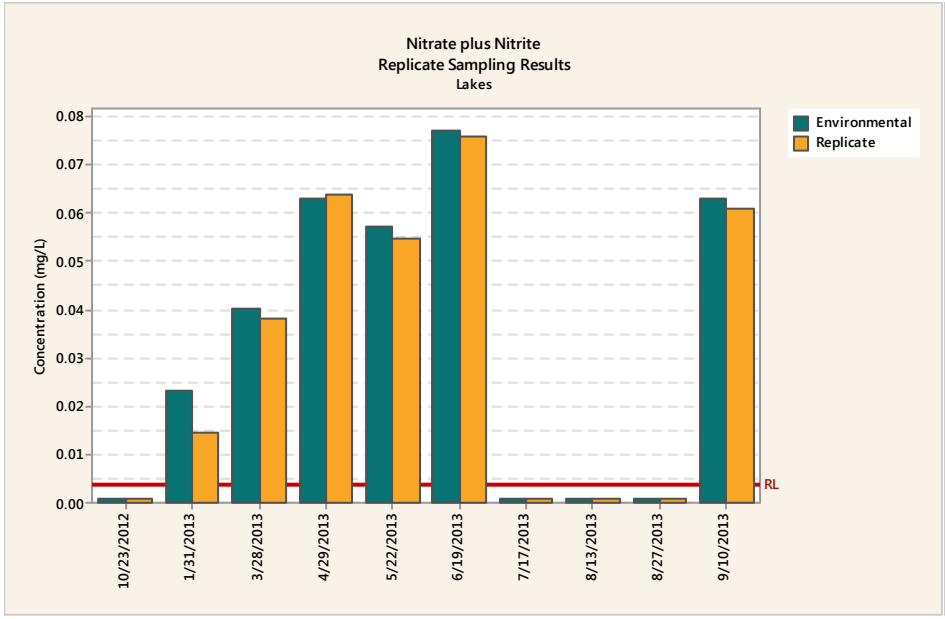

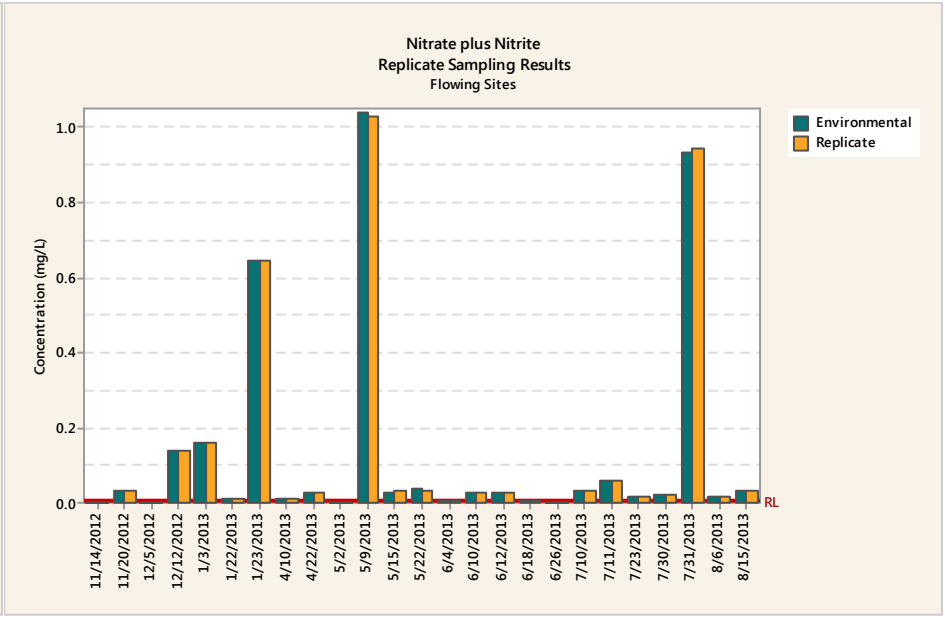

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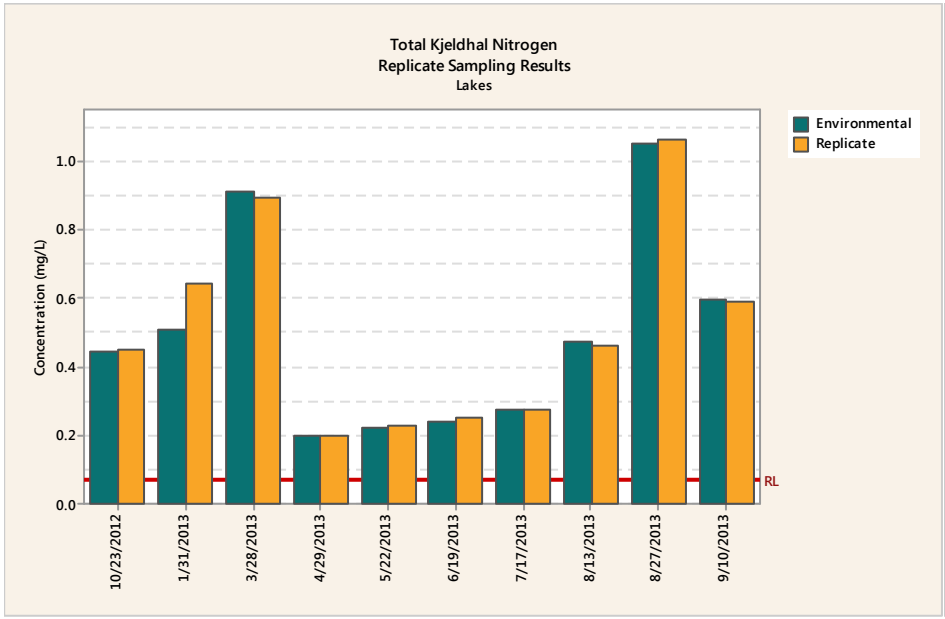

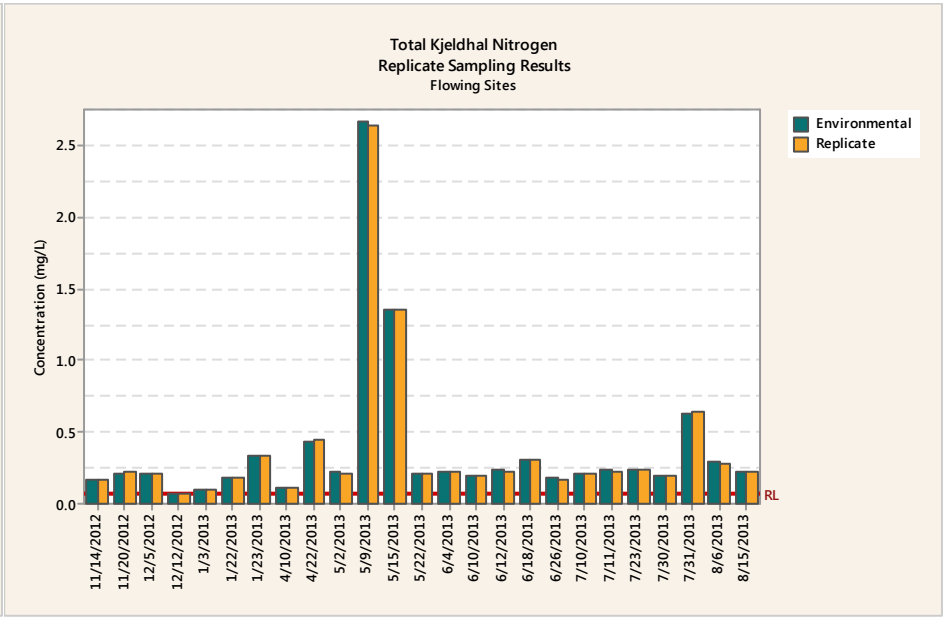

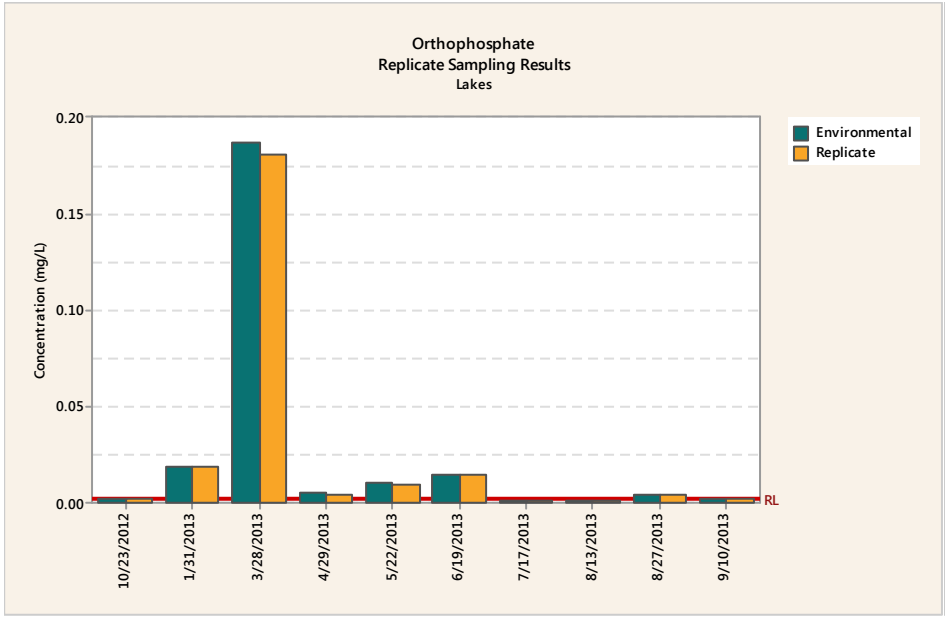

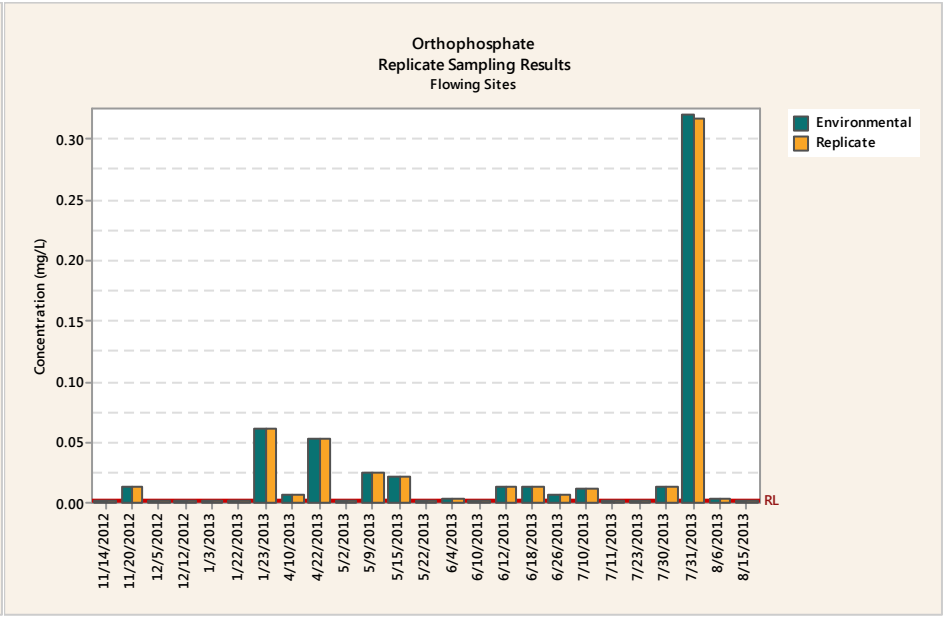

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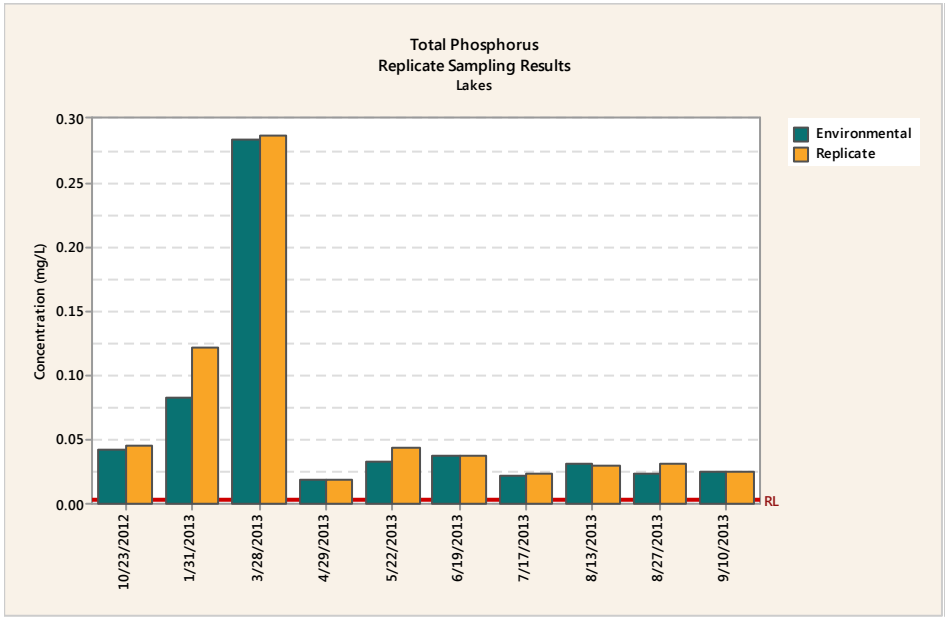

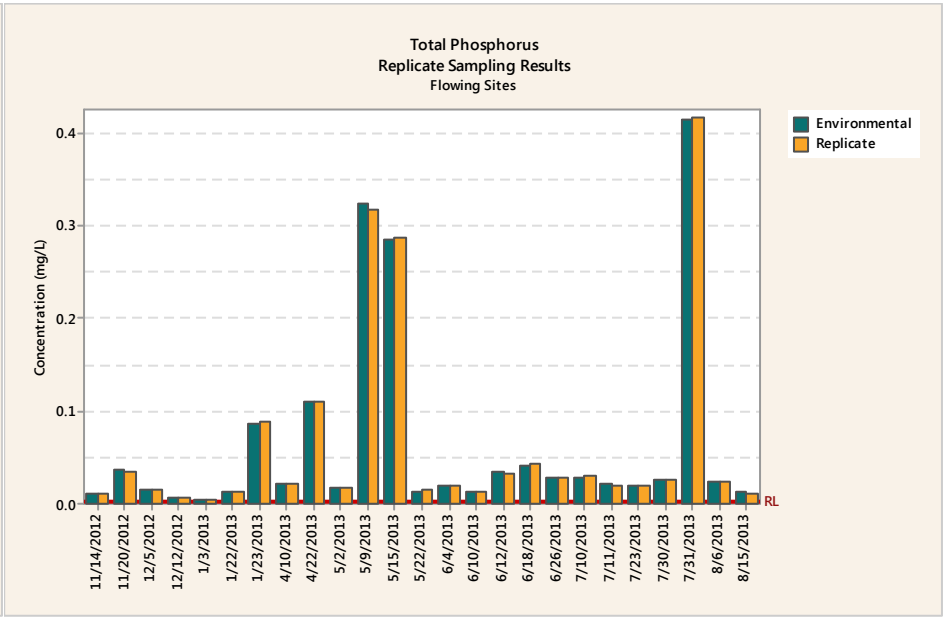

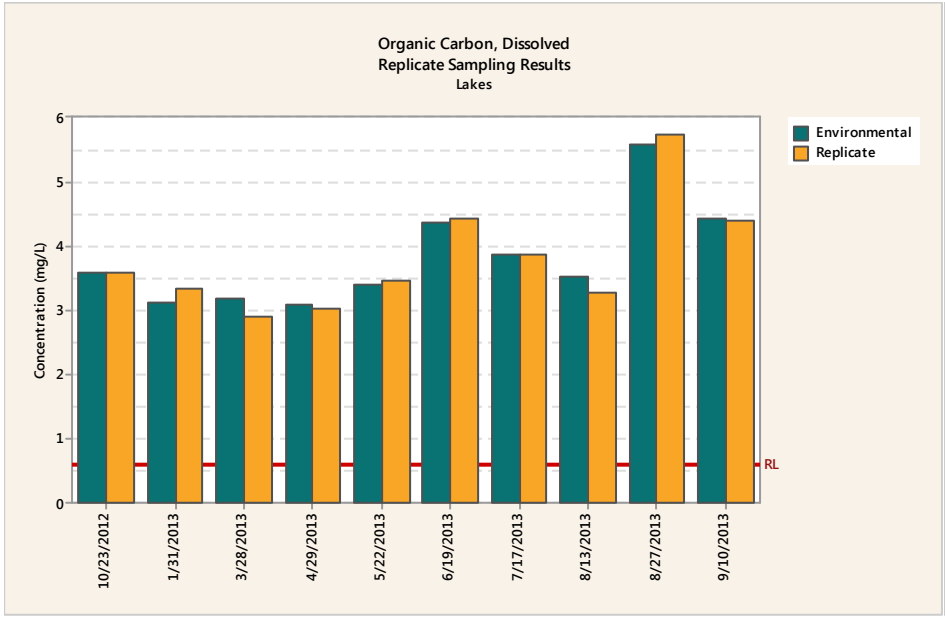

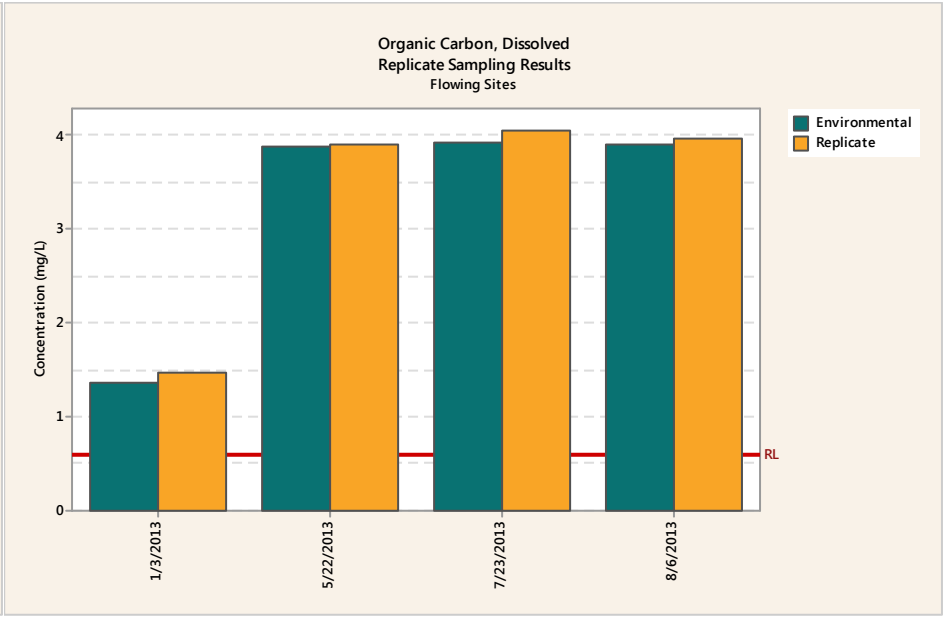

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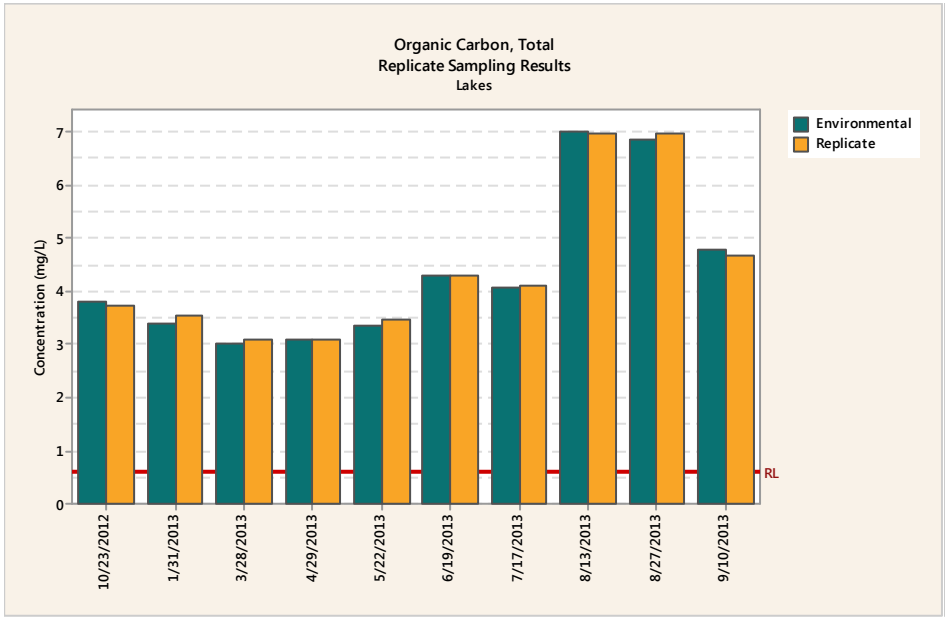

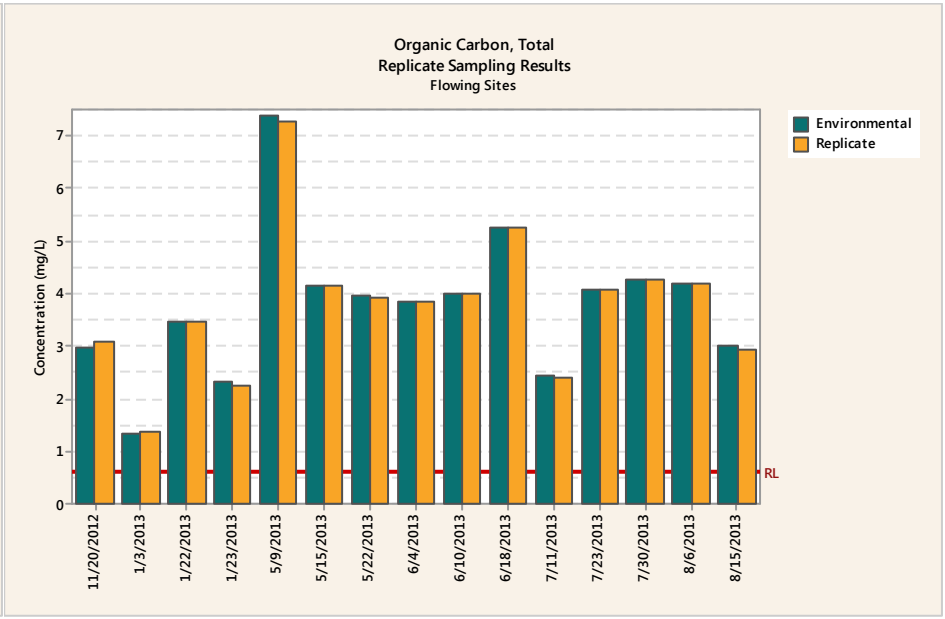

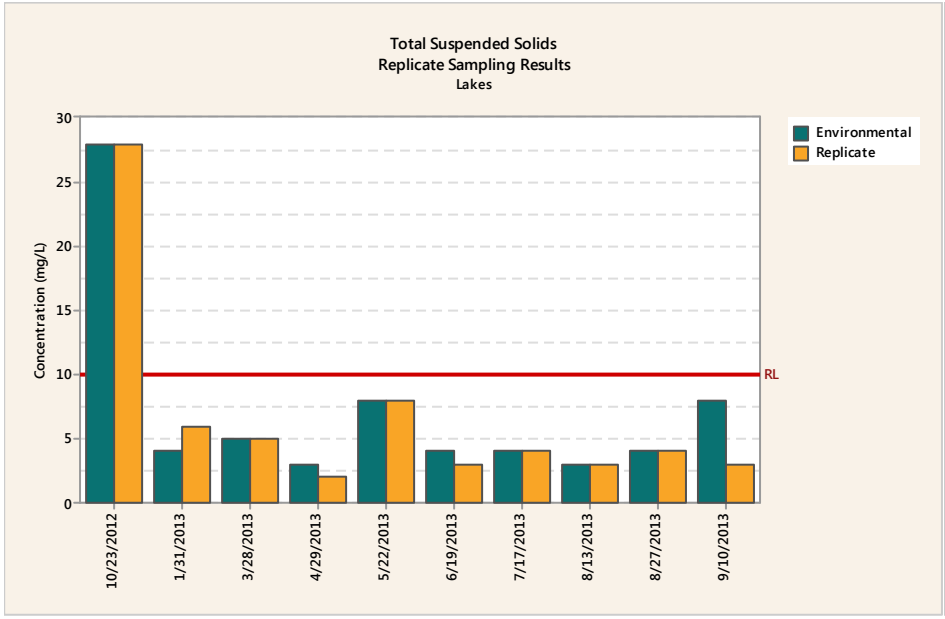

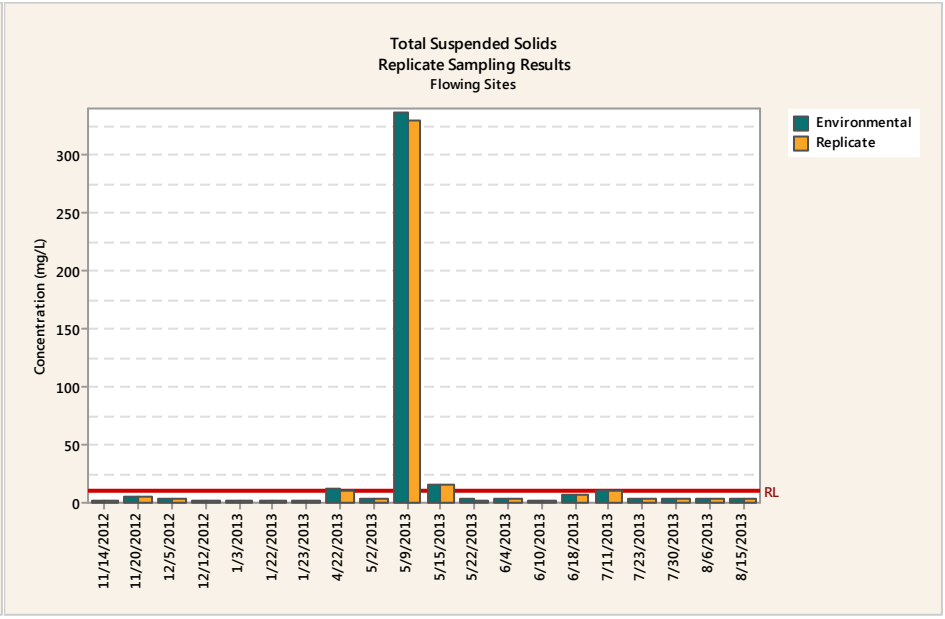

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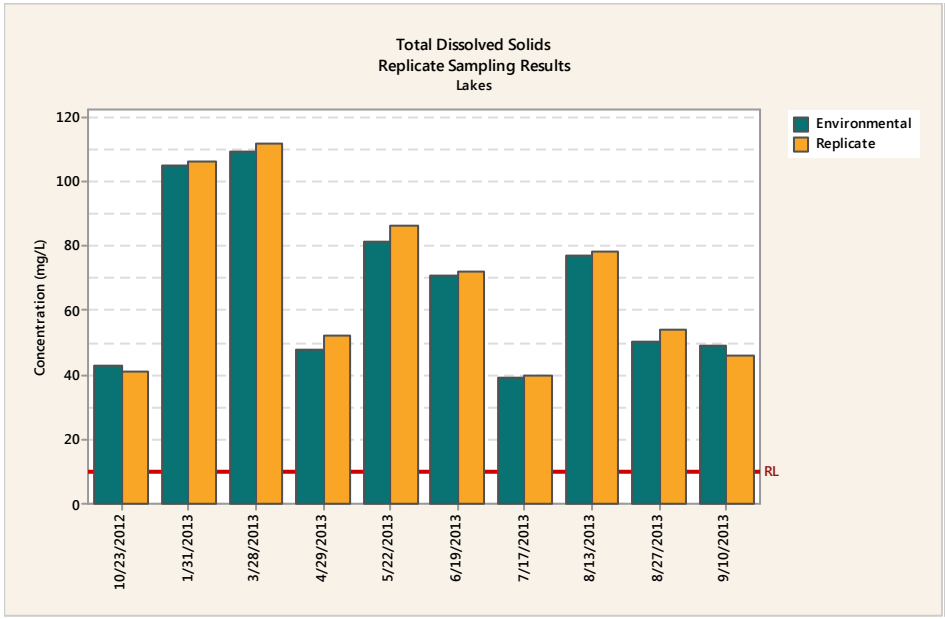

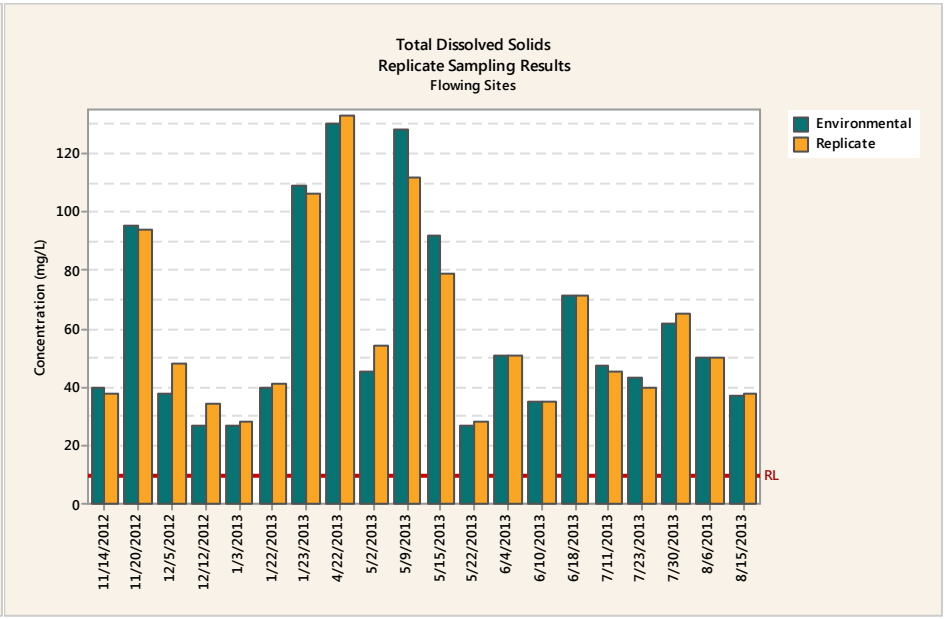

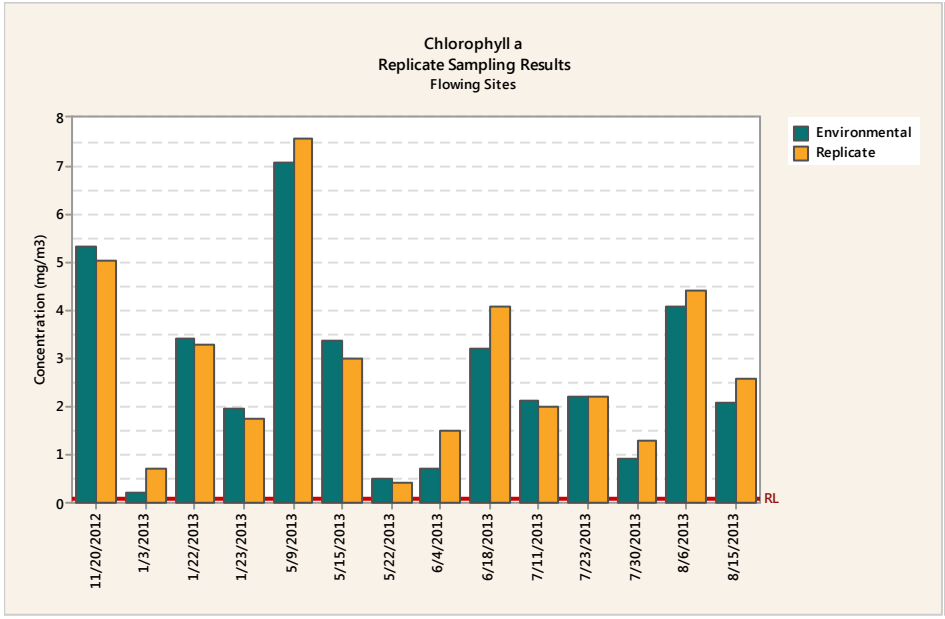

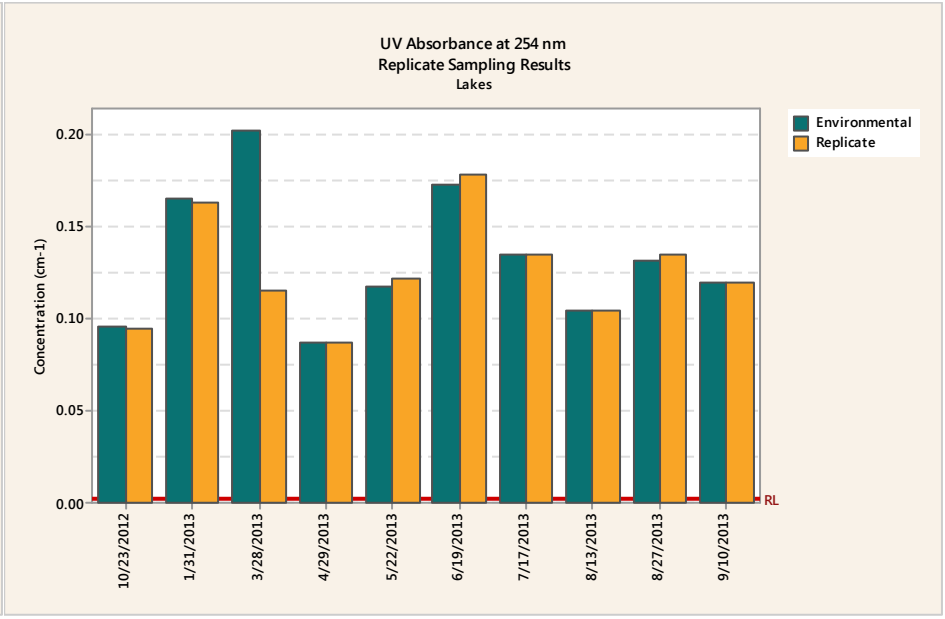

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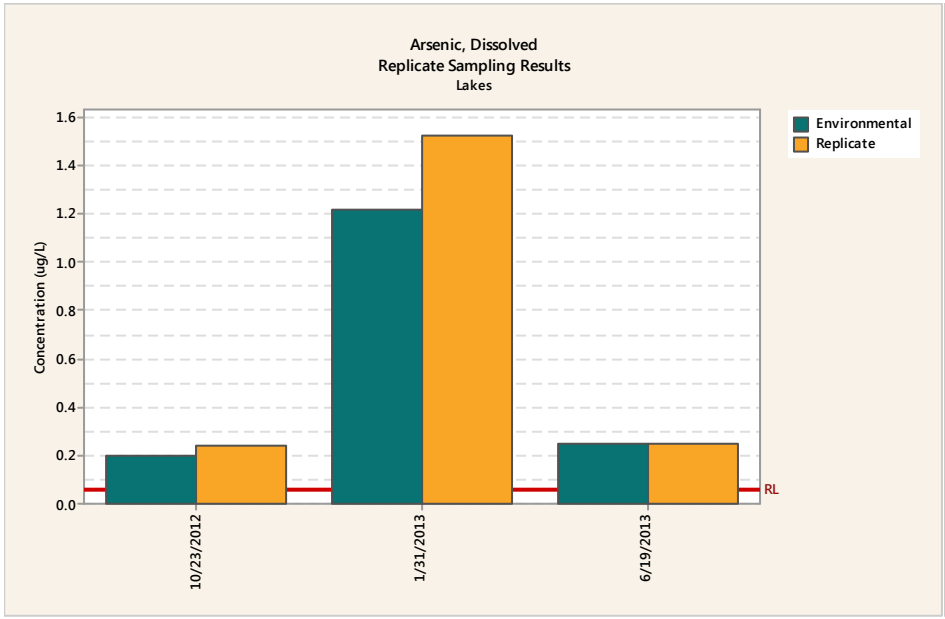
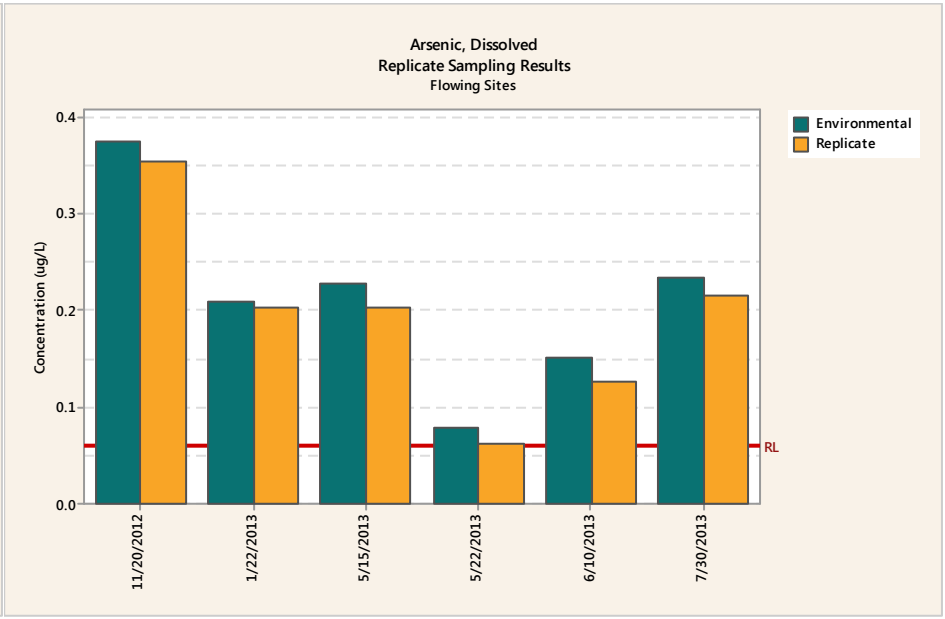
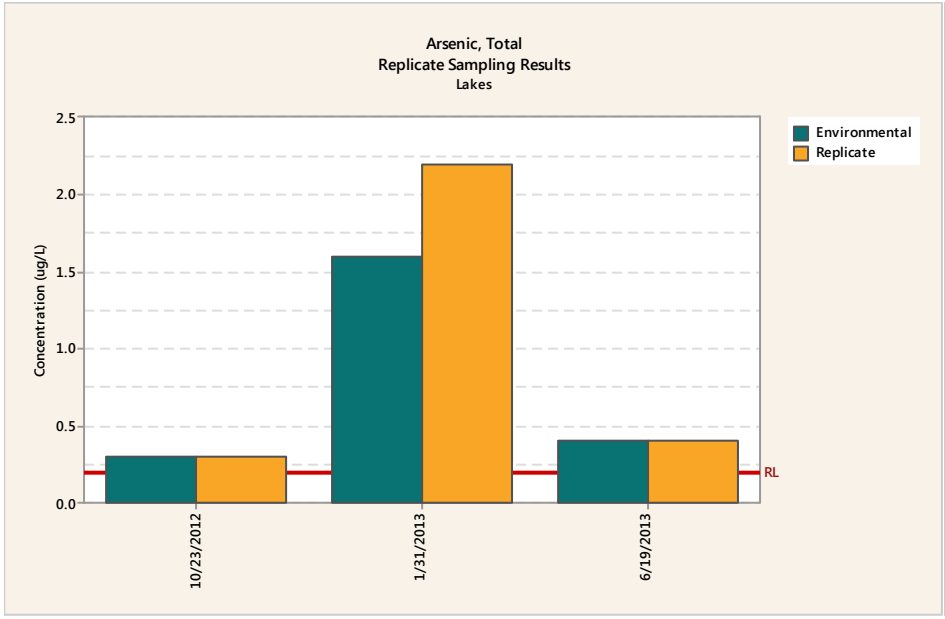
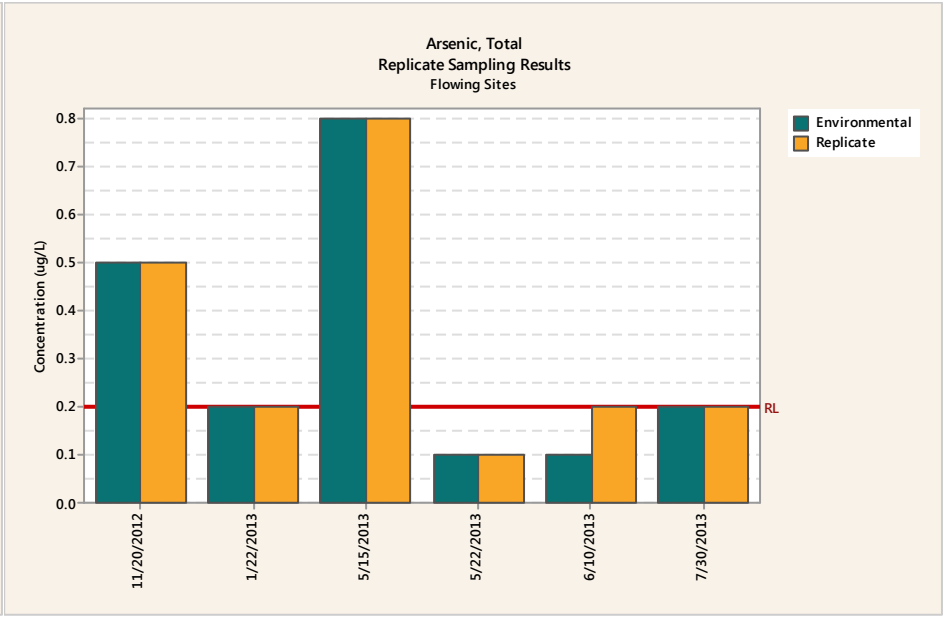
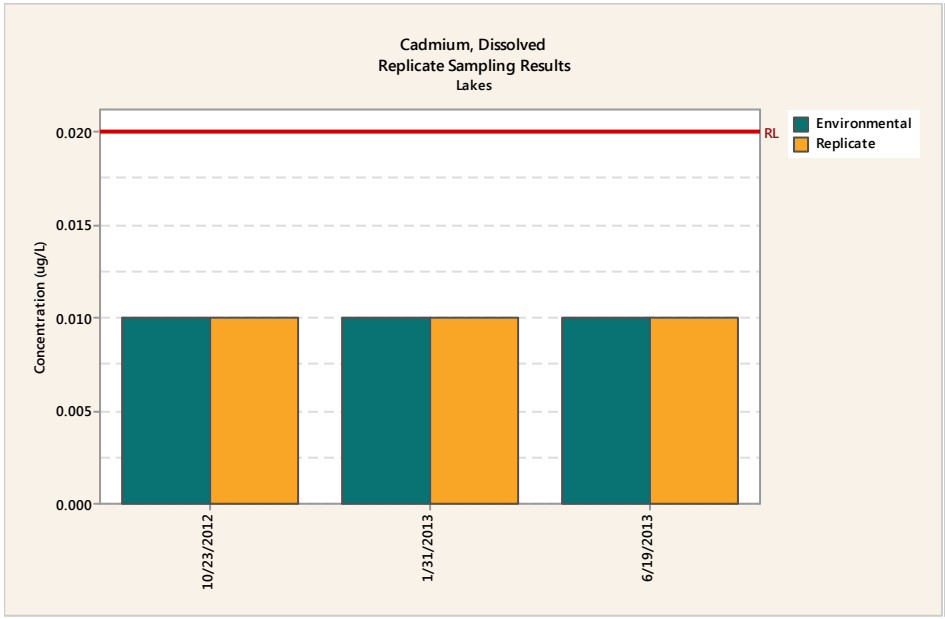


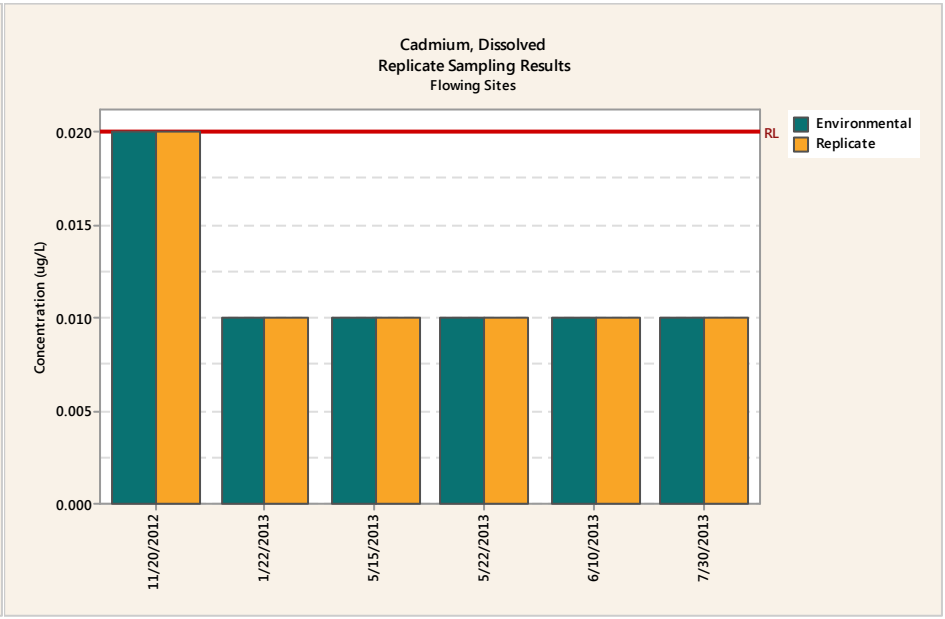


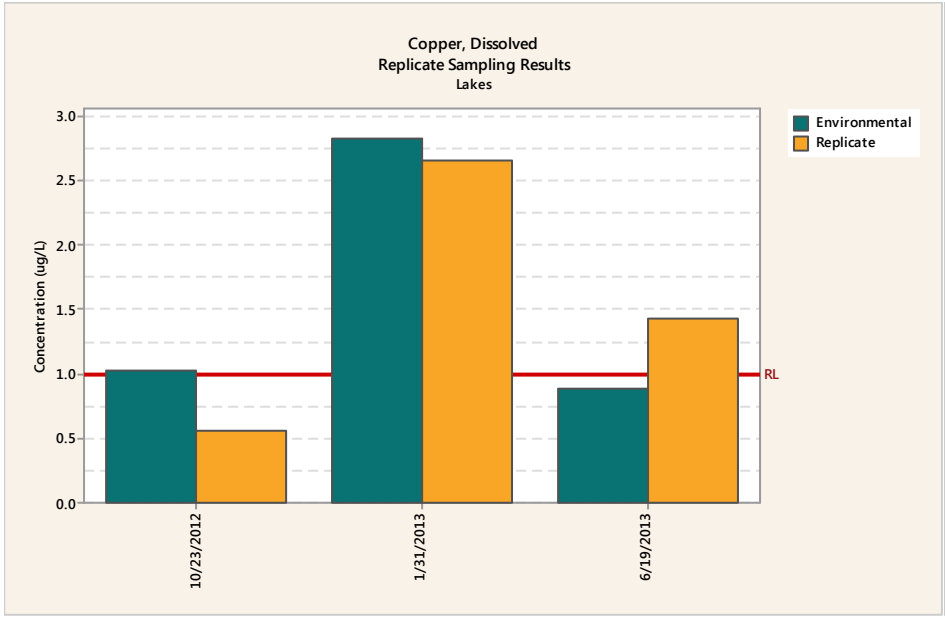


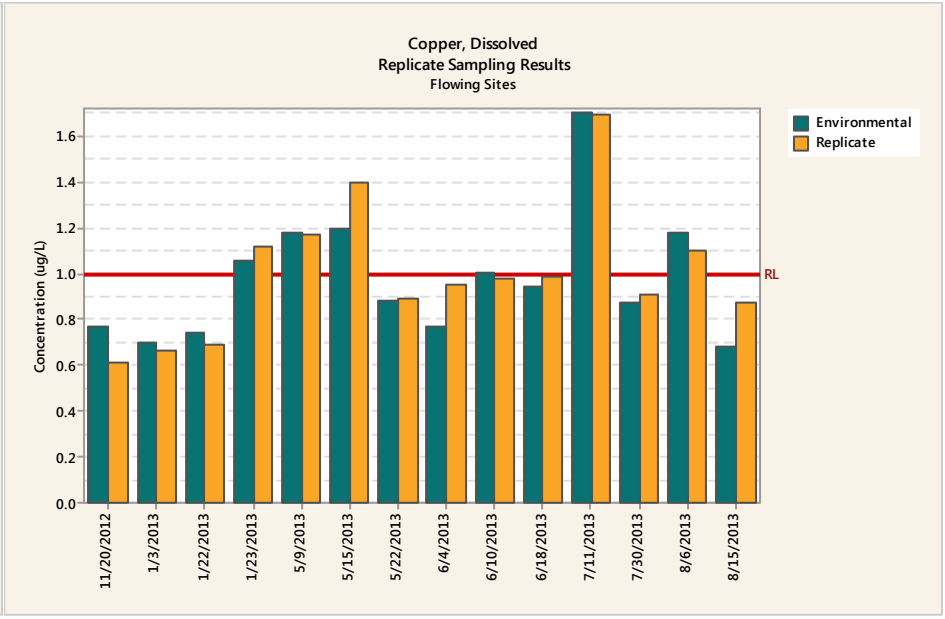


Appendix 2 – Field Replicate Results

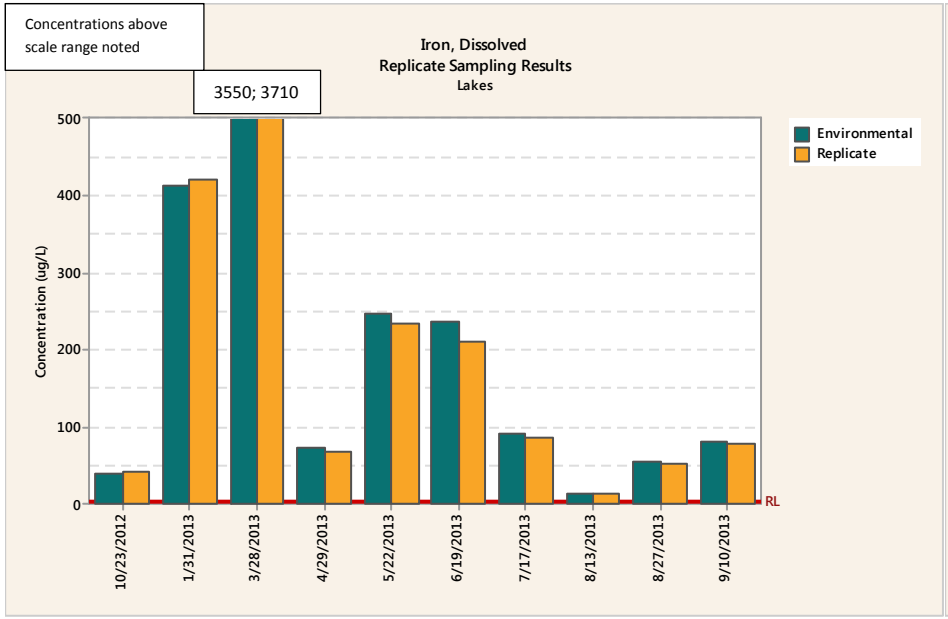


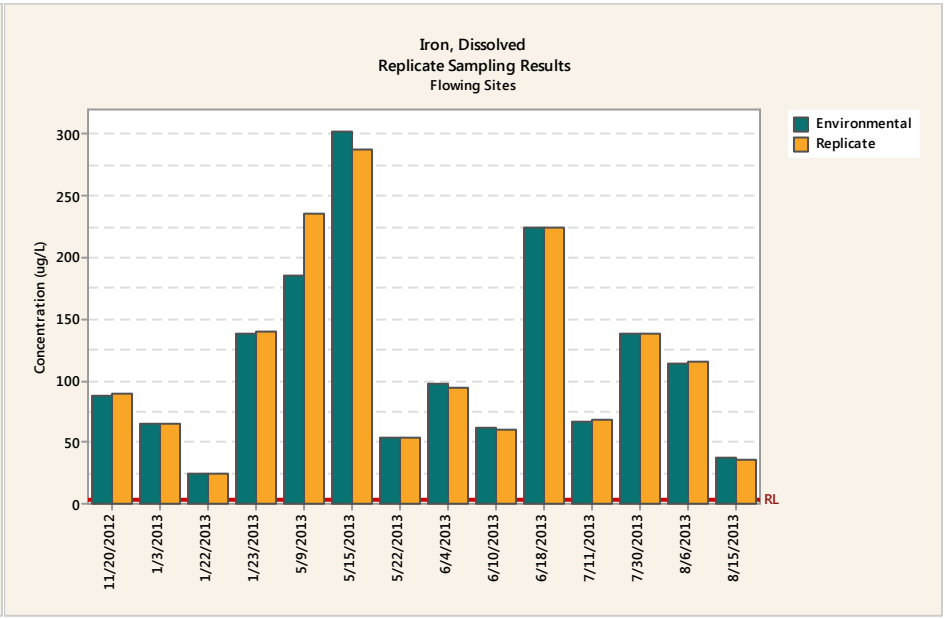


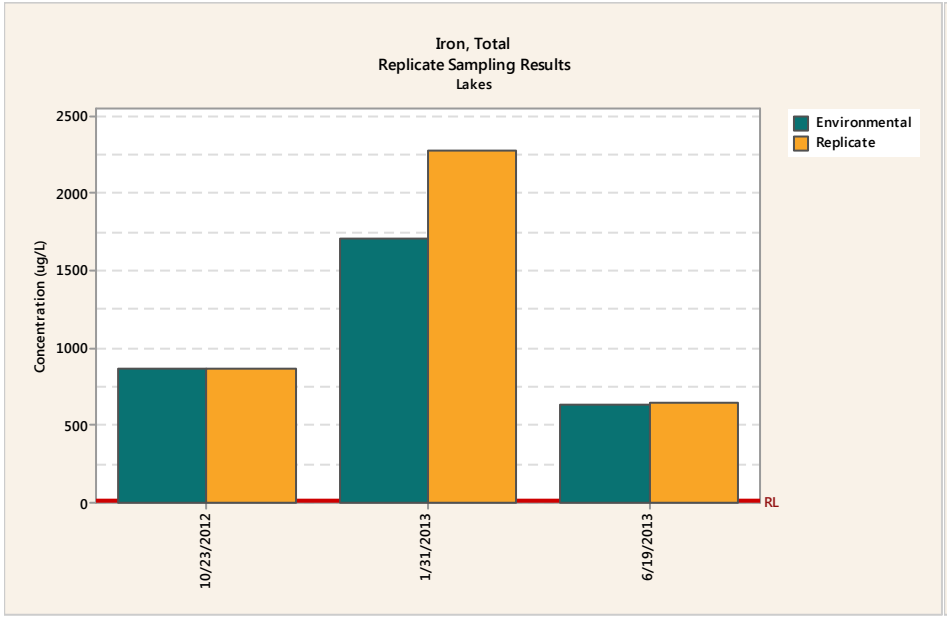


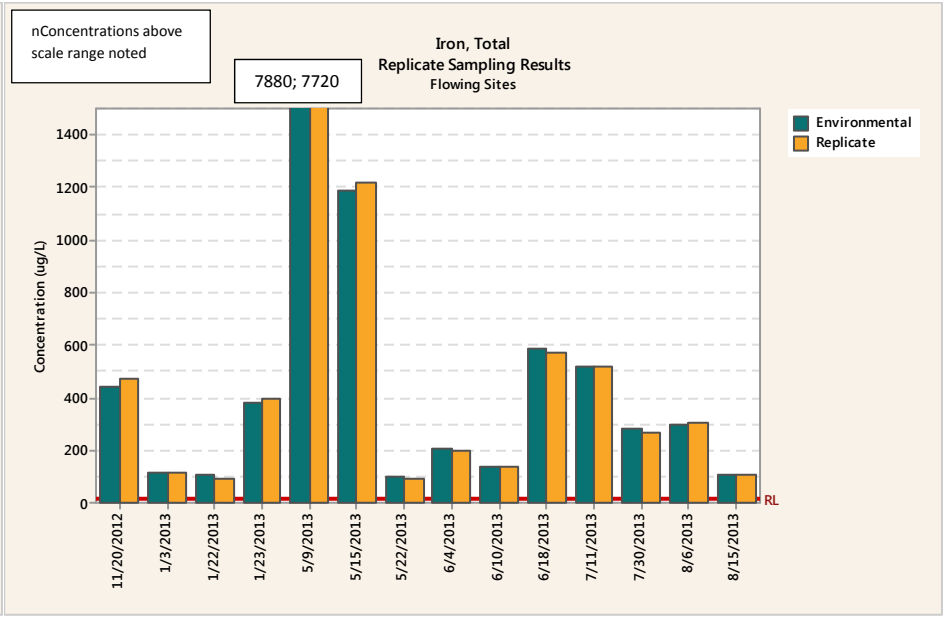


Appendix 2 – Field Replicate Results

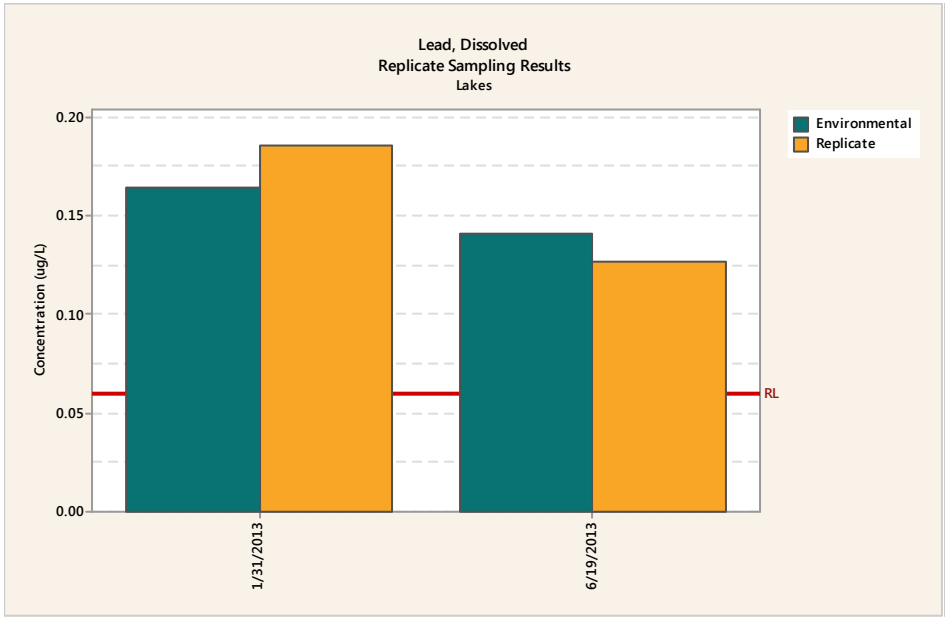


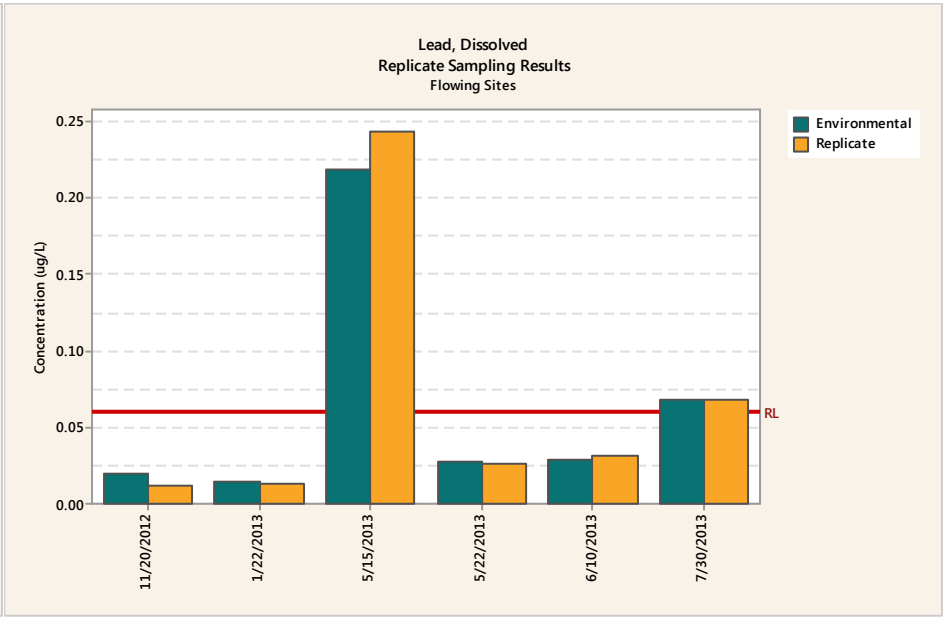


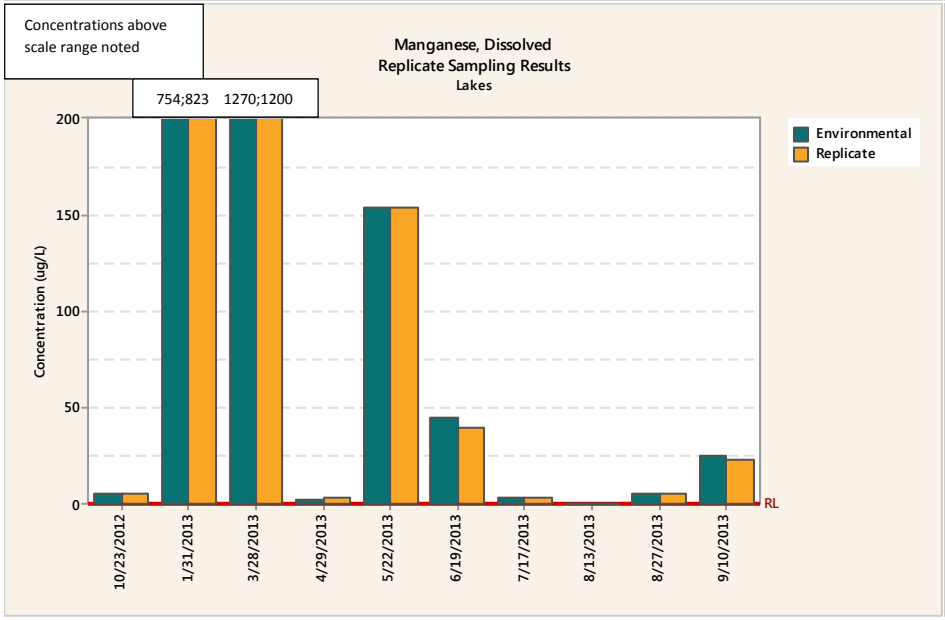


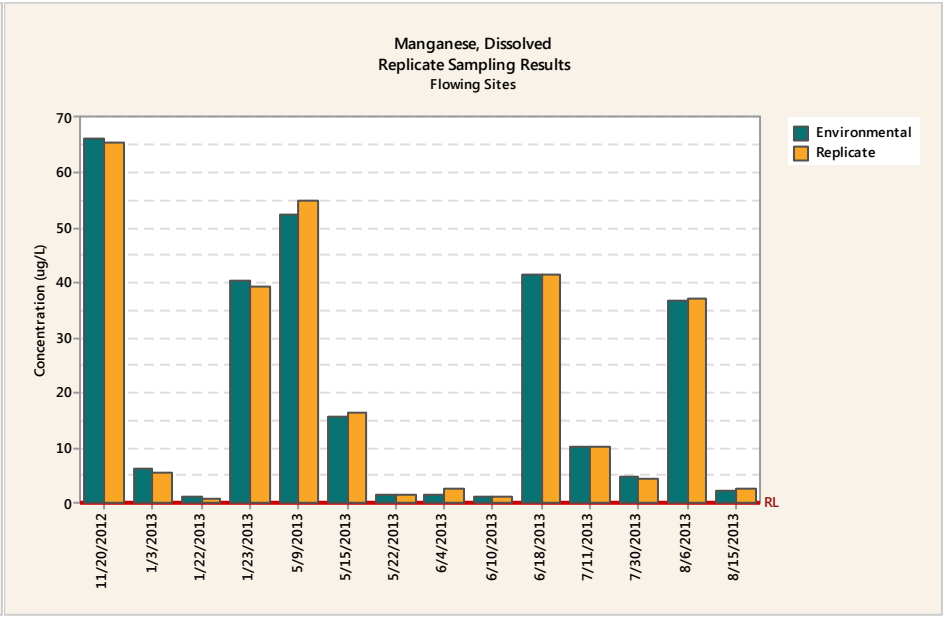


Appendix 2 – Field Replicate Results

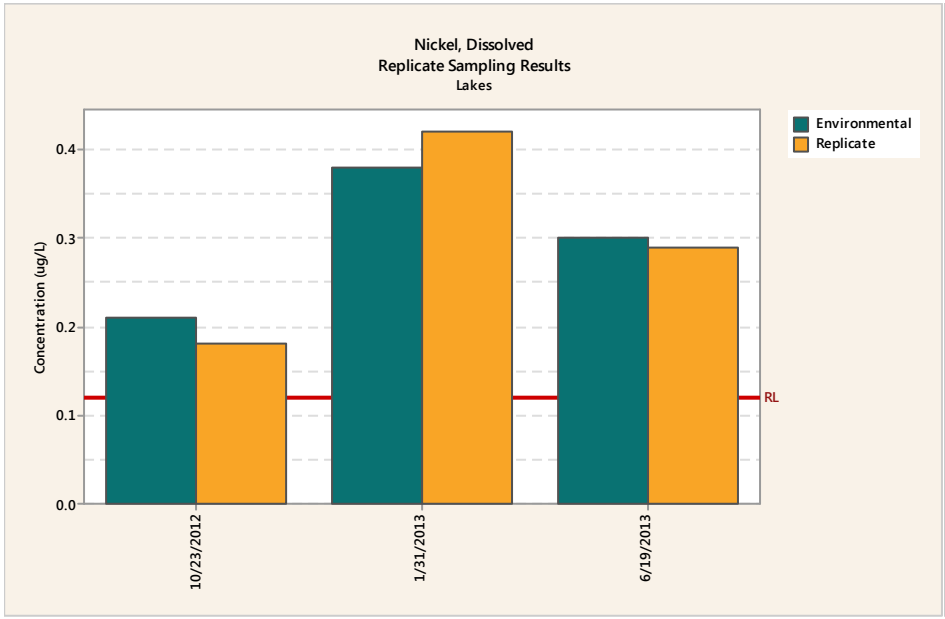


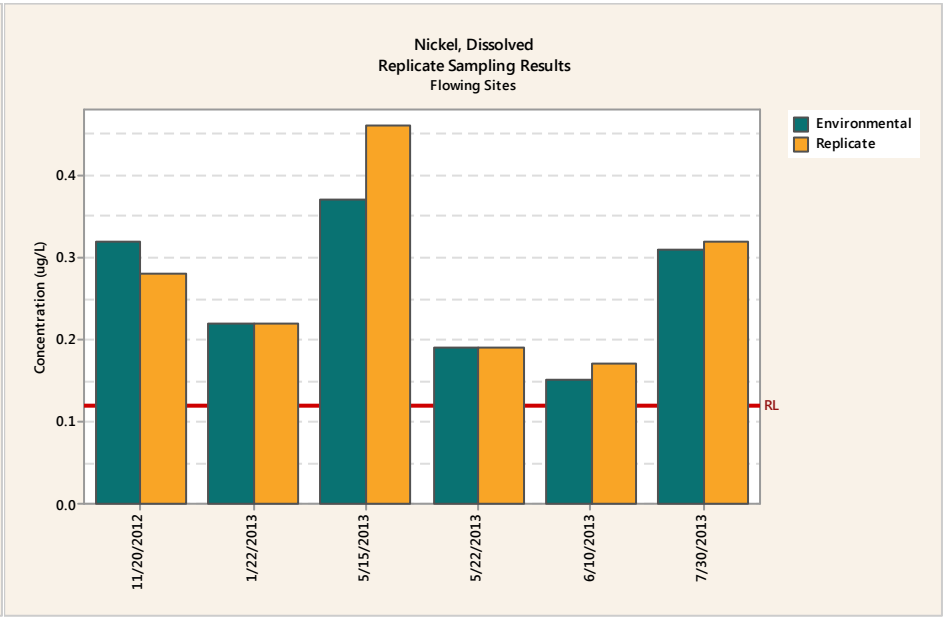


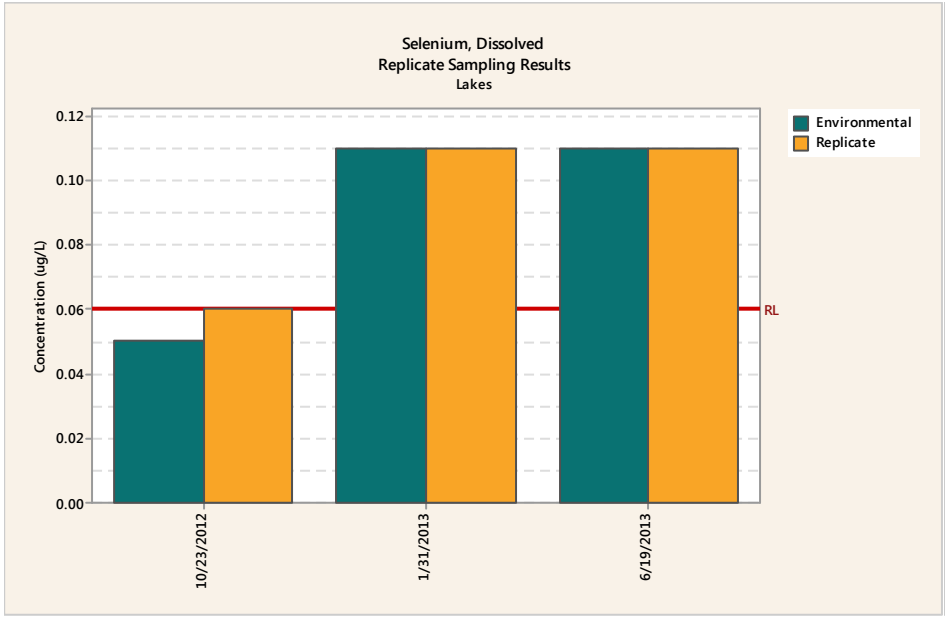


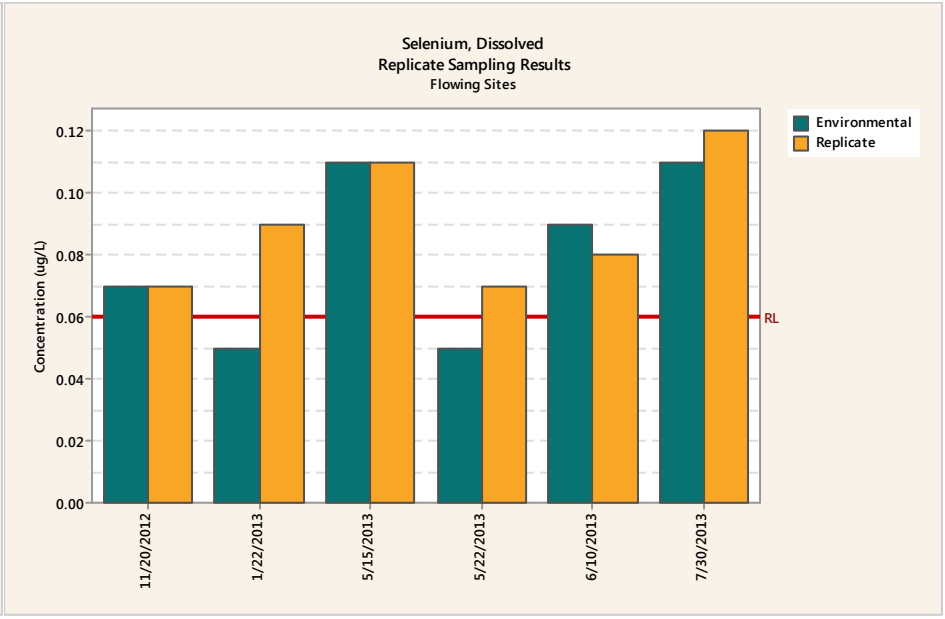


Appendix 2 – Field Replicate Results

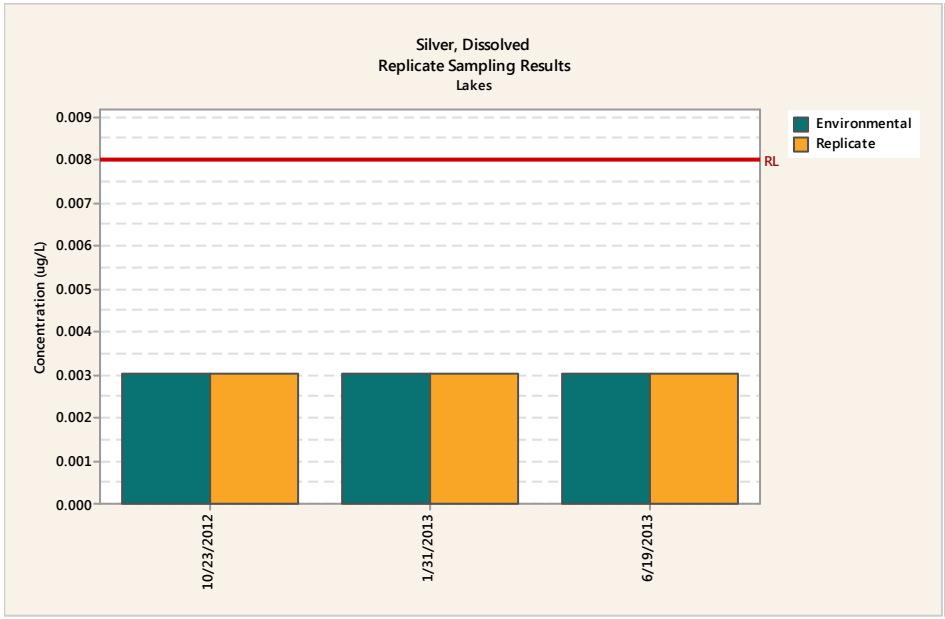


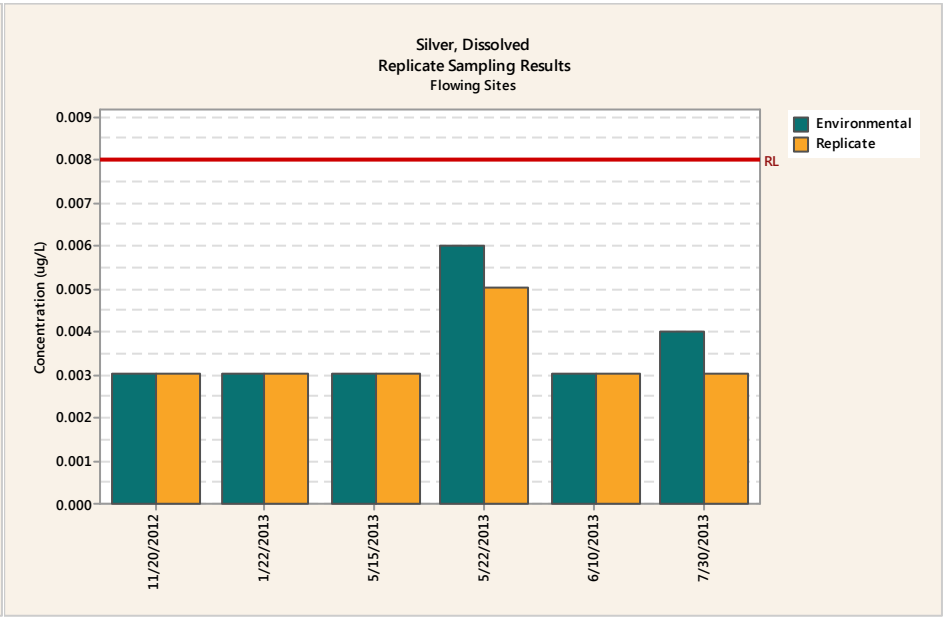


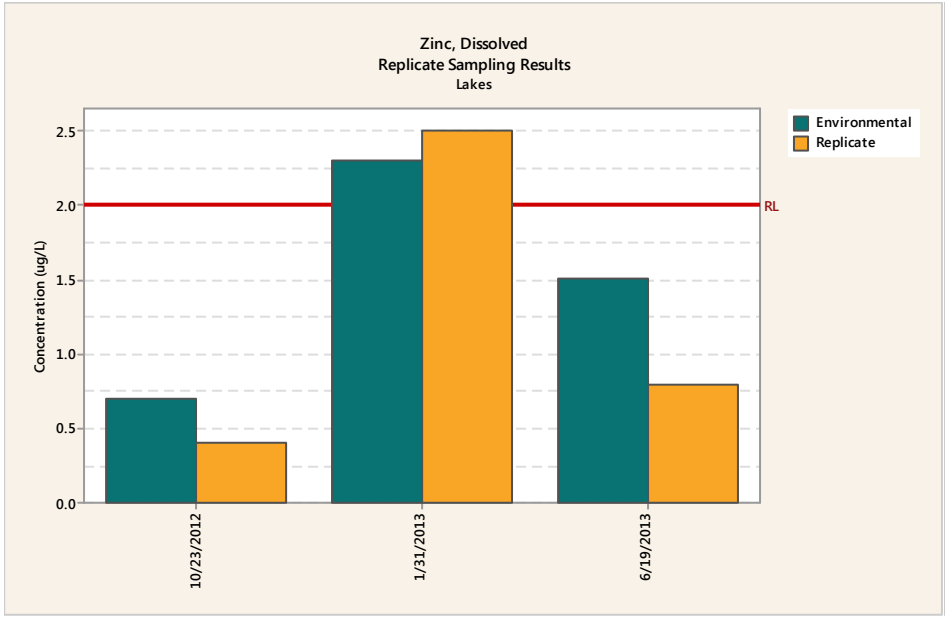


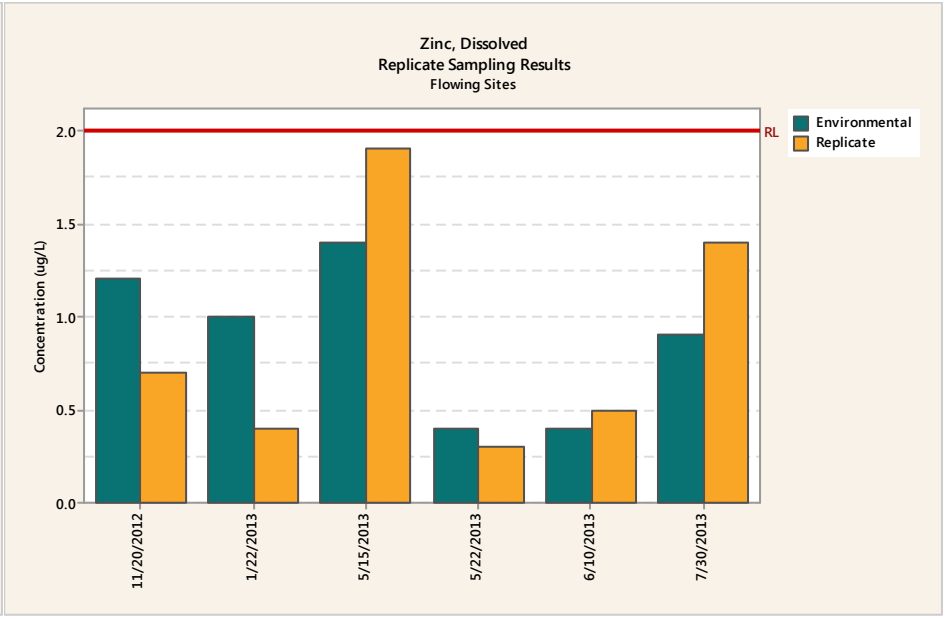


Appendix 2 – Field Replicate Results

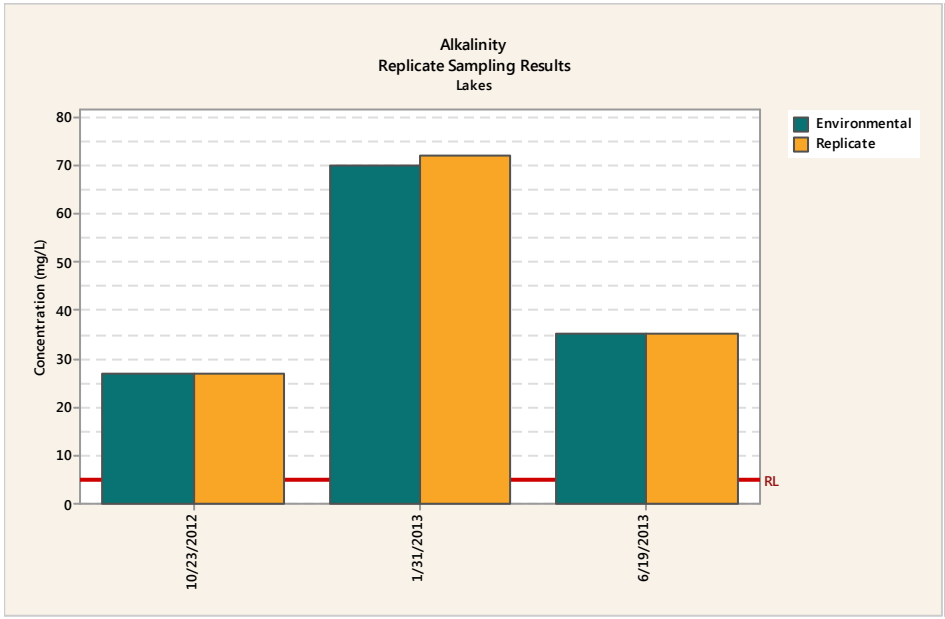


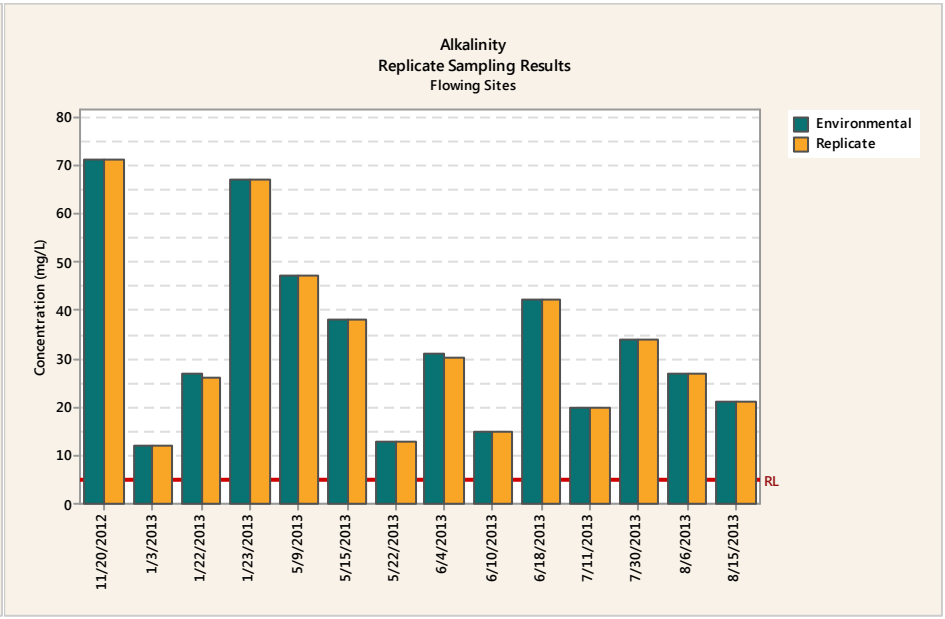


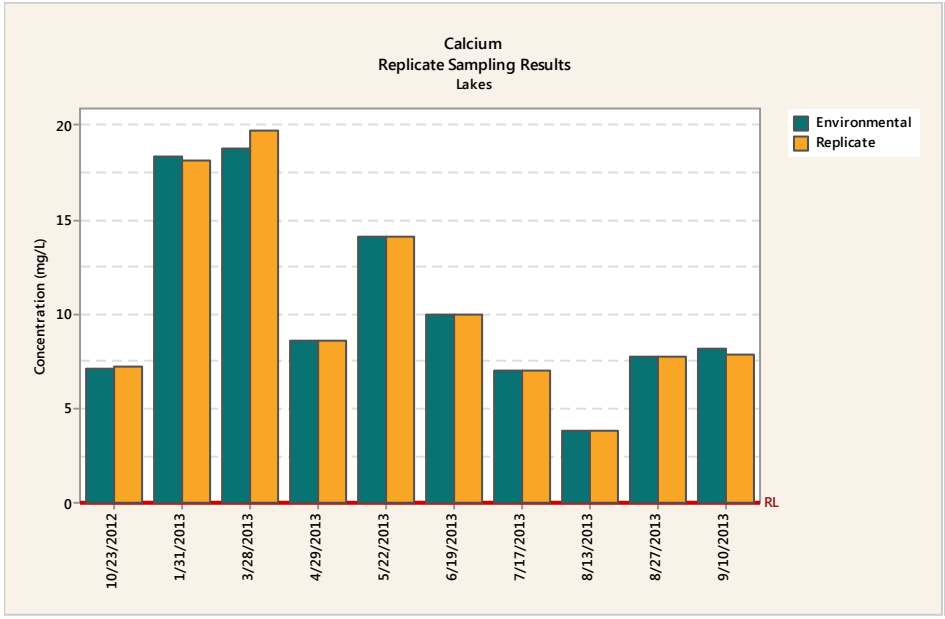


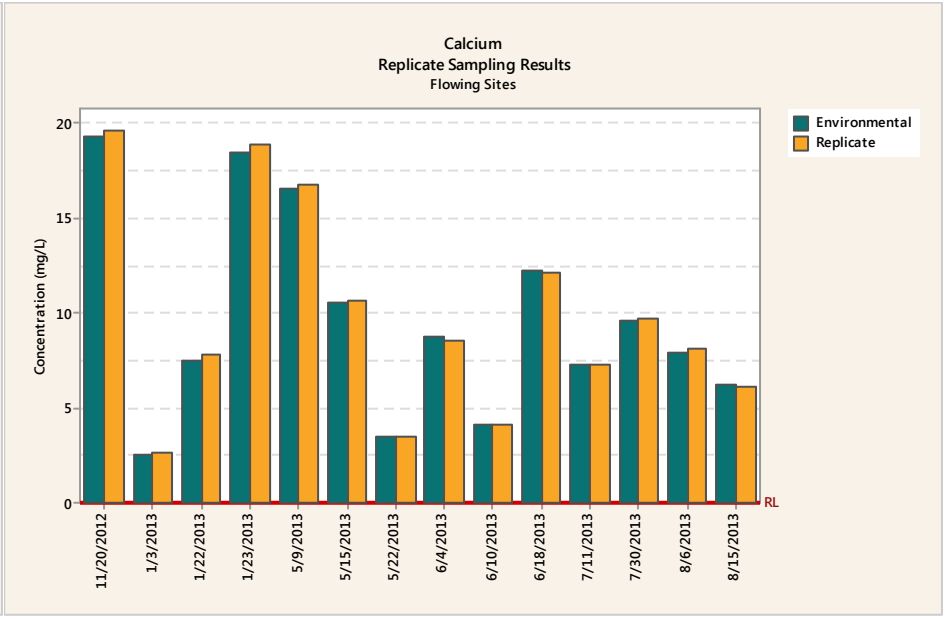


Appendix 2 – Field Replicate Results









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