

Appendix B

Quality Control/Quality Assurance

Kendra L. Zamzow, Ph.D.
Center for Science in Public Participation
Sutton, Alaska 99674

Joel Reynolds, PhD
Solutions Consulting
Anchorage, Alaska 99502

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1.0 Introduction

Quality assurance (QA) and quality control (QC) are performed in order to assess the accuracy and precision of analyte measurements and identify potential sources of bias. Biases and contamination can be introduced in the field due to equipment preparation, field methodology and from sample handling and transport. They can be introduced at the laboratory due to lab methodology or equipment limitations.

Field sampling was conducted according to the 2009 and 2010 Quality Assurance Project Plans (QAPP).¹ Chain of custody protocol was followed. Lab processing was conducted by Columbia Analytical Services (CAS) in Kelso, Washington in accordance with their NELAP²-approved quality assurance program. Sample results were analyzed for accuracy, precision, representativeness, and completeness. Prior to comparing this data set with data collected by other groups, the comparability of the data sets was reviewed. Precision and accuracy are quantitative, while representativeness and completeness have quantitative and qualitative aspects; comparability is entirely qualitative.

2.0 Methods

2.1 Completeness

Completeness is the portion, per analyte, of all field samples for which analyses were completed successfully, i.e., without any reason to reject. Completeness was calculated per analyte.

Completeness = $100 * (\text{total number of valid lab results}) / (\text{total number of field sample analyses})$

2.2 Accuracy (bias)

Accuracy is a measure of the agreement of a known value with a measured value, and was assessed in the lab using lab control samples (LCS) and matrix spikes (MS). Lab control samples were lab water spiked with known concentration of analyte, then analyzed to determine what percent of the analyte could be recovered. Matrix spikes were field samples spiked with a known concentration of analyte, then analyzed to determine what percent of the analyte could be recovered. Both were processed at a rate of 10% or one per lab order, whichever was more frequent, to assess lab accuracy (Table 1).

LCS accuracy: $\% \text{ recovery} = 100 * (\text{measured concentration} / \text{actual spike concentration})$

MS accuracy: $\% \text{ recovery} = 100 * (\text{measured concentration of spiked aliquot} - \text{measured concentration of un-spiked aliquot}) / (\text{actual spike concentration})$

¹ Zamzow 2009; Zamzow 2010

² National Environmental Laboratory Accreditation Program

Table 1. Frequency of QAQC sampling, 2009-2010. The number of samples, quality assurance samples, and quality control samples is shown. SMPL= sample (includes field replicates), LCS= lab control sample, MS=matrix spike, MB=method blank, EB=equipment blank, TB = trip blank, DUP= laboratory duplicates, DMS=duplicate matrix spike. In DUP, all possible sets are considered, although only sets with samples greater than MRL were included in the final analysis.

	Lab Order	SMPL	Accuracy		Representativeness			Reproducibility	
			LCS	MS	MB	EB	TB	DUP	DMS
May 2009	3825	1215	95	96	97	0	0	123	1
	3897	739	58	84	58	76	55	85	1
June 2009	5121	804	48	64	49	0	0	75	1
	5175	443	56	32	56	0	0	37	1
	5186	200	47	29	46	0	20	35	0
	5300	123	35	1	36	102	21	0	1
	7344	90	32	15	32	0	0	20	0
June 2010	5914	180	29	18	31	0	0	28	3
	5972	138	30	16	34	0	26	23	2
	6091	508	51	33	55	0	0	48	3
	6103	426	50	43	54	96	25	63	2
	sum 2009 - 2010	4866	531	431	548	274	147	537	15
	% of total samples		11%	9%	11%	6%	3%	11%	0.3%

2.3 Representativeness

Representativeness measures how well the sample accurately and precisely represents a "true" characteristic of a parameter, i.e. whether lab processing, field equipment, or the field environment introduced analytes or changed analyte concentrations from the "true" stream water quality. This was assessed by analyzing trip blanks and equipment blanks in the field, and method blanks in the lab. The frequency of blank collection is provided in Table 1.

Trip blanks (TB) were bottles of lab-certified water (provided by the lab) that were never opened but were subjected to the same sample handling and transport to the field, in the field, and from the field to the lab to determine if the field environment or transport methods introduced contaminants.

Equipment blanks (EB) were bottles of lab-certified water (provided by the lab) that were processed by field personnel in the same manner as stream water. Lab-certified water was pumped from the lab bottle into a sample bottle using a peristaltic pump and clean tubing in the same manner and by the same personnel as for stream water collection. They were used to determine if the field equipment introduced contaminants.

Method blanks (MB) were vials of lab-certified water made up in the lab and run with the field samples in the lab to determine if the lab processing equipment introduced contaminants.

The trip blanks and equipment blank sample bottles were transported from the field to the lab in the same coolers as the field samples.

"Representativeness" has both quantitative and qualitative aspects. Unlike precision, samples are not considered "out of control" when they exceed MRL, but rather are used to determine whether systemic contamination has been introduced. For purposes of this study, analytes detected above method reporting limit (MRL) were reported, and considered to be of concern when detected at greater than 5 times the MRL. When an analyte consistently exceeds the MRL, concentrations as reported in field sample results may be higher than true water quality.

2.4 Reproducibility (Precision)

Reproducibility is a measure of agreement between repeated measurements to determine variability among replicates. Reproducibility was summarized as the relative percent difference (RPD) for duplicates or relative standard deviation (RSD) for triplicate or quadruplicate samples. Only aliquots whose results exceeded the method reporting limits were used in the reproducibility calculations. All lab precision was assessed as RPD except gross alpha and beta, which were assessed as RSD (triplicates). For field samples, metals were assessed as RSD (triplicates or quadruplicates) and non-metals as RPD (duplicates).

$$\text{RPD} = 100 * (\text{absolute value of the difference in measurements}) / (\text{mean of the two results})$$

$$\text{RSD} = 100 * (\text{standard deviation in results}) / (\text{mean of replicates})$$

The lab assessed precision by dividing an incoming field sample into more than one aliquot ('lab duplicates', denoted DUP) and measuring analyte concentrations in each. The lab ran duplicates on 10% or more of the samples from each lab order (Table 2). Duplicate matrix spikes (DMS) – a procedure in which a field sample is divided into aliquots and both are spiked with a known concentration of analyte – were also performed on at least one sample for each lab order and for low-level mercury.

Table 2. Frequency of samples analyzed for lab duplicates, 2009-2010. Percent of samples that were split by the lab and analyzed as duplicate lab samples.

Lab order	Total # samples	# samples with duplicate aliquots	% DUP	DUP sample ID
3825	27	3	11%	NW-11-01 NW-11-02 SY-11-03
3897	13*	2	15%	UT-01-01 UT-01-02
5121	19	2	11%	CH-11-04 GH-01-01
5175	11	1	9%	SY-11-01
5186	4*	1	25%	RC-01-01
7344	2	1	50%	Aquafina
*not including trip blanks and equipment blanks; also note that lab order 5300 was all trip and equipment blanks and did not have any DUP				

In the field, in May 2009 all sites had duplicates collected for non-metal analytes (except single samples for gross alpha and gross beta radioactivity) and triplicates for metal analytes (except single samples for low-level mercury). In June 2009, this was modified. Replicates were taken at every 5th site, with duplicates collected for non-metal analytes and quadruplicates for total and dissolved metals (Table 3); gross alpha and gross beta sampling was not conducted, and low – level mercury samples were not collected as replicates. In June 2010, at every 5th site duplicates were collected for non-metal analyte analysis and triplicates for total and dissolved metals. Specifically:

In May 2009, replicates were taken at all 14 sample sites for a total of 40 filtered and unfiltered samples for metal and major cation analysis, 28 samples for non-metals analysis, 15 samples for low-level mercury and 14 samples for gross alpha and gross beta radioactivity.

- 11 sites had metal analysis samples collected in triplicate
 - 33 bottles for total (unfiltered) metals and total major cations
 - 33 bottles for dissolved (filtered) metals and dissolved major cations
- 3 sites had metals analysis samples collected in duplicate
 - 6 bottles for total (unfiltered) metals and total major cations
 - 6 bottles for dissolved (filtered) metals and dissolved major cations
- 1 of the 3 sites with duplicates had an additional sample collected the following day.
- 14 sites had samples for non-metals analysis collected in duplicate
 - 28 bottles for DOC, nitrate + nitrite, and ammonia analysis
 - 28 bottles for TDS, TSS, and alkalinity analysis
 - 28 bottles for fluoride, chloride, sulfate, and cyanide analysis
- 14 sites had single samples collected for low-level mercury and radioactivity analysis
 - 14 bottles for low-level total mercury, and one site had duplicates for 15 total
 - 14 bottles for gross alpha and gross beta radionuclides

In June 2009, replicates were collected at every 5th site of 22 total sites total for 34 samples for filtered and unfiltered metals and total cations analysis, 26 samples for each set of non-metals, and 22 samples for low-level mercury.

- 4 sites had quadruplicate samples collected for metals and major cations analysis (16)
- 4 sites had duplicate samples collected for non-metals analysis (8)
- 4 sites had duplicate samples for low-level mercury analysis
- 18 sites had single samples collected for low-level mercury, metals and non-metals analysis (18)
- 1 site had a sample collected for dissolved low-level mercury
- no sites had samples for radioactivity analysis or dissolved major cations

Additionally in June a bottle of Aquafina water was submitted to the lab and duplicates run for all analytes except dissolved cations and radionuclides.

In June 2010, replicates were collected at every 5th site of 18 sites. Collection was at four sites and in the same manner as in June 2009, except for the following:

- Mercury was analyzed as part of the metals suite; there was no low-level mercury analysis
- Mercury was only analyzed at 3 of the four sites that had quadruplicate samples, and at only 7 of the 14 sites that had single samples, for a total of 19 samples instead of 30.
- One site did not have analyses conducted on several elements (total selenium and total mercury, and dissolved aluminum, antimony, arsenic, cadmium, chromium, copper, manganese, molybdenum, selenium, and uranium) due to a misunderstanding with the lab, resulting in 29 analyses instead of 30 for many elements.
- Dissolved iron was not analyzed in four of the sites with single samples, due to an error by the lab, resulting in 26 analyses instead of 30.

The method for determining the acceptability of replicates varies depending on whether concentrations are near the method reporting limit (MRL). For lab duplicates, the EPA³ defines unacceptable those samples for which

- (i) 2 or more duplicates met or exceeded 5 MRL and the RPD calculated from those duplicates that met or exceeded 5 MRL was 20% or greater;
- (ii) 2 or more duplicates exceeded MRL, but less than 2 exceeded 5 MRL, and the difference between the two duplicates exceeded the MRL.

For field replicates, RPD values of +/- 35% are acceptable.

The procedure used for assessing lab duplicates:

- If both concentrations are greater than 5 MRL, they are acceptable when the RPD < 20%
- If one has a concentration less than 5 MRL, they are acceptable if the absolute difference is less than the MRL

The procedure for assessing field replicates was more complicated, in that there might be duplicates, triplicates, or quadruplicates depending on the site and element. For sites with duplicates, the same assessment is used except that RPD is allowable up to 35%. For triplicates:

- If all concentrations are greater than 5 MRL, the RSD should be less than 35%
- If concentration #1 is less than 5 MRL but the concentrations #2 and #3 are greater, then
 - are acceptable if the absolute difference is less than the MRL
 - Concentrations #1 compared to #2
 - Concentrations #1 compared to #3
 - are acceptable if the RPD is less than 35%
 - Concentration #2 compared to #3

Quadruplicates are similarly assessed by determining first which samples have concentrations greater than 5 MRL and proceeding accordingly.

³ US EPA 2005

Table 3. Frequency of field replicate sets and analytes, 2009-2010. In May 2009, replicates were collected at every sample site. In later sampling, replicates were collected at approximately 20% of sample sites. In May 2009, low level mercury was analyzed; in later years mercury was included as part of the ICP-MS metals suite. In June 2010, due to a miscommunication with the lab, the full suite of metals was not analyzed at all sites. In addition to the mercury, selenium, and iron listed in the table, the following dissolved metals were analyzed 29 times instead of 30: aluminum, antimony, arsenic, cadmium, chromium, copper, manganese, molybdenum, uranium (for a 161% coverage instead of 167%).

	May 2009		June 2009		June 2010	
	Number	%	Number	%	Number	%
Unique sites	14		22		18	
Sites with replicates	14	100%	4	18%	4	22%
Non-metal replicates	28	200%	26	118%	22	122%
Metal and cation replicates	40	286%	34	155%	30*	167%
Mercury replicates	15	107%	<i>included in metals</i>		19	106%
Selenium replicates	<i>included in metals</i>		<i>included in metals</i>		19	106%
Iron (dissolved)	<i>included in metals</i>		<i>included in metals</i>		26	144%

3.0 Results

Lab QA QC involved analysis of blanks, replicates, and matrix spikes. Lab accuracy was within method-specific acceptance limits, and method blanks were all less than the method reporting limit (MRL), except one blank for gross alpha and gross beta. Of 1084 analyses in lab duplicates, all but three were acceptable; two for total zinc and one for total lead.

Field QA QC included blanks and replicates. Upon arrival at the lab, the temperature of coolers was occasionally slightly greater than optimal, but was not expected to affect analytical results.⁴ In May 2009, zinc

- exceeded 5 MRL in all three of the trip blanks carried on a single day
- exceeded 5 MRL in an equipment blank
- showed variable concentrations in field replicates, often associated with total suspended solids

Other than for zinc, virtually all blanks and replicates were acceptable.

- No analytes other than zinc exceeded acceptable limits in trip blanks in May 2009
- All analytes in trip blanks were acceptable in June 2009 and June 2010
- No analytes were detected above 5 MRL in June 2009 equipment blanks
- Manganese and zinc were >5 MRL in May 2009, and calcium, copper, magnesium, and manganese exceeded 5 MRL in June 2010
- In field replicates, variability was rarely above +/- 35%

⁴ personal communication with CAS lab manager Jeff Christian

3.1 Completeness

All analyses were 100% complete.

3.2 Accuracy

All lab control samples, 'on-going precision and recovery samples' (run as part of the analysis of total mercury), and matrix spike samples had accuracies within the analyte and method specific acceptance limits (Figure 1). Additionally, a spot-check on percent recovery calculated by hand for 2010 data agreed well with lab calculations (Figure 2).

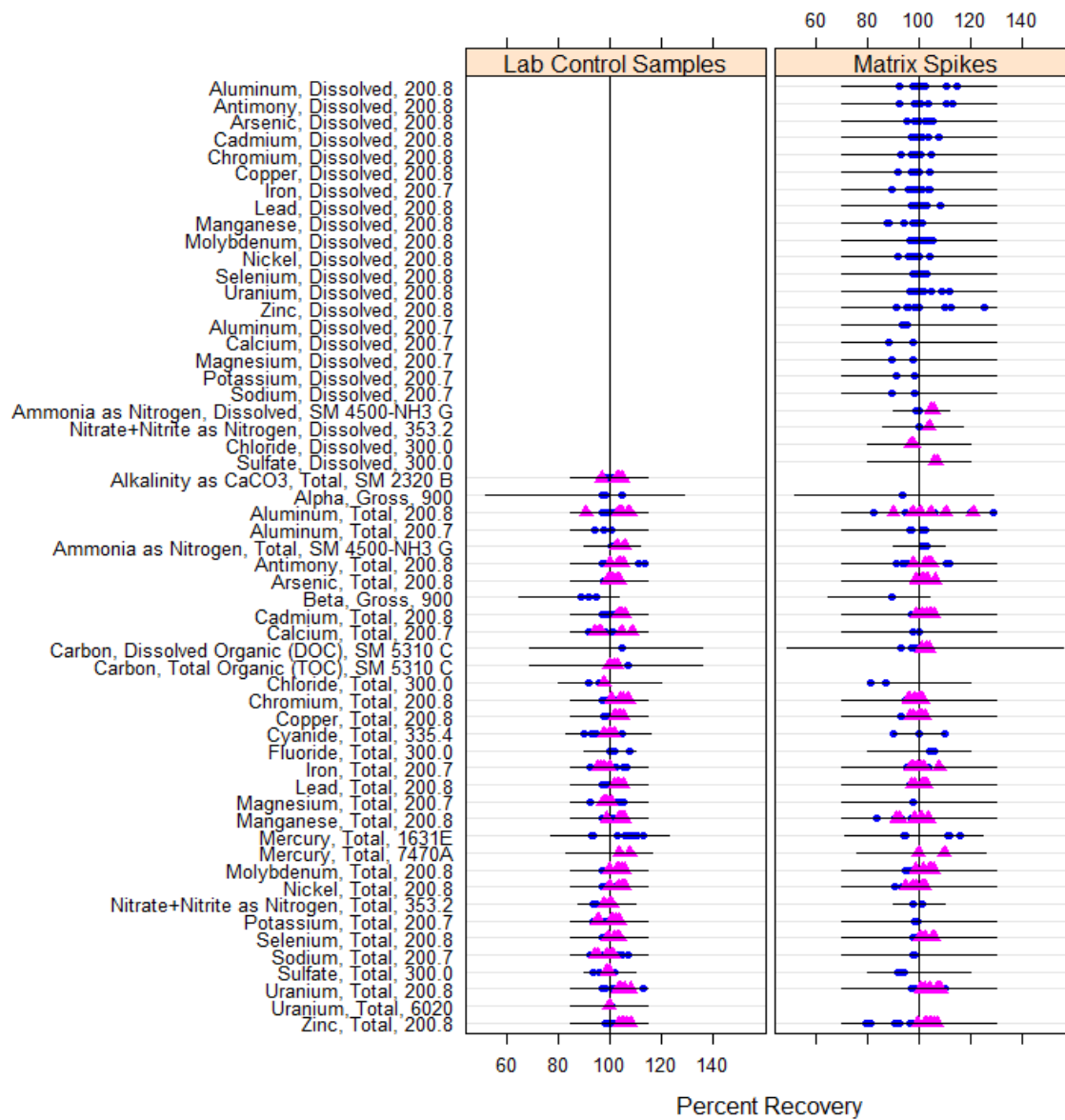


Figure 1. Accuracy of lab control samples and matrix spikes, 2009-2010. The accuracy of all lab control samples (left column) and matrix spikes (right column), by component and method combination (row), and year of collection and analysis (symbol: blue dot = 2009, magenta triangle = 2010). The lab reported Percent Recovery is shown. The dark line segment shows that component and method's acceptance limits. All lab control samples were within acceptance limits.

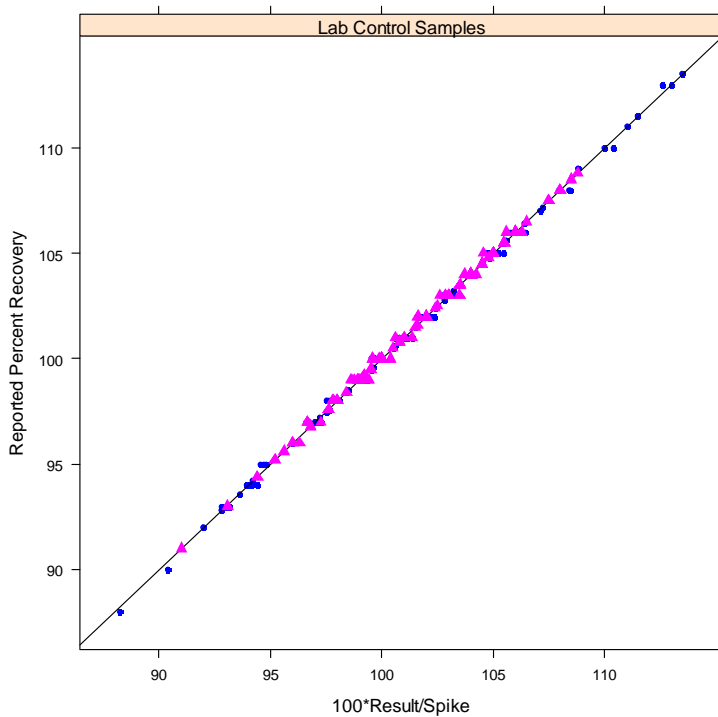


Figure 2. Percent recovery in lab control samples, 2009-2010. Assessing reported percent recovery (vertical axis) for lab control samples versus the percent recovery calculated directly from the reported result and spike concentration (horizontal axis). The values were approximately identical (within rounding error) as shown by the points falling along the identity reference line. Blue dots results from 2009; magenta triangles – results from 2010.

3.3 Representativeness

3.3.1 Method blanks

Of the 548 method blank results, 498 (90.9%) were less than method detection limits. Of the 9.1% that exceeded detection limits, all were less than their method reporting limits except one for gross alpha and one for gross beta (Figure 3). Gross alpha and gross beta, measures of radioactivity, were not analyzed in-house at CAS labs, but were sent by CAS to ACZ labs of Steamboat Springs, CO; CAS and ACZ are NELAC-certified labs.⁵

3.3.2 Trip blanks

Triplicate trip blanks were carried in 2009 and analyzed for metals and organic carbon; two trip blanks were carried in 2010 and subjected to the same analysis as regular samples. Of the 147 blank analyses, 114 (77%) were non-detect. Of the 34 analyses above detection limit, four exceeded 5 MRL; these were three blanks carried on May 2, 2009 exceeding in total zinc and one blank exceeding slightly in dissolved organic carbon (Figure 4 and Table 4).

⁵ National Environmental Laboratory Accreditation Certified

The data for the trip blank carried on June 8, 2010 showed no analytes above detection limit other than pH and TDS. However, the blank carried on June 10, 2010 had puzzling results. Total metal and non-metal analytes were non-detect except pH and alkalinity. However, there were nine analyses for dissolved metals, four of which were in concentrations above detection limit. This is puzzling in that trip blank samples were never opened and never pumped through a filter, therefore analysis for dissolved concentrations had not been requested; this was verified by examining the chain of custody form, on which were listed which samples were to have which analyses done, and were confirmed by the lab. By the time the lab was contacted, the samples had been discarded. The dissolved analytes were excluded from the calculations for representativeness and from graphic representations.

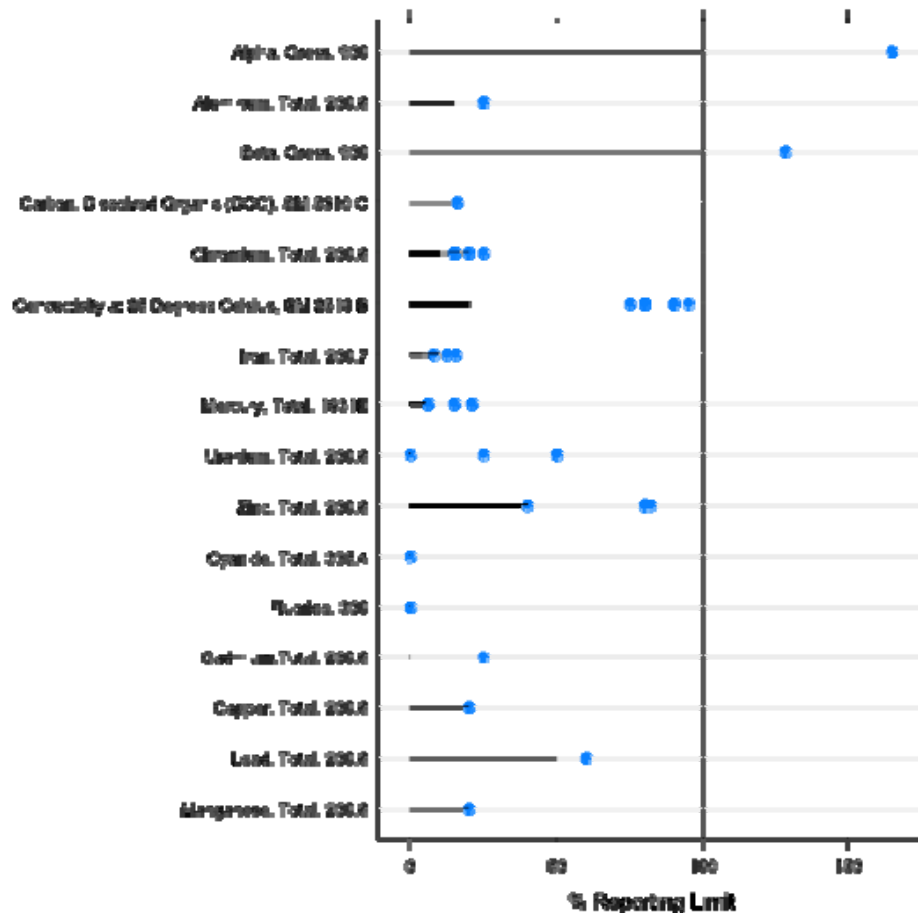


Figure 3. Method Blank Results, 2009-2010. Method blanks whose results met or exceeded the associated detection limit, presented as percent of the reporting limit. Only method blanks for gross alpha and gross beta exceeded their reporting limit (values to the right of the vertical reference line), and these had concentrations less than twice the method reporting limit (MRL). The solid line segment for each component and method combination denotes the detection limit (as percentage of the reporting limit). Method detection limits were not provided for 2010, so the figure represents data from 2009 only. However, all but two samples in 2010 were non-detect, and the remaining two were below method reporting limits, therefore the figure is representative of all sampling events. In 2010, total lead was detected at 50% of MRL and total molybdenum was detected at 20% of MRL.

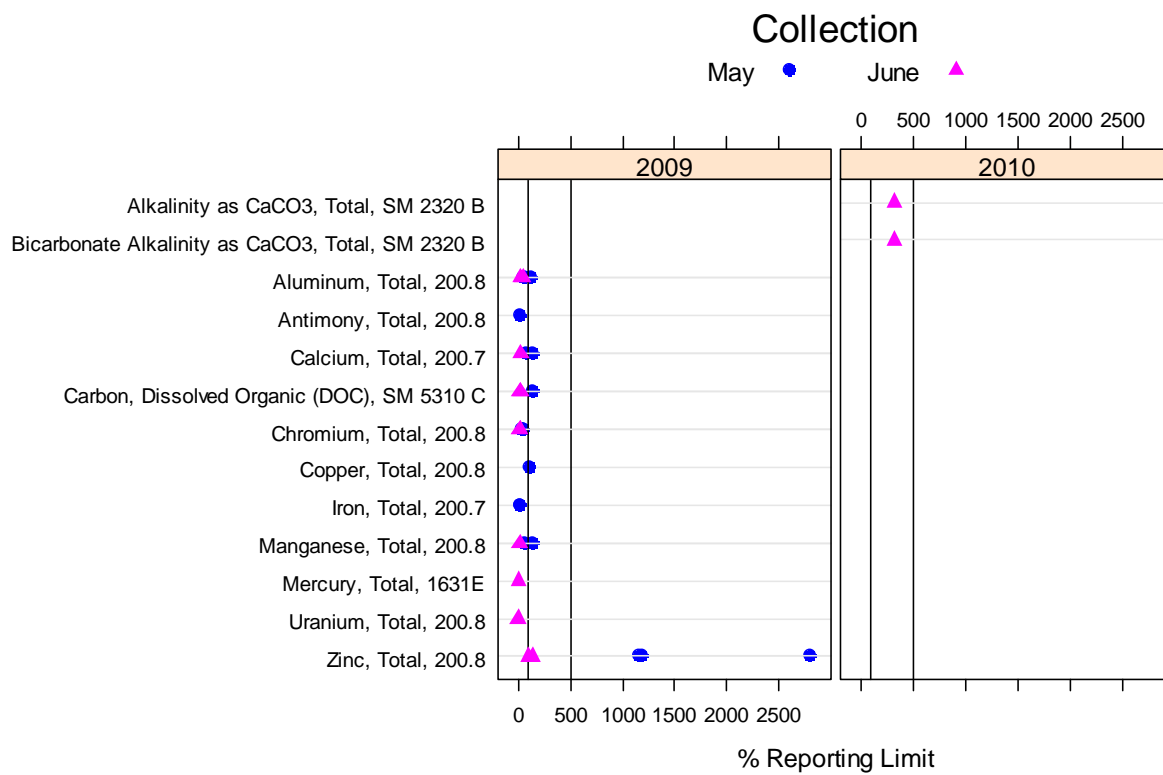


Figure 4. Trip Blank Results, 2009-2010. All analytes above detection limit are shown. The line furthest to the left represents the method reporting limit (MRL), the line to the right represents 5MRL. Analytes above detection limit but less than MRL fall to the left of the line on the left.

Table 4. Trip Blank Results and MRL, 2009-2010. Trip blanks that exceeded the method reporting limit (MRL) are shown. Those exceeding 5 MRL are shown in bold.

Sample	Lab Code	Date Collected	Component	Result	MRL	> 5 MRL?
TB-01-ME	K0903897-012	2009-05-02	Aluminum (total), ug/L	2.70	2.00	No
TB-01-ME	K0903897-012	2009-05-02	Copper (total), ug/L	0.11	0.10	No
TB-01-ME	K0903897-012	2009-05-02	Zinc (total), ug/L	5.79	0.50	YES
TB-01-OC	K0903897-015	2009-05-02	DOC – dissolved organic carbon, mg/L	0.70	0.50	YES
TB-02-ME	K0903897-013	2009-05-02	Calcium (total) , mg/L	74	50	No
TB-02-ME	K0903897-013	2009-05-02	Manganese (total), ug/L	0.07	0.05	No
TB-02-ME	K0903897-013	2009-05-02	Zinc (total), ug/L	14.00	0.50	YES
TB-03-ME	K0903897-014	2009-05-02	Zinc (total), ug/L	5.95	0.50	YES
TB2	K0905186-007	2009-06-08	Zinc (total)	0.70	0.50	No
Sample	Lab Code	Date Collected	Component	Result	MRL	> 5 MRL?
TB-01-01	K1006103-009	2010-06-10	Alkalinity as CaCO ₃	29.10	9.00	No
TB-01-01	K1006103-009	2010-06-10	Bicarbonate alkalinity as CaCO ₃	29.10	9.00	No

3.3.3 Equipment blanks

Lab water passed through field sampling equipment should have analytes within 5 times the MRL. Two sets of blanks were processed in May 2009 and three sets were processed in June 2009 and June 2010. Of the 274 analyses of analytes in equipment blanks, 176 (64.0%) were non-detects (Table 5 and 6; Figure 5 and 6). Nine exceeded 5 MRL: two in May 2009 (3%), none in June 2009, and seven in June 2010 (7%).

Table 5. Frequency of non-detects and concentrations greater than MRL in equipment blanks, 2009-2010. MRL= method reporting limit.

	total	#>MRL	#>5MRL	#ND
May 2009	76	7	2	51
June 2009	102	5	0	59
June 2010	96	28	7	66
sum	274	40	9	176

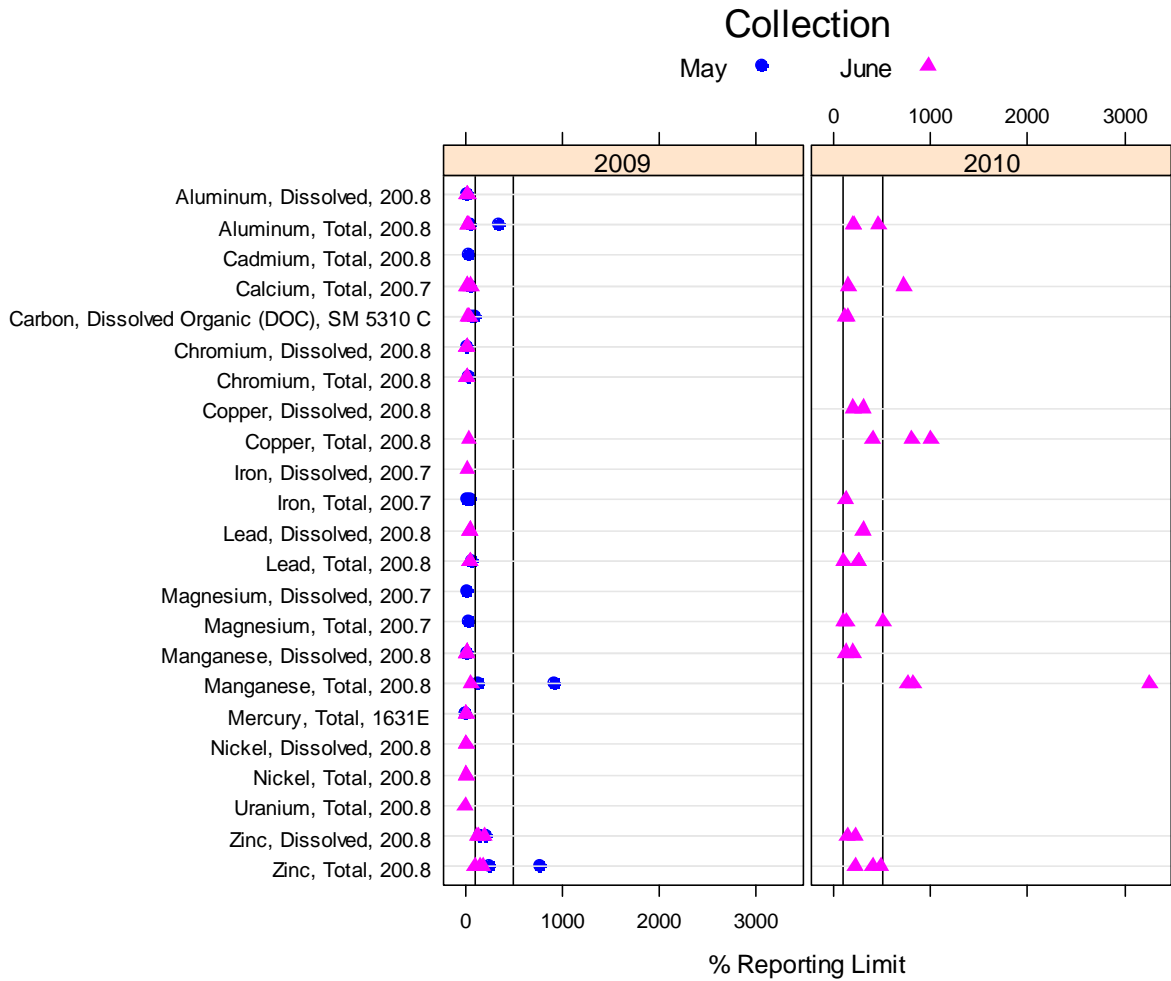


Figure 5. Equipment Blank Results, 2009-2010. The leftmost vertical line represents the method reporting limit (MRL); the rightmost line represents 5MRL.

Table 6. Equipment Blank Results, 2009-2010. MRL= method reporting limit. The MRL is provided by CAS labs. The right-most column lists equipment blanks for which analytes were detected in concentrations greater than five times the MRL. All equipment blanks should be lower than 5 MRL for all analytes.

Sample	Lab Code	Date Collected	Component	Result (ug/L)	MRL (ug/L)	> 5 MRL?
EB-01	K0903897-011	2009-05-03	Aluminum (total)	7.10	2.00	No
			Manganese (total)	0.46 *	0.05	YES
			Zinc (total)	1.27	0.50	No
EB-01	K0903897-011DISS	2009-05-03	Zinc (dissolved)	0.75	0.50	No
EB-02	K0903897-016	2009-05-04	Manganese (total)	0.07	0.05	No
			Zinc (total)	3.88 *	0.50	YES
EB-02	K0903897-016DISS	2009-05-04	Zinc (dissolved)	1.07	0.50	No
Sample	Lab Code	Date Collected	Component	Result (ug/L)	MRL (ug/L)	> 5 MRL?
EB-01-01	K0905300-002	2009-06-10	Zinc (total)	0.80	0.50	No
EB-01-01	K0905300-002DISS	2009-06-10	Zinc (dissolved)	0.60	0.50	No
EB-01-02	K0905300-003	2009-06-10	Zinc (total)	0.90	0.50	No
EB-01-02	K0905300-003DISS	2009-06-10	Zinc (dissolved)	1.00	0.50	No
EB-01-03	K0905300-004DISS	2009-06-10	Zinc (dissolved)	0.70	0.50	No
EB-01-01	K1006103-007	2010-06-10	DOC	0.72	0.50	No
			Aluminum	9.20	2.00	No
			Calcium	361	50	YES
			Copper	1.00	0.10	YES
			Copper (dissolved)	0.30	0.10	No
			Iron	24.00	20.00	No
			Lead	0.05	0.02	No
			Lead (dissolved)	0.06	0.02	No
			Magnesium	102.00	20.00	YES
			Manganese	1.63	0.05	YES
			Manganese (dissolved)	0.10	0.05	No
			Zinc	2.40	0.50	No
			Zinc (dissolved)	1.10	0.50	No
EB-01-02	K1006103-015	2010-06-10	DOC	0.57	0.50	No
			Aluminum	3.90	2.00	No
			Copper	0.80	0.10	YES
			Copper (dissolved)	0.20	0.10	No
			Lead	0.05	0.02	No
			Magnesium	20.20	20.00	No
			Manganese	0.41	0.05	YES
			Manganese (dissolved)	0.06	0.05	No
Zinc	2.00	0.50	No			

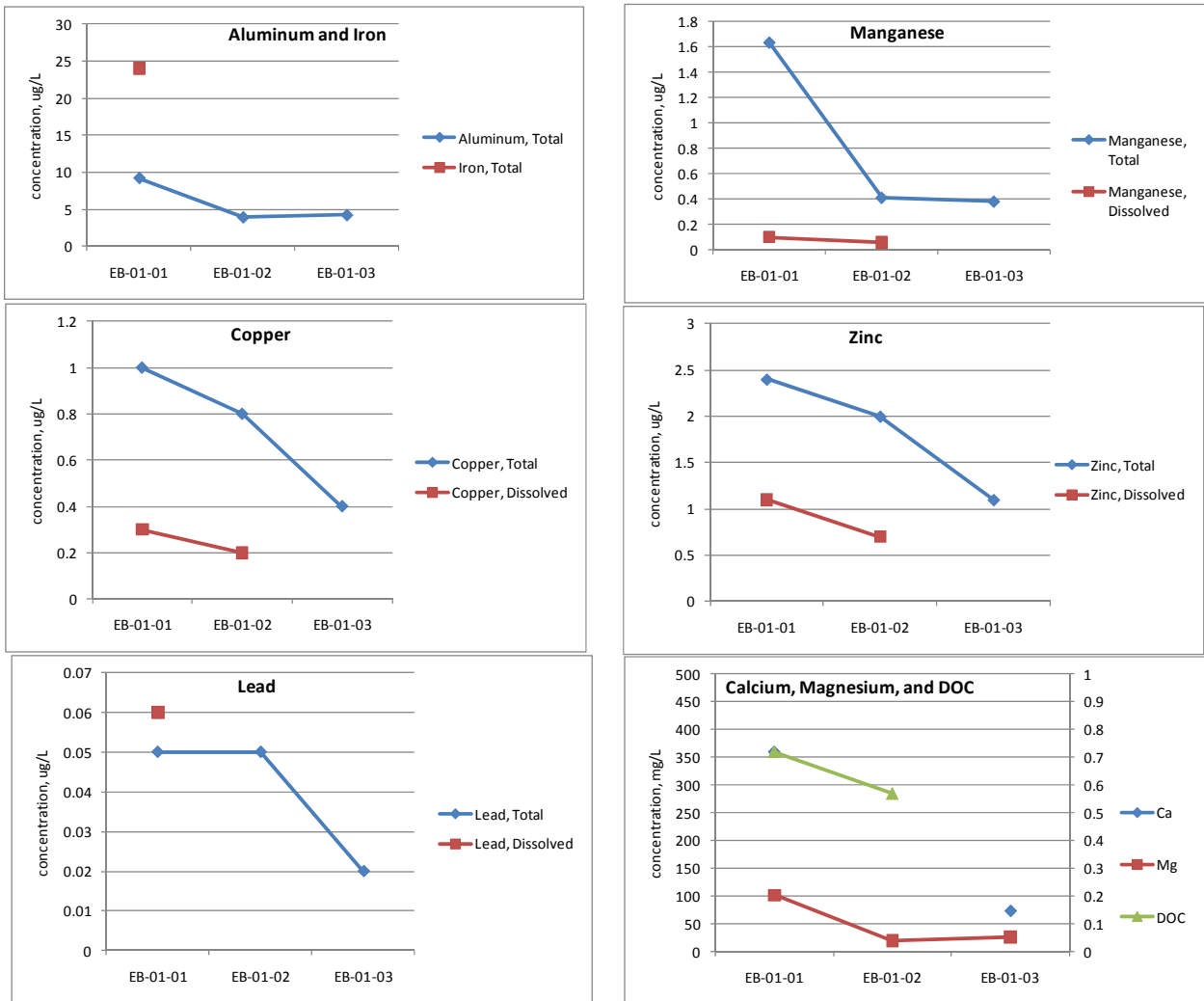


Figure 6. Analyte concentrations in sequence of equipment blanks, 2010. Three sets of equipment blanks were collected sequentially during 2010 field sampling. Source water came initially from a sealed container provided by CAS labs; when that water ran out, a sealed container from TTT labs was utilized to continue running water through equipment and collecting equipment blanks. The sharp decline in analyte concentrations between initial and final collection indicates the wrong water was provided by CAS, and that sampling equipment itself was not a source of contamination.

3.4 Reproducibility

3.4.1 Lab Duplicates

Lab duplicates are considered acceptable according to EPA standards⁶ when:

- (i) 2 or more duplicates met or exceeded 5*MRL and the RPD calculated from those duplicates that met or exceeded 5*MRL was 20% or greater;
- (ii) 2 or more duplicates exceeded MRL, but less than 2 exceeded 5*MRL, and the difference between the two duplicates exceeded the MRL.

Of the 1084 individual analyses associated with lab duplicates or triplicates, 454 resulted in non-detects or concentrations below MRL and caused the set to be removed from reproducibility analysis (Table 7). In all, 315 sets of analyses were conducted. Only three samples exceeded guidelines: dissolved zinc (twice in 2009) and total lead (2010) (Table 8 and Figure 7). All sets were run as lab duplicates except gross alpha, gross beta, and three total and dissolved aluminum samples in May 2009, which were analyzed as triplicates by the labs and as RSD instead of RPD in the reproducibility calculations. In general these reflect the very low concentrations of analytes in the field samples, as nearly all samples with RPD > 10% had concentrations within three times the MRL.

Table 7. Frequency of lab duplicate samples, 2009-2010. The lab split a subset of samples into duplicates and analyzed them as part of the lab QC for reproducibility to determine if lab equipment caused variation in reported sample concentrations. Samples below MRL are not utilized for reproducibility analysis. MRL = method reporting limit.

Summary of information on individual samples	5/09	6/09	6/10
Total individual samples	426	334	324
Number of samples with concentration below detection limit	87	54	90
Number of samples with concentration below MRL	76	116	31
Number of samples with concentration above 5 MRL	160	76	135
Number of samples with concentrations above MRL but below 5 MRL	103	88	68
Summary of information on analyte-site sets			
Total possible analyte-site sets	208	167	163
Total analyses conducted after removal of low concentration samples	135	80	100

Table 8. Lab Duplicate Results, 2009-2010. Only analytes that exceed compliance guidelines are listed. None of the sets exceeding guidelines had both sample and duplicate greater than 5MRL, therefore compliance was noted as whether the absolute difference in concentrations was greater than MRL.

Year	Sample number	Site	Analyte	MRL	SMPL Result	DUP1 Result	Absolute Difference
2009	K0905175	SY-11-01	Zinc, total	0.50	1.10	2.10	1.00
	K0905186	RC-01-01	Zinc, dissolved	0.50	2.20	2.90	0.7
2010	K1006091	UT-41-04	Lead, total	0.02	0.06	0.023	0.37

⁶ US EPA 2005

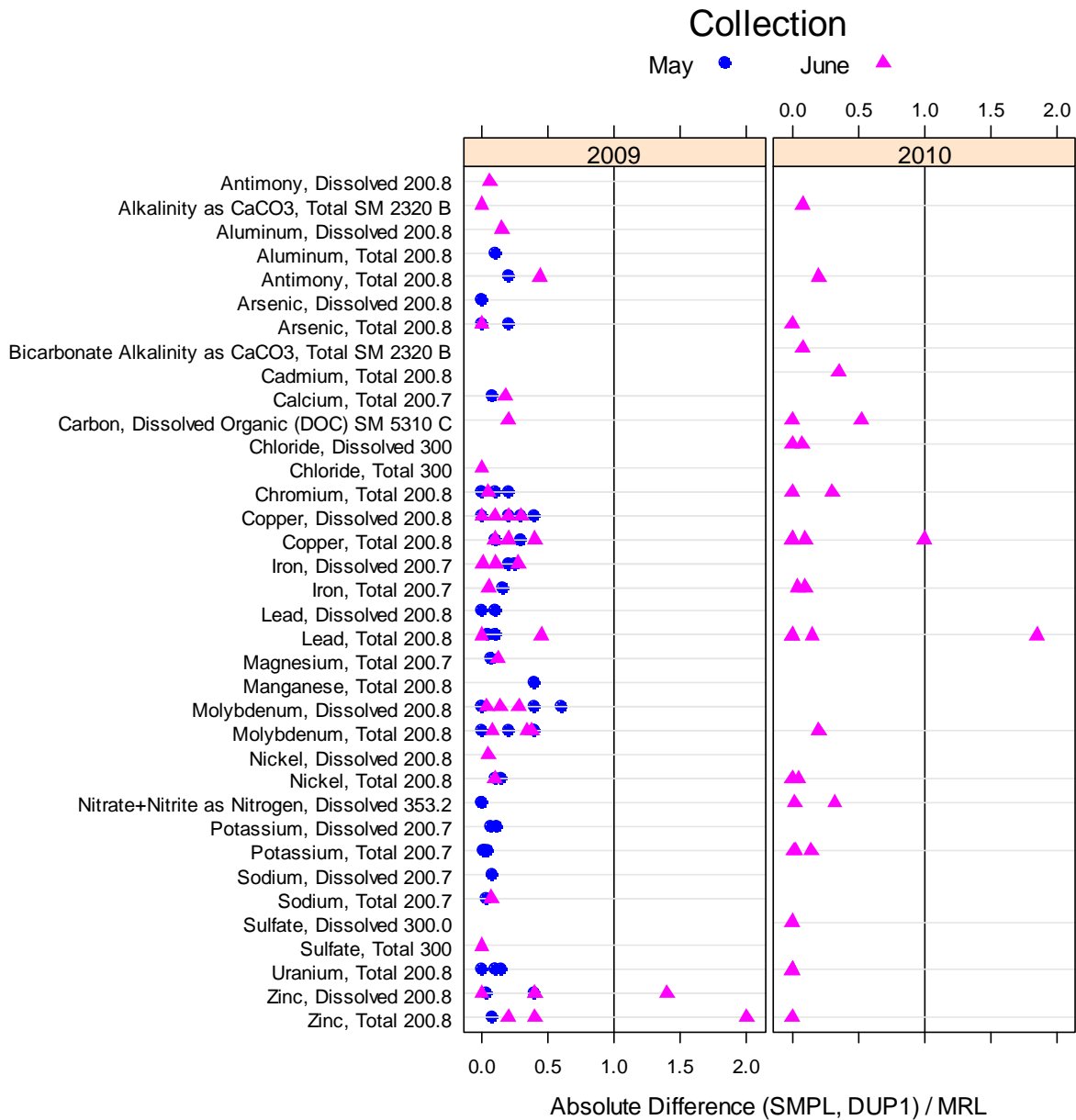


Figure 7. Lab Duplicate Results, 2009-2010. Lab duplicates consisted of sets of samples with either one or two associated duplicates. Sets with single duplicates were assessed as RPD or as absolute difference compared to MRL; samples with two duplicates were assessed as RSD if all were greater than MRL. Sample-duplicate sets with concentrations below MRL were not included in the reproducibility analysis. The figure shows the difference between sample aliquot result and lab duplicates divided by MRL, by year (panel) and month of collection (dot color and shape), for those pairs of aliquots where the SMPL and DUP1 were not both over 5*MRL.

3.4.2 Matrix Spike Duplicates

Five duplicate matrix spike sets were run for total low-level mercury, with relative percent difference of measured concentrations in duplicate aliquots ranging from 0 to 3%, indicating very high precision (Table 9). Matrix spikes for anions were also within acceptable percent recovery ranges (Table 10, Figure 8). A summary of compliance results for all QAQC sample types, excepting field replicates, is provided in Table 11.

Table 9. Precision for Low Level Mercury, 2009. Matrix spike duplicates determined precision based on relative percent difference of spiked field samples. Samples for low-level mercury analysis were only collected in 2009.

Site	RPD	measured sample concentration (ng/L)	spike concentration (ng/L)	final concentration (ng/L)	
				#1	#2
NW-11-01	0	2.17	25	25.6	25.4
NK-21-01	0	1.65	25	25.3	25.2
GH-01-01	2%	2.28	25	30.3	30.9
SY-11-02	3%	1.44	25	29.3	30.3
EB-01-01	2%	0.11	25	29.0	28.4

Table 10. Duplicate Matrix Spike Results, analytes other than mercury, 2010.

Analytes are assessed as percent recovery.

Sample Name	Analyte	RPD	MS % recovery	DMS % recovery	Acceptable % recovery
CH-11-01	Chloride	1.2%	98%	96%	80-120%
SK-41-01	Chloride	0.5%	97%	97%	80-120%
CH-11-01	Sulfate	0.4%	106%	106%	80-120%
SK-41-01	Sulfate	0.8%	106%	105%	80-120%
SK-12-01	Ammonia	0.0%	106%	106%	90-112%
UT-02-01	Ammonia	0.9%	105%	104%	90-112%
UT-11-01	Ammonia	0.5%	106%	105%	90-112%
SK-51-01	Nitrate+nitrite	0.0%	104%	104%	86-117%
UT-02-01	Nitrate+nitrite	0.5%	104%	104%	86-117%
UT-11-01	Nitrate+nitrite	0.9%	107%	105%	86-117%

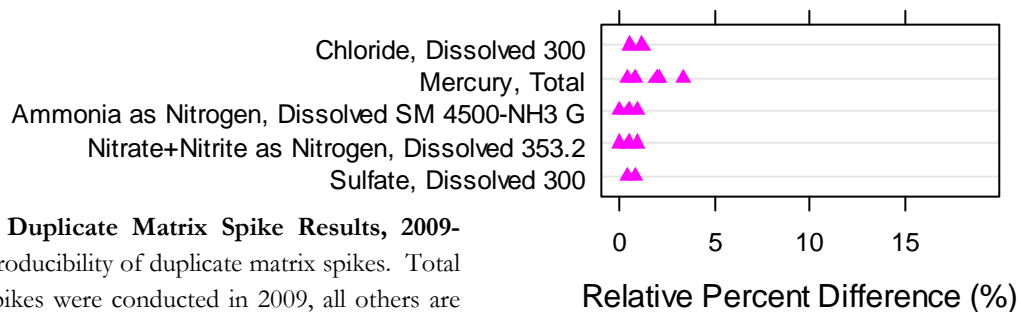


Figure 8. Duplicate Matrix Spike Results, 2009-2010. Reproducibility of duplicate matrix spikes. Total Mercury spikes were conducted in 2009, all others are from 2010. All RPD results were within EPA standards of less than 20%.

Table 11. Summary of QAQC compliance results, 2009-2010. Results for accuracy, representativeness, and reproducibility are summarized. Accuracy is assessed as % recovery, with acceptable recovery determined by the lab. Representativeness is qualitative, but of concern when analytes are in concentrations greater than 5MRL or consistently greater than MRL. Duplicate matrix spikes are assessed as both RPD (for precision) and as percent recovery (for accuracy). Lab duplicates are assessed as RPD, RSD, or the relationship of the absolute difference in concentrations to the MRL (see section on Lab Duplicates). The row "Sample and Duplicate <MRL" refers to sets where both are less than MRL and one or both are less than 5MRL. When samples and replicates are both less than MRL, they are not counted as part of the reproducibility analysis.

Type of QAQC test		2009		2010		Total
		In compliance	Out of compliance	In compliance	Out of compliance	
Accuracy	Lab Control Samples (% recovery)	371	0	160	0	531
	Matrix Spikes (% recovery)	321	0	110	0	431
Representativeness	Equipment Blank					
	Total	178		96		274
	Non-detects	110		66		176
	Exceeded MRL	10	2	21	7	40
	Trip Blank					
	Total	96		51		147
	Non-detects	57		47		104
	Exceeded MRL	6	3	4	0	13
	Method Blank					
	Total	374		174		548
Non-detects	326		172		498	
Exceed MRL	2	0	0	0	2	
Reproducibility (lab)	Duplicate Matrix Spikes (% recovery and RPD)	5	0	10	0	15
	Lab Duplicate Sets					
	Sample and Duplicate both >5MRL	115	0	68	0	183
	Sample and Duplicate >MRL	98	2	31	1	132
	Sample or Duplicate <MRL	168		62		230

3.4.3 Field Replicates

To collect field samples, one person held clean peristaltic pump tubing at mid-stream while a pump operator filled bottles on the stream bank. To collect replicate samples, bottles were filled sequentially (e.g. to collect triplicate samples for total metals, Bottle 1 was filled, then Bottle 2, then Bottle 3). Therefore, "field reproducibility" was a measure of the variation in natural stream water collected using the same equipment and personnel within a short time period, as well as a measure of precision of field methods. Natural stream samples were expected to have some variability while lab duplicates were not expected to vary.

Laboratory duplicates with concentrations >5 times the MRL should have RPD values of +/-20%. For comparison of field duplicates, RPD or RSD values of +/- 35% would be acceptable. However, when concentrations are very low, the absolute difference of concentrations should be less than the MRL.⁷

In May 2009, replicates were taken at all 14 sample sites. In June 2009 and June 2010, replicates were taken at every 5th site at 22 sites and 18 sites respectively. Replicates taken at a single site on a single day were compared to determine similarity of concentrations. Reproducibility calculations were performed based on concentration.

- If an individual sample was below the method reporting limit, it was not included in calculations for reproducibility/variability.
- If all replicates were greater than 5 MRL, an RPD or RSD calculation was performed.
- When replicates were greater than MRL but less than 5 MRL, replicates were assessed in pairs to determine whether the absolute difference in concentrations exceeded the MRL.

For example, at site SY-11 in June 2009 four replicates were collected and analyzed for total zinc. This would be considered one site-analyte set, but it had six different pair-wise calculations made because all concentrations were between the MRL and 5MRL (see Table 17). However, at site SY-11 in May 2009, three replicates were collected and analyzed for total zinc; because all concentrations were greater than 5MRL, a single RSD calculation was performed (see Table 17). Because the RSD was greater than 35%, the sample set was considered to have variability. A third example is evident at site UT-41, where four replicates were collected in June 2010 and analyzed for total lead. One replicate was less than the MRL and not utilized in calculations; the remaining three (all between MRL and 5MRL) had pair-wise calculations found, with two of the three found to have variability based on the difference in sample concentrations greater than the MRL.

Although often all pair-wise comparisons yielded an answer that the samples were "yes, variable" or "no, not variable", several sets yielded mixed results.

Due to the complexity of the variability possibilities, the exercise is conducted primarily to determine whether field replicates have variability consistently over time or space. The variability is presumed to be due to natural conditions unless evidence indicates otherwise.

The frequency of field replicates utilized in reproducibility calculations of site-analyte sets is provided in Table 12.

There were 40 site and component combinations out of 1040 whose field replicate RSD or RPDs exceeded the EPA guidelines for variability (see Methods section). Of these, non-zinc analytes accounted for 14 instances and zinc (total or dissolved) accounted for 26 instances, primarily in May 2009. A summary of the variable samples is provided in Tables 13-15, with details in Tables 16-18. A series of graphical representations is provided in Figure 9.

⁷ US EPA 2005

Table 12. Frequency of field replicates for reproducibility analysis, 2009-2010.

Summary of information on individual samples		note
Total individual samples collected for field replicate analysis	2979	
Number of samples with concentration below detection limit	669	not included in variability analysis
Number of samples with concentration below MRL	520	not included in variability analysis
Number of samples with concentration above 5 MRL	1053	analyzed using RPD or RSD
Number of samples with concentrations above MRL but below 5 MRL	737	analyzed by comparing absolute difference of a pair to the MRL
Summary of information on analyte-site sets		
Total possible analyte-site sets	1040	e.g. a single site with replicates for a single metal would be one set, no matter how many replicates or whether concentrations were ND
Total individual analysis conducted	1087	e.g. a site with triplicates and concentrations greater than MRL but less than 5 MRL would have 3 individual pair wise comparisons; sites at which concentrations were ND would have zero analyses

Table 13. Field replicate site-analyte sets with variability, analytes other than zinc, 2009-2010.

Zinc is not included. Details of concentrations and calculations are in Table 15.

Analyte	Site	Date	Number of replicates	Total number of reproducibility calculations	Number of calculated sets with variability
Alkalinity	SK-01	6/09	duplicates	1	1
	SK-21	5/09	duplicates	1	1
	UT-01	5/09	duplicates	1	1
	NK-21	5/09	duplicates	1	1
TDS	SK-21	5/09	duplicates	1	1
	SK-12	6/10	duplicates	1	1
Nitrate + Nitrite	UT-41	6/10	duplicates	1	1
Aluminum, Dissolved	SK-21	5/09	triplicates	1	1
	UT-03	6/10	quadruplicates	6	3
Copper, Total	KC-01	6/09	quadruplicates	6	3
Iron, Total	SK-01	5/09	triplicates	3	2
Lead, Total	KC-01	5/09	duplicates	1	1
	UT-41	6/10	quadruplicates	3	2

Table 14. Field replicate site-analyte sets with variability in zinc, 2009-2010. Site-analyte sets for both total zinc and dissolved zinc are listed. The number of calculations performed at each site may be different for total zinc than for dissolved zinc, depending on concentrations. Details of concentrations and calculations are in Table 17.

Site	Date	Number of replicates	Total number of reproducibility calculations (Total, Dissolved)	Number of calculated sets with variability	Number of calculated sets with variability
				Total Zinc	Dissolved Zinc
NW-11	5/09	triplicates	3, 3	2	3
UT-11	5/09	triplicates	3, 3	3	3
UT-02	5/09	triplicates	1, 3	1	2
LT-11	5/09	triplicates	3, 3	2	2
SY-11	5/09	triplicates	1, 1	1	1
SK-21	5/09	triplicates	3, 0	3	0
NK-01	5/09	triplicates	3, 0	3	0
UT-01	5/09	duplicates	1, 1	1	1
NK-21	5/09	duplicates	1, 1	1	1
NK-11	5/09	triplicates	3, 3	2	3
SK-01	6/09	quadruplicates	6, 6	4	5
CH-11	6/09	quadruplicates	6, 0	3	5
SY-11	6/09	quadruplicates	6, 0	2	0
SK-01	5/09	triplicates	0, 3	0	2
KC-01	5/09	triplicates	0, 3	0	3
CH-11	5/09	triplicates	0, 3	0	2

Table 15. Field replicate site-analyte sets with variability, non-metal analytes, 2009-2010. Details of replicate concentrations, pair-wise or other calculations performed, and results.

Analyte	MRL	5 MRL	Date	Site	Replicate concentrations (mg/L)		Assessment based on	Calculation	Variability?
					#1	#2			
Alkalinity as CaCO ₃ , total	2	10	5/09	NK-21	#1	6	#1 to #2 < MRL	5	Y
					#2	11			
			6/09	SK-01	#1	12	RPD < 35%	RPD = 55%	Y
					#2	21			
			5/09	SK-21	#1	7	#1 to #2 < MRL	4	Y
					#2	11			
			5/09	UT-01	#1	15	RPD < 35%	RPD = 46%	Y
					#2	24			
TDS	5	25	5/09	KC-01	#1	9	#1 to #2 < MRL	7	Y
					#2	16			
			5/09	SK-21	#1	10	#1 to #2 < MRL	6	Y
					#2	16			
			6/10	SK-12	#1	55	RPD < 35%	RPD = 58%	Y
					#2	30			
Nitrate + Nitrite, as Nitrogen	0.05	0.25	6/10	UT-41	#1	0.95	#1 to #2 < MRL	0.07	Y
					#2	0.25			

Table 16. Field replicate site-analyte sets with variability in metals, except zinc, 2009-2010. Details of replicate concentrations, pair-wise or other calculations performed, and results.

Analyte	MRL	5 MRL	Date	Site	Replicate concentrations (ug/L)		Assessment based on	Calculation	Variability?
					#	Value			
Aluminum, dissolved	2	10	5/09	SK-21	#1	24	RSD > 35%	RSD = 40%	Y
					#2	24			
					#3	45			
			6/10	UT-03	#1	9	#1 to #2 < MRL	1	N
					#2	8	#1 to #3 < MRL	0	N
					#3	9	#1 to #4 < MRL	3	Y
					#4	12	#2 to #3 < MRL	1	N
							#2 to #4 < MRL	4	Y
							#3 to #4 < MRL	3	Y
Copper, Total	0.1	0.5	6/09	KC-01	#1	0.35	#1 to #2 < MRL	0.19	Y
					#2	0.16	#1 to #3 < MRL	0.17	Y
					#3	0.18	#1 to #4 < MRL	0.18	Y
					#4	0.17	#2 to #3 < MRL	0.02	N
							#2 to #4 < MRL	0.01	N
							#3 to #4 < MRL	0.01	N
					Iron, Total	20	100	5/09	SK-01
#2	75	#1 to #3 < MRL	38	Y					
#3	76	#2 to #3 < MRL	1	N					
Lead, Total	0.02	0.1	5/09	SY-11	#1	0.17	#1 to #2 < MRL	RPD = 1%	N
					#2	0.17	#1 to #3 < MRL	0.06	Y
					#3	0.09	#2 to #3 < MRL	0.06	Y
			6/10	UT-41	#1	0.03	#1 to #2 < MRL	0	N
					#2	0.03	#1 to #4 < MRL	0.03	Y
					#3	less than MRL	#2 to #4 < MRL	0.03	Y
					#4	0.06			

Table 17. Field replicate site-analyte sets with variability in total zinc, 2009-2010. Details of replicate concentrations, pair-wise or other calculations performed, and results.

Analyte	MRL	5 MRL	Date	Site	Replicate concentrations (ug/L)		Assessment based on	Calculation	Variability?
					#	Concentration			
Zinc, Total	0.5	2.5	6/09	CH-11	#1	0.7	#1 to #2 < MRL	0.4	N
					#2	2.1	#1 to #3 < MRL	0.6	Y
					#3	1.3	#1 to #4 < MRL	1.1	Y
					#4	1.8	#2 to #3 < MRL	0.8	Y
							#2 to #4 < MRL	0.3	N
							#3 to #4 < MRL	0.5	N
			5/09	LT-11	#1	1.5	#1 to #2 < MRL	7.4	Y
					#2	8.9	#1 to #3 < MRL	0.4	N
					#3	1.1	#2 to #3 < MRL	7.8	Y
			5/09	NW-11	#1	2.4	#1 to #2 < MRL	0.7	Y
					#2	3.1	#1 to #3 < MRL	2.1	Y
					#3	4.5	#2 to #3 as RPD	33%	N
			5/09	NK-01	#1	2.0	#1 to #2 < MRL	11.0	Y
					#2	6.6	#1 to #3 < MRL	4.6	Y
					#3	13	#2 to #3 as RPD	66%	Y
			5/09	NK-11	#1	3	#1 to #2 as RPD	11%	N
					#2	2.7	#1 to #3 < MRL	1.6	Y
					#3	1.4	#2 to #3 < MRL	1.3	Y
			5/09	NK-21	#1	2.4	#1 to #2 < MRL	11.1	Y
					#2	13.5			
			6/09	SK-01	#1	1.4	#1 to #2 < MRL	1.1	Y
					#2	2.5	#1 to #3 < MRL	1.6	Y
					#3	2	#1 to #4 < MRL	1.3	Y
					#4	2.7	#2 to #3 < MRL	0.5	Y
							#2 to #4 < MRL	0.2	N
							#3 to #4 < MRL	0.7	N
			5/09	SK-21	#1	2.5	#1 to #2 as RPD	77%	Y
					#2	3.4	#1 to #3 < MRL	5.1	Y
					#3	7.6	#2 to #3 < MRL	0.9	Y
			5/09	UT-01	#1	3.3	#1 to #2 as RPD	RPD=71%	Y
					#2	7.0			
			5/09	UT-02	#1	3.0	RSD < 35%	RSD=48%	Y
					#2	6.1			
					#3	8.6			
			5/09	UT-11	#1	1.7	#1 to #2 < MRL	2.1	Y
					#2	3.8	#1 to #3 < MRL	5.4	Y
					#3	7.1	#2 to #3 as RPD	64%	Y
			5/09	SY-11	#1	3.9	RSD < 35%	RSD=61%	Y
					#2	9.1			
					#3	15.3			
6/09	SY-11	#1	1.1	#1 to #2 < MRL	0.3	N			
		#2	1.4	#1 to #3 < MRL	0.1	N			
		#3	1.2	#1 to #4 < MRL	0.7	Y			
		#4	1.8	#2 to #3 < MRL	0.2	N			
				#2 to #4 < MRL	0.4	N			
				#3 to #4 < MRL	0.6	Y			

Table 18. Field replicate site-analyte sets with variability in dissolved zinc, 2009-2010. Details of replicate concentrations, pair-wise or other calculations performed, and results.

Analyte	MRL	5 MRL	Date	Site	Replicate concentrations (ug/L)		Assessment based on	Calculation	Variability?
					#	Concentration			
Zinc, dissolved	0.5	2.5	5/09	CH-11	#1	2.2	#1 to #2 < MRL	3	Y
					#2	5.2	#1 to #3 < MRL	0.2	N
					#3	2.4	#2 to #3 < MRL	2.8	Y
			5/09	KC-01	#1	10.5	#1 to #2 as RPD	54%	Y
					#2	6.0	#1 to #3 < MRL	8.9	Y
					#3	1.6	#2 to #3 < MRL	4.4	Y
			5/09	LT-11	#1	1.2	#1 to #2 < MRL	1.9	Y
					#2	3.1	#1 to #3 < MRL	0.2	N
					#3	1.4	#2 to #3 < MRL	1.7	Y
			5/09	NW-11	#1	1.4	#1 to #2 as RPD	1.6	Y
					#2	3.0	#1 to #3 < MRL	3.3	Y
					#3	4.8	#2 to #3 < MRL	46%	Y
			5/09	NK-11	#1	2.5	#1 to #2 < MRL	1.7	Y
					#2	0.8	#1 to #3 < MRL	0.8	Y
					#3	1.7	#2 to #3 < MRL	0.9	Y
			5/09	NK-21	#1	1.3	#1 to #2 < MRL	5.5	Y
					#2	6.9			
			5/09	SK-01	#1	2.1	#1 to #2 < MRL	1.6	Y
					#2	3.7	#1 to #3 < MRL	2	Y
					#3	4.1	#2 to #3 as RPD	11%	N
			6/09	SK-01	#1	1.1	#1 to #2 < MRL	0.1	N
					#2	1	#1 to #3 < MRL	0.8	Y
					#3	1.9	#1 to #4 < MRL	2.3	Y
					#4	3.4	#2 to #3 < MRL	0.9	Y
							#2 to #4 < MRL	2.4	Y
					#3 to #4 < MRL	1.5	Y		
			5/09	UT-01	#1	2.4	#1 to #2 < MRL	1.1	Y
					#2	3.5			
			5/09	UT-02	#1	3.1	#1 to #2 as RPD	1%	N
					#2	3.1	#1 to #3 < MRL	1	Y
					#3	2.1	#2 to #3 < MRL	1	Y
			5/09	UT-11	#1	1.5	#1 to #2 < MRL	2.2	Y
					#2	3.7	#1 to #3 < MRL	5.2	Y
					#3	6.6	#2 to #3 < MRL	57%	Y
			5/09	SY-11	#1	3.0	RSD > 35%	43%	Y
					#2	4.5			
					#3	7.1			

Figure 9 graphically demonstrates the actual analyte concentrations for each replicate at each site over the three sampling periods, and the low concentrations at which most samples were measured. Field replicate results are illustrated by month (symbol), site (row within panel), and component (panel). The horizontal axis is log base 10 of the ratio of the Field Result / MRL, so a level exactly equal to MRL will be plotted as $\log_{10}(1/1) = 0$. Results < MRL will give logs < 0. Three reference lines are shown: the dashed line denotes the MDL (anything to the left denotes a non-detect), the solid line the MRL (anything to left is non-quantifiable), and the dotted line (when it appears on the panel) is the relevant criteria in $\mu\text{g/L}$ (not all components have relevant criteria). Non-detects are plotted at $\frac{1}{2}$ MDL. Total Sodium & Total Aluminum have multiple MDLs & MRLs; the maximum MDL has been shown, though all resulting Relevant Standard/MRL reference lines are plotted.

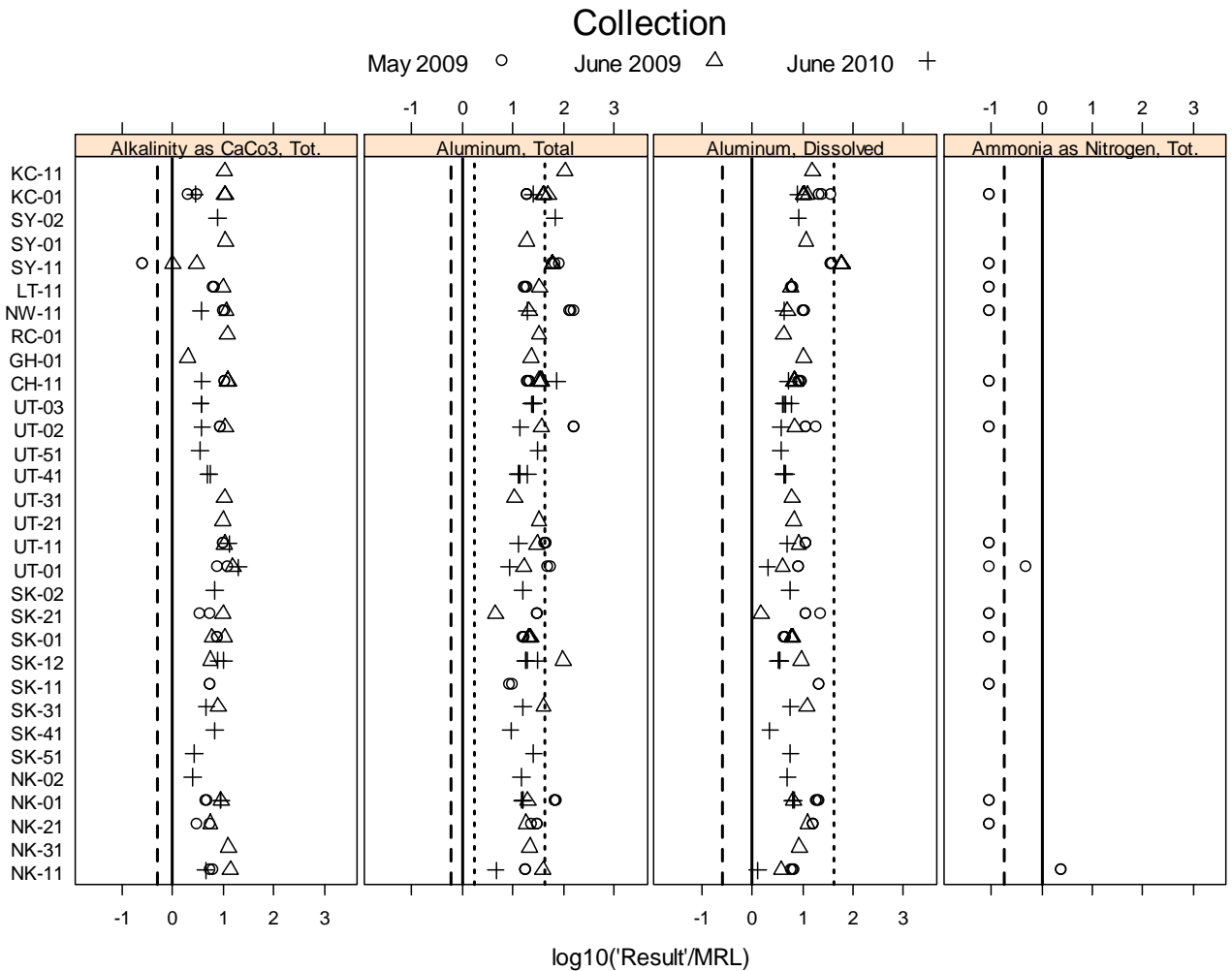
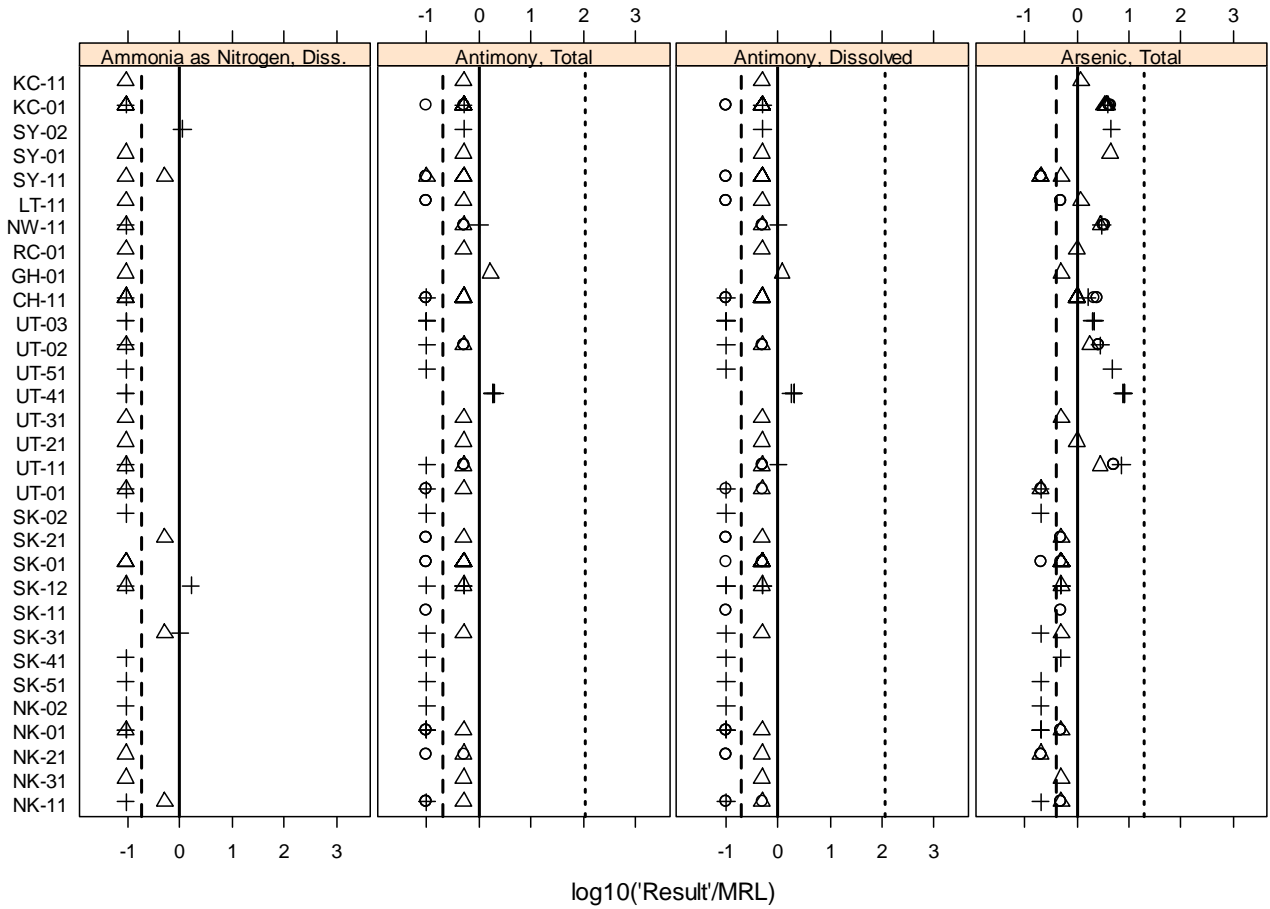


Figure 9. Field replicate results in relation to MRL, 2009-2010. All replicates and all analytes are shown in this and the following pages. They graphically demonstrate the low concentration of most analytes. Graphs developed by J Reynolds.

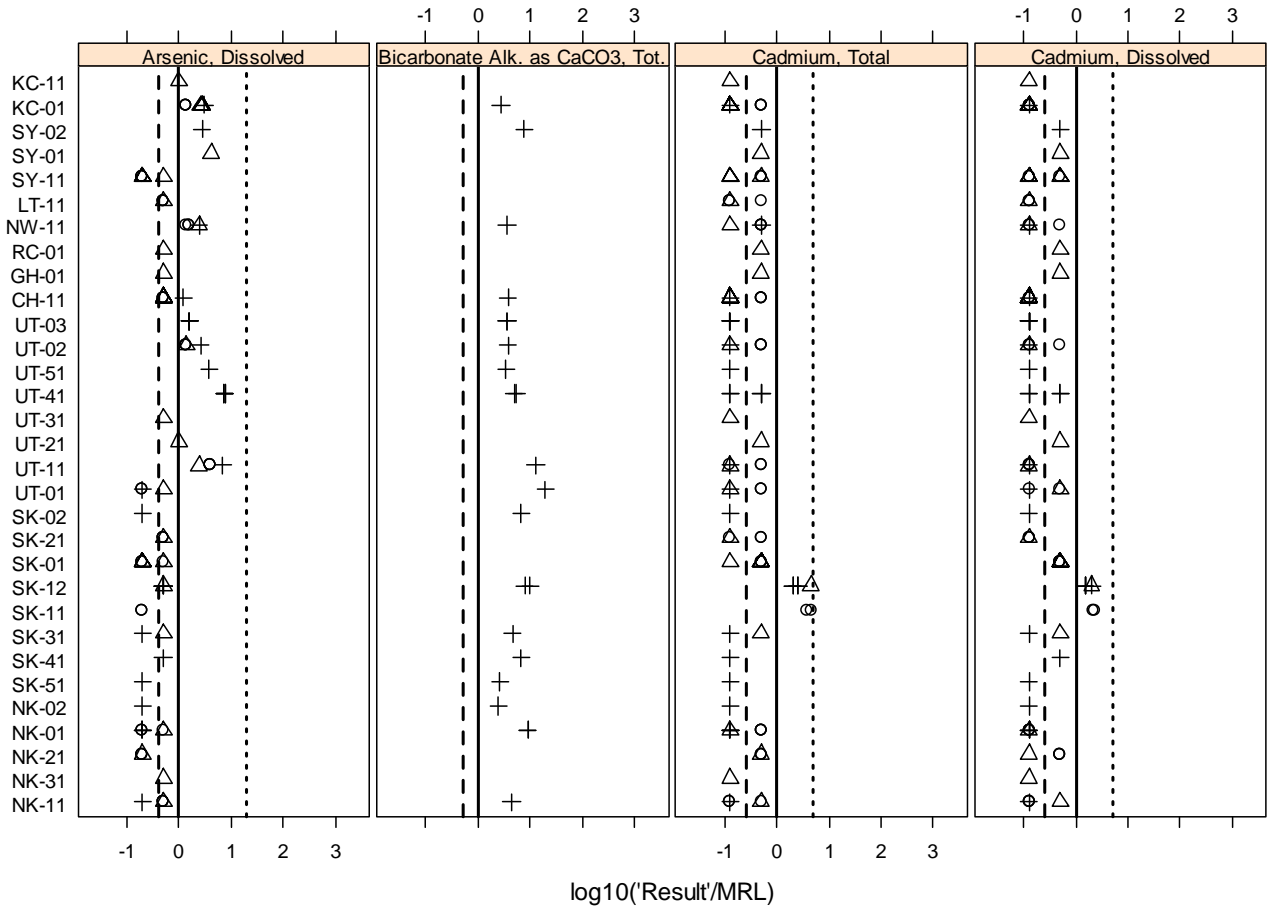
Collection

May 2009 ○ June 2009 △ June 2010 +



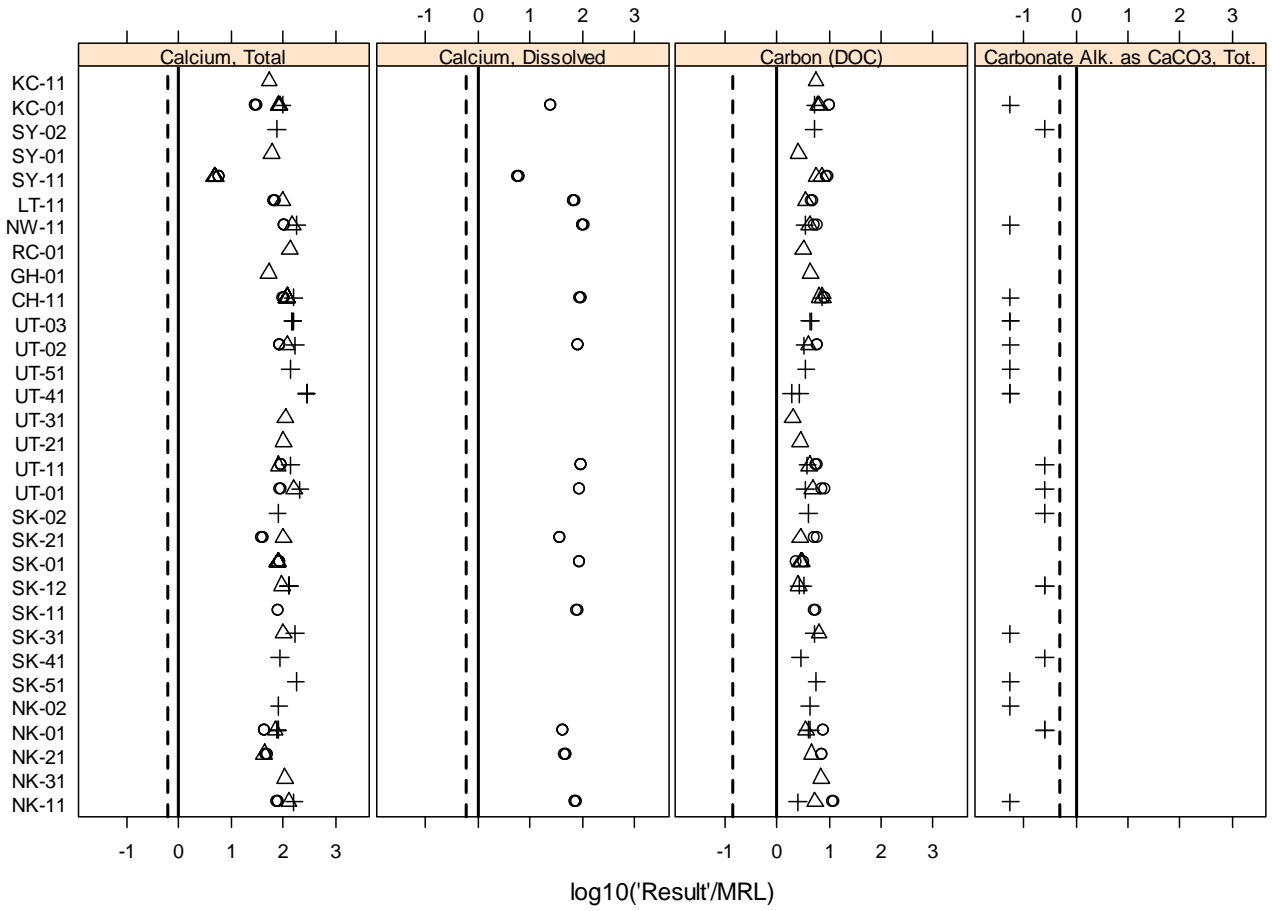
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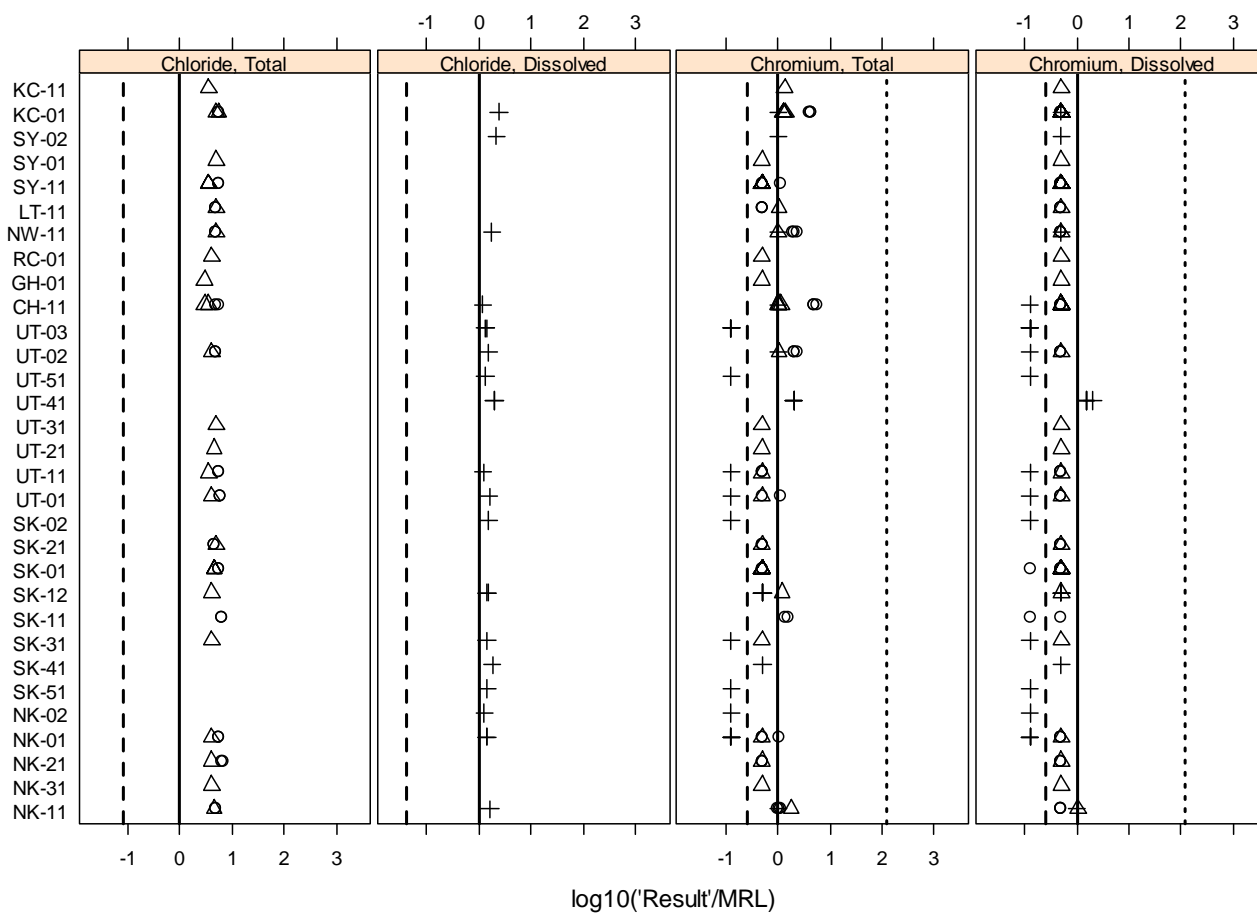
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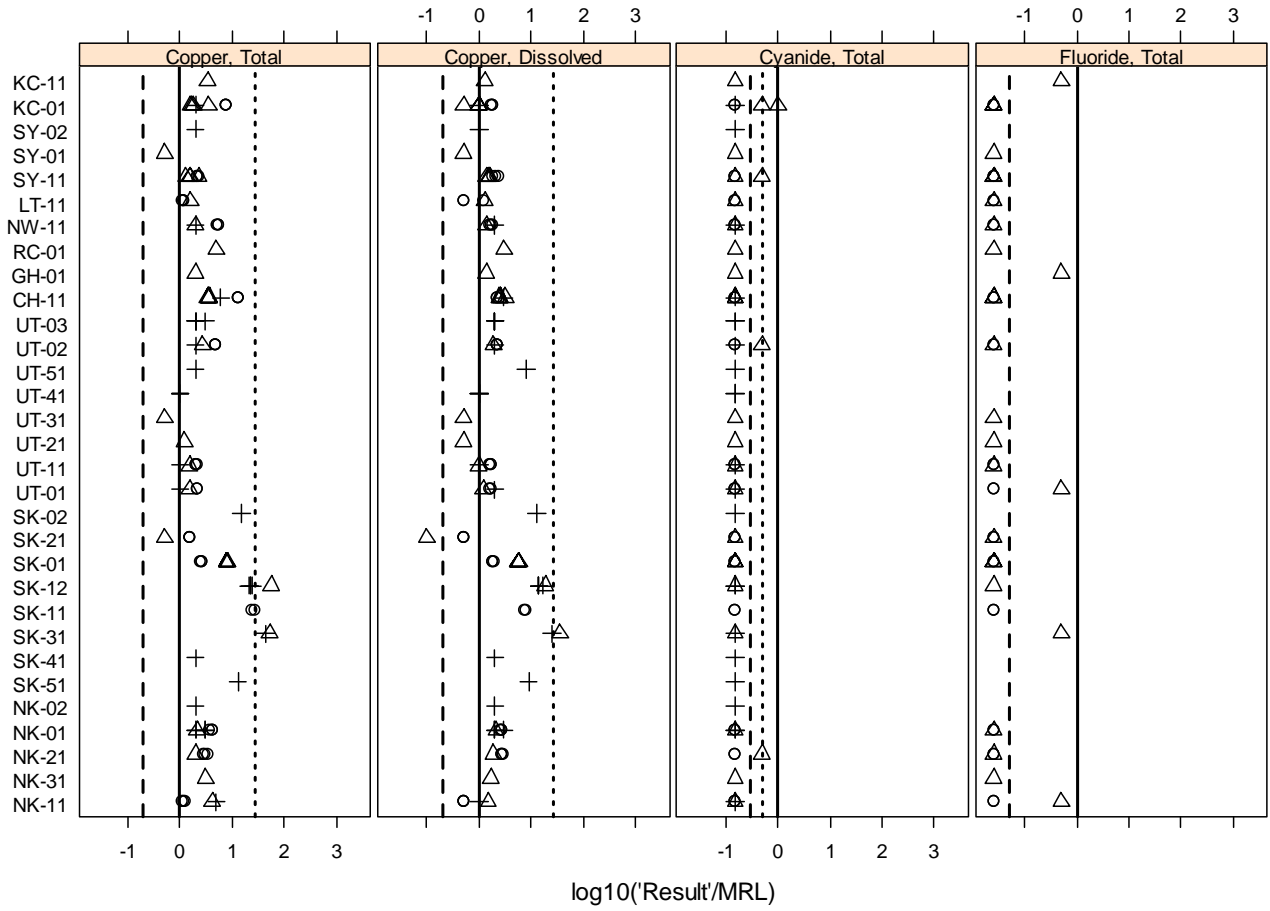
Collection

May 2009 ○ June 2009 △ June 2010 +



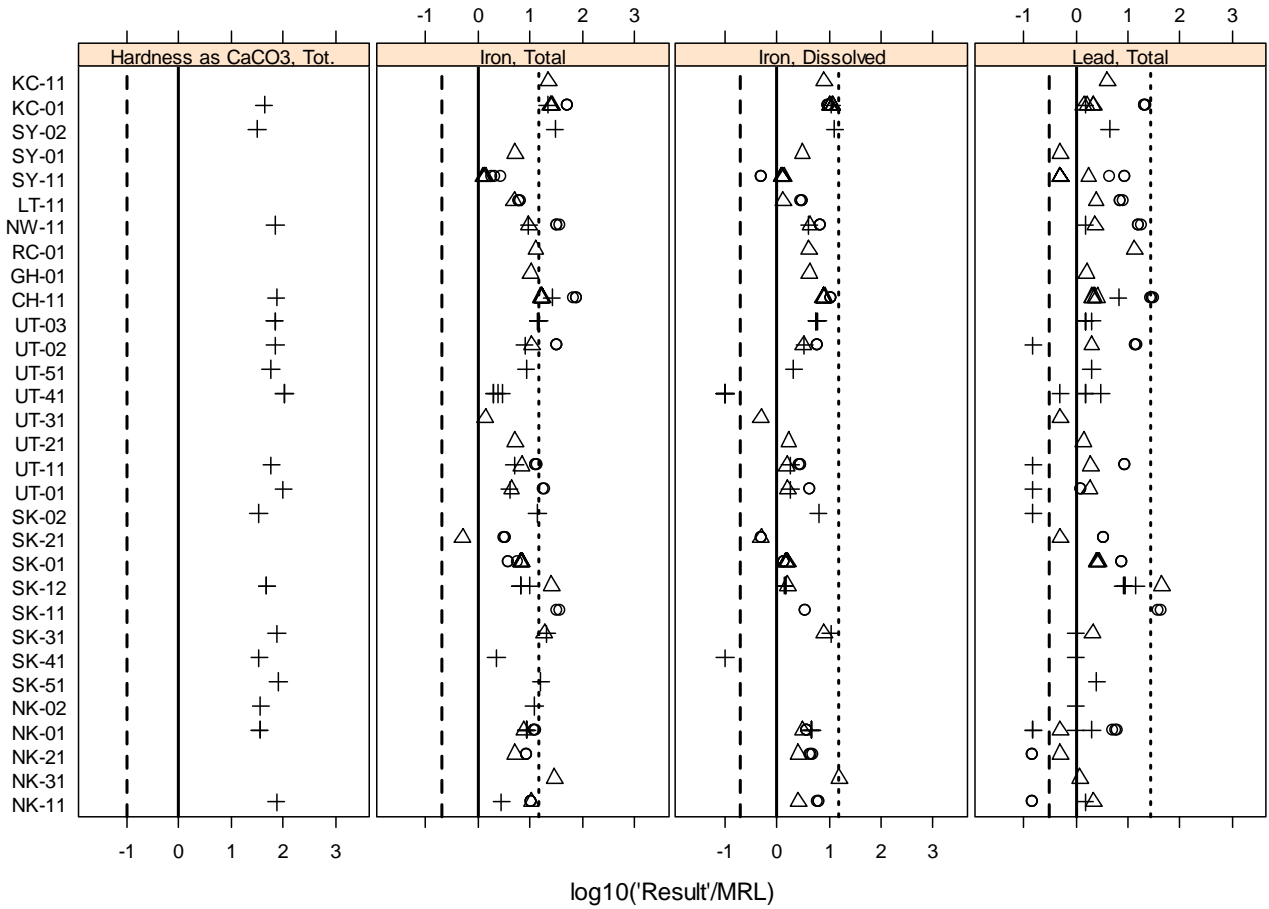
Collection

May 2009 ○ June 2009 △ June 2010 +



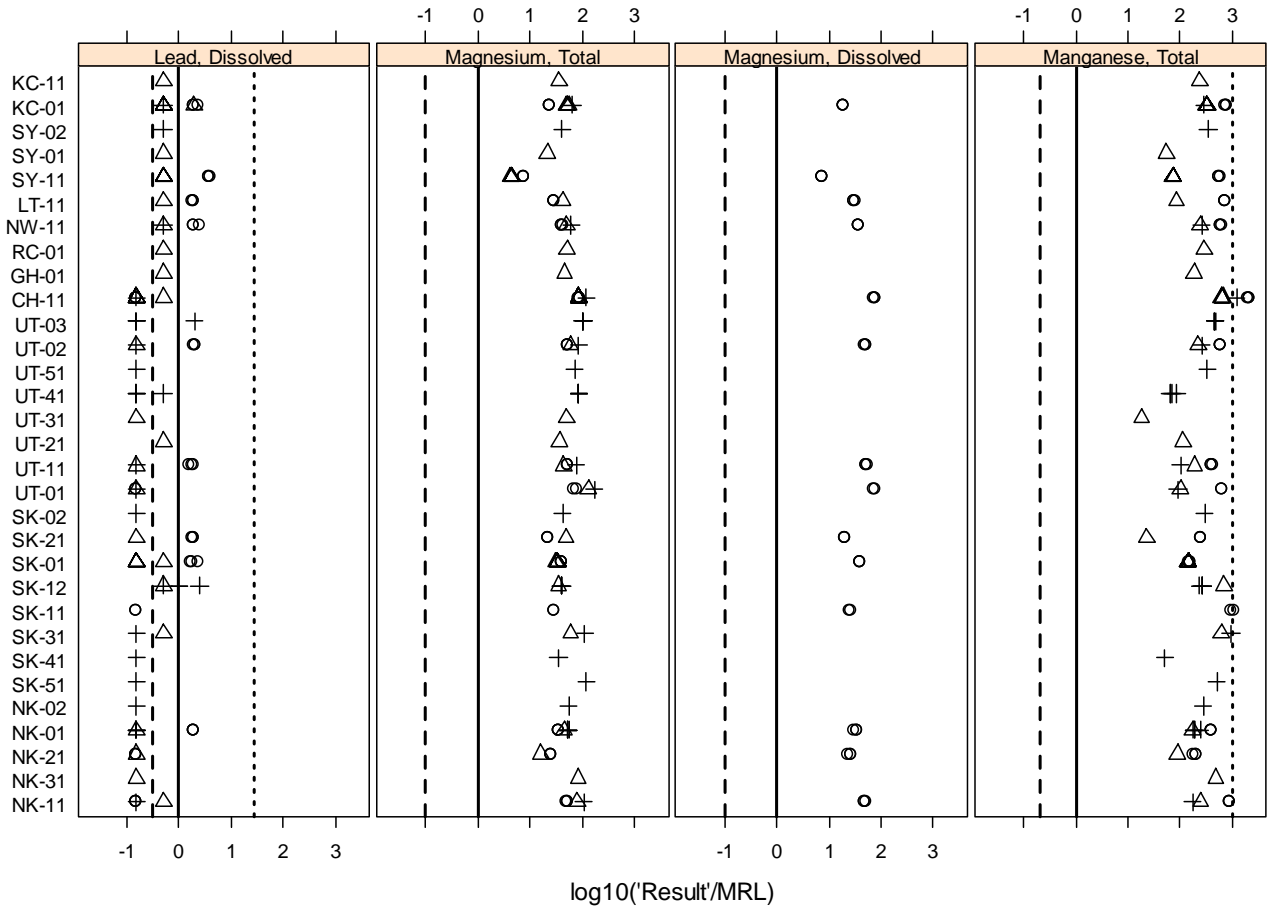
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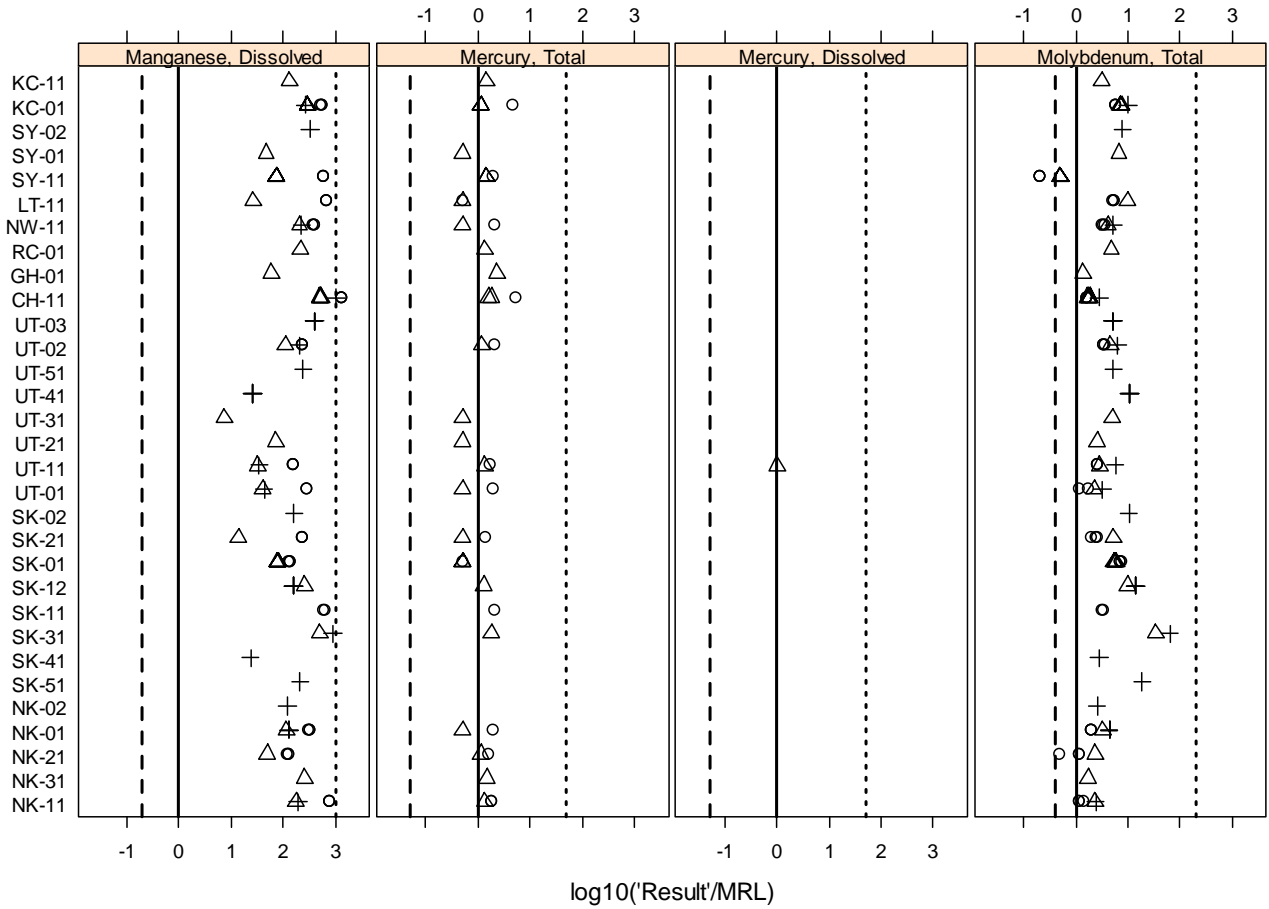
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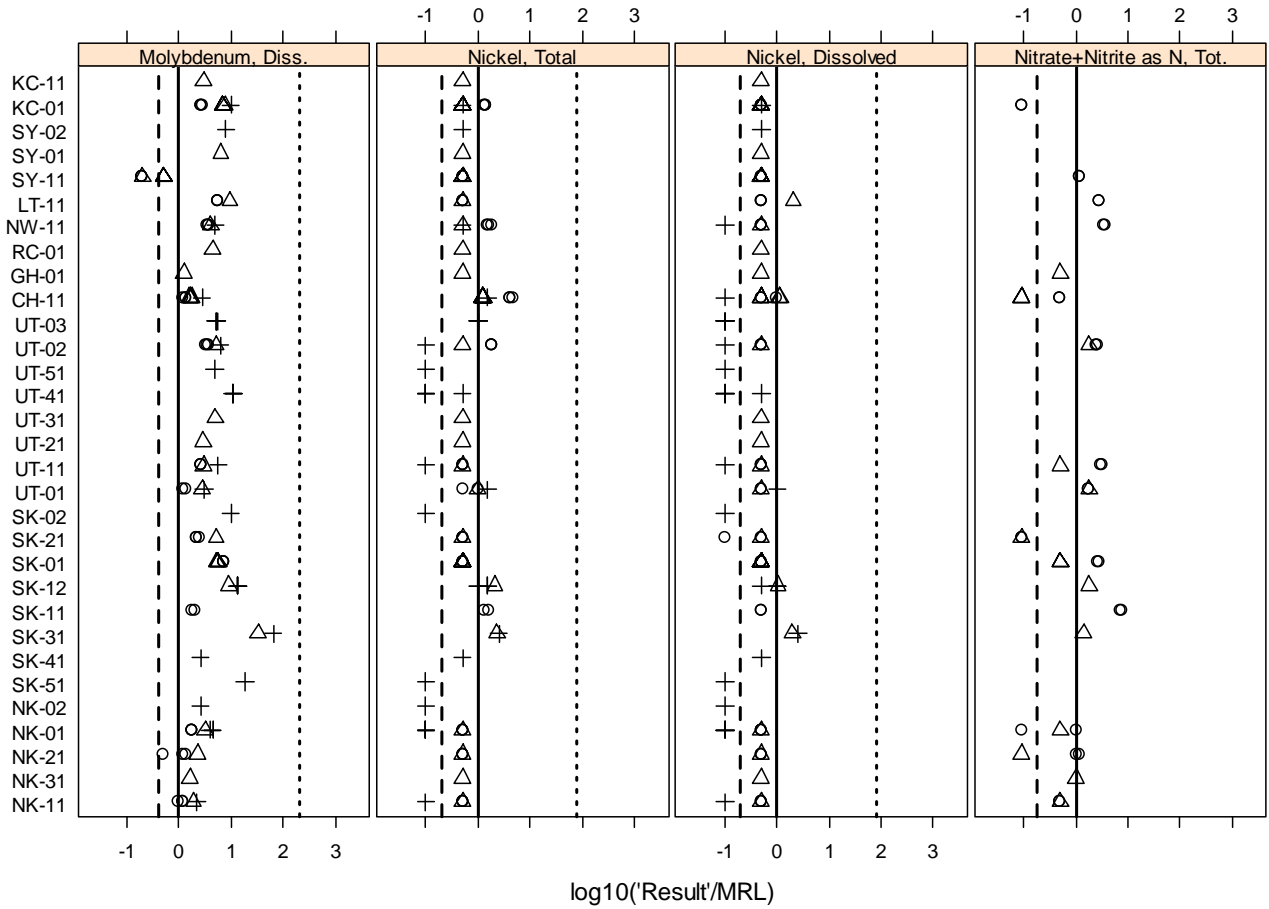
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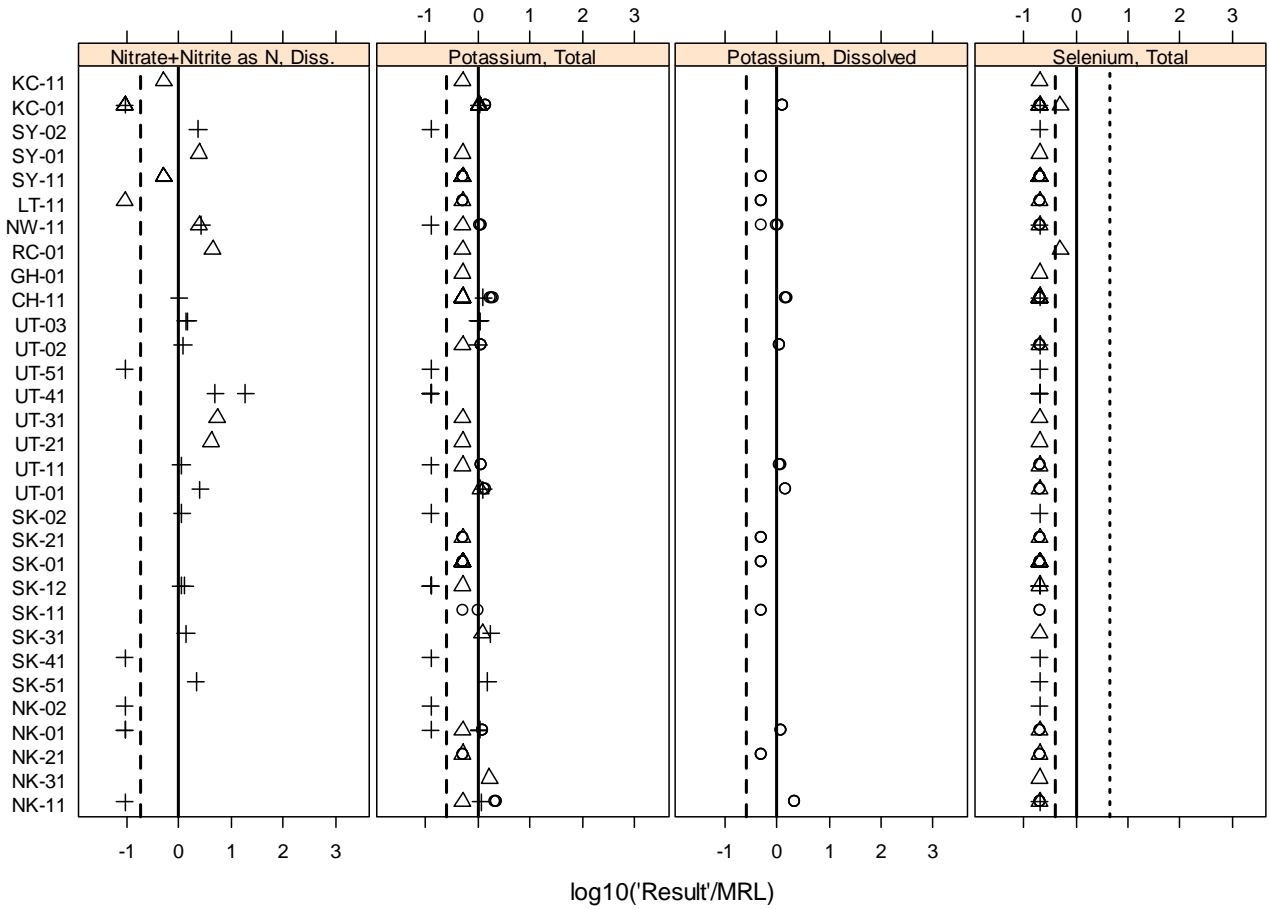
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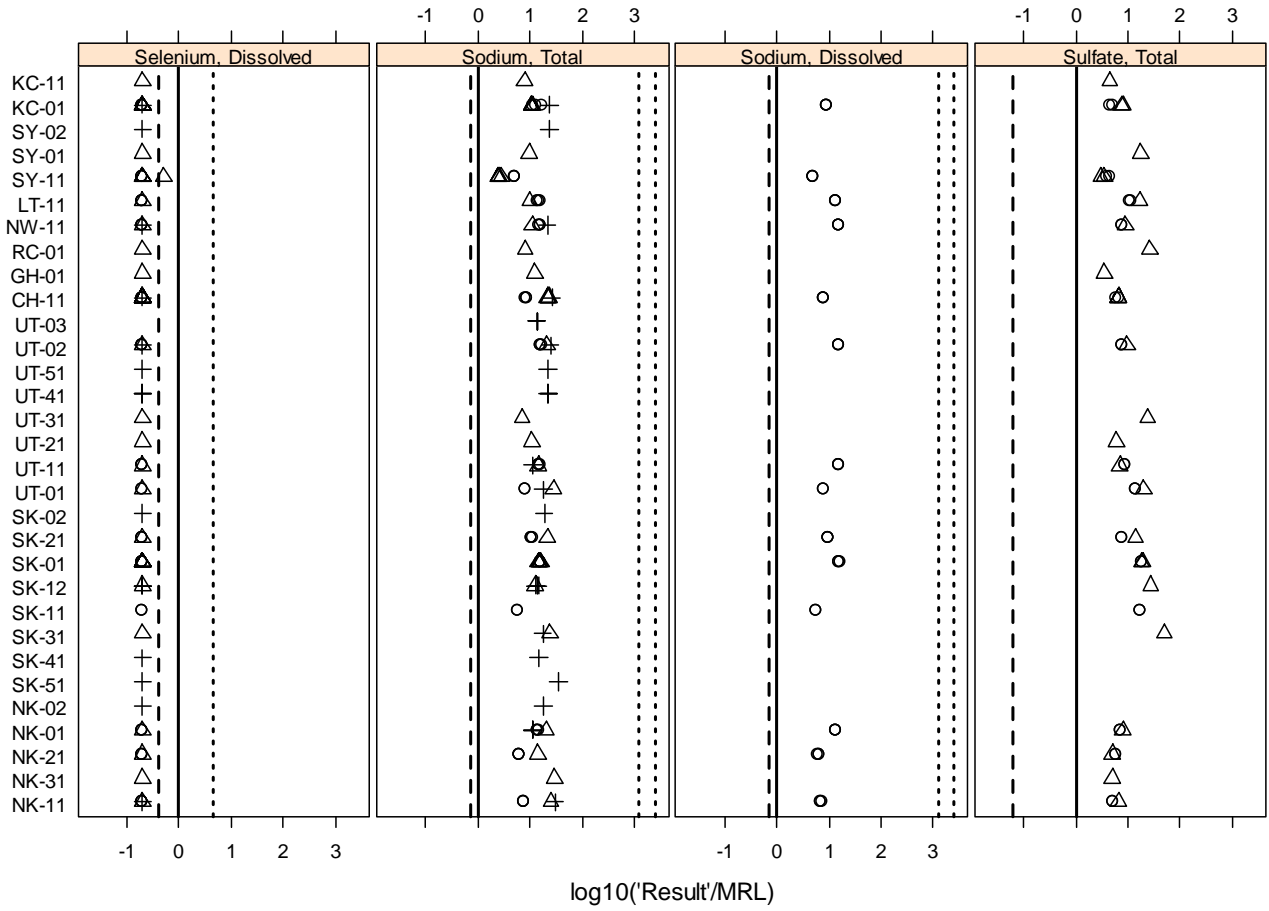
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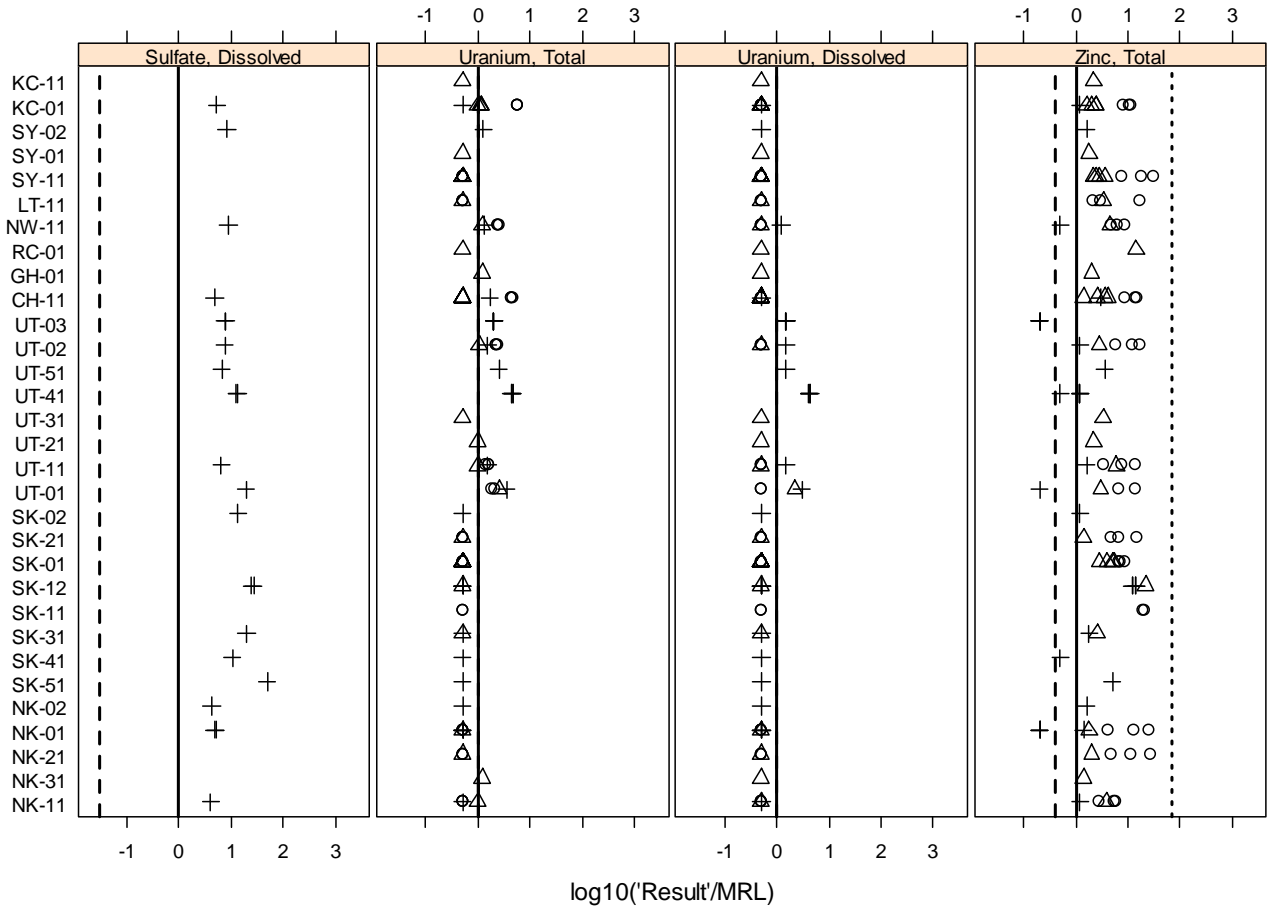
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May 2009 ○ June 2009 △ June 2010 +



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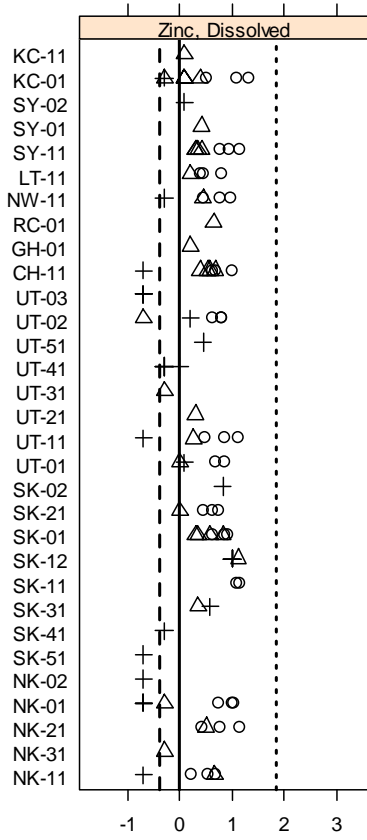


Collection

May 2009 ○

June 2009 △

June 2010 +



log10('Result'/MRL)

3.5 Other indicators of sample quality

3.5.1 Cation-Anion Balance

Water is electrically balanced: the sum of cations (generally calcium, magnesium, sodium, and potassium) should be the same as the sum of anions (generally bicarbonate, sulfate, chloride, nitrate) in milliequivalents per liter (mEq/L). Imbalances may be due to the lab not including an important anion or cation, which would indicate a site with an unusually high ion compared to other sites. It may also be due to poor sample handling technique, such as filtering several hours after collection, which can lead to particulates in the sample that dissolve when acid is added, or precipitation that removes constituents from the dissolved fraction. An unbalance may also result from allowing headspace in the sample container that is used for measuring alkalinity, potentially allowing carbon dioxide in air to partition into water (or carbonate to off-gas from water into air), which can cause the lab-measured alkalinity to be different from actual alkalinity in the field.

A charge balance error (CBE) within 10% is acceptable. The balance was determined by the lab. Of 76 sample sets analyzed by the lab, 19 had CBE > 10% and four samples had CBE > 20% (Table 19). Many had anions in concentrations less than 5MRL. Of the four with CBE > 20%, three were sites sampled in June 2009 and had one to three anions at less than 5 MRL (chloride, bicarbonate; sulfate). One of these sites, on Groundhog Mountain, had a charge balance difference of 41%.

Of sets with charge balances greater than 10%, twelve sets had replicates, and replicates were within acceptable CBE in ten of the twelve sets; only sites SY-11 (a site with very low cation concentrations) and SK-12 (a mineralized tributary) had measurements in which both replicates had charge balances greater than 10%. SY-11 and GH-01 were two of only four sites in which cations were in greater concentration than anions.

3.5.2 Total and Dissolved Metal Concentrations

Comparison of the dissolved and total fractions of metals also provides information on the quality of the sampling procedure (the dissolved fraction should always be lower). In nearly all instances when the dissolved fraction was reported as greater than total, analyte concentrations were less than MRL and/or the difference in concentrations was within the limits of the filter.⁸ Sets in which both total and dissolved concentrations were greater than MRL are listed in Table 20. The differences in concentrations were generally a small fraction of the total analyte concentration. Analyte concentrations in all sets but one listed in Table X were greater than 5MRL. When the RPD was calculated (or the difference as compared to MRL for the one set with analyte concentration less than 5 MRL), all but three sets had RPD over 5%:

- May 2009, site KC-01, zinc with RPD at 32%
- June 2009, site SK-01, zinc with RPD at 11%
- June 2009, site CH-11, zinc with RPD at 55%

⁸ Water samples were passed through a 0.45 um filter during collection for analysis of dissolved analytes. The 0.45 um filter has "limits of detection" for 67 metals and two anions as assessed by an independent EPA-certified lab listed on the package.

Table 19. Charge balance error in samples, 2009-2010. The major cations should be approximately equal to the major anions as milliequivalents per liter. Analysis and calculations were provided by CAS labs. Cation concentrations were well over 5MRL unless noted, but anions were occasionally in low concentrations (columns "alkalinity", "sulfate", and "chloride"). Charge balances may be upset if a site is elevated in dissolved metals (e.g. iron or aluminum) that contribute substantially to the ion balance but was not included in the charge balance calculation, as may have occurred at SY-11, where dissolved aluminum was high (near 120 ug/L) and calcium low (near 300 ug/L).

Sample Name	Cation Sum (meq/L)	Anion Sum (meq/L)	Charge balance error	Date	Alkalinity < 5MRL	Sulfate < 5MRL	Chloride < 5MRL	Notes on cations
CH-11-01	0.45	0.47	2%	May 2009				
CH-11-02	0.44	0.49	5%	May 2009				
CH-11-01	0.56	0.54	2%	June 2009			x	
CH-11-02	0.55	0.52	3%	June 2009			x	
CH-11-01	0.72	0.72	0%	June 2010	x		x	
GH-01-01	0.26	0.11	41%	June 2009	x	x	x	
KC-01-01	0.13	0.17	13%	May 2009	x	x		
KC-01-02	0.16	0.13	10%	May 2009				
KC-01-01	0.4	0.47	8%	June 2009				
KC-01-02	0.4	0.5	11%	June 2009				
KC-01-01	0.46	0.56	10%	June 2010	x		x	
KC-11-01	0.27	0.45	25%	June 2009		x	x	
LT-11-01	0.29	0.35	9%	May 2009				
LT-11-02	0.3	0.33	5%	May 2009				
LT-11-01	0.4	0.49	10%	June 2009			x	
NK-01-01	0.24	0.24	0%	May 2009	x			
NK-01-02	0.23	0.26	6%	May 2009				
NK-01-01	0.36	0.41	6%	June 2009			x	
NK-01-01	0.38	0.41	4%	June 2010			x	
NK-01-02	0.39	0.42	4%	June 2010			x	
NK-02-01	0.38	0.49	13%	June 2010			x	
NK-11-01	0.36	0.27	14%	May 2009				
NK-11-02	0.36	0.3	9%	May 2009				
NK-11-01	0.58	0.6	2%	June 2009			x	
NK-11-01	0.73	0.83	6%	June 2010			x	
NK-21-01	0.24	0.28	8%	May 2009				
NK-21-02	0.24	0.18	14%	May 2009	x			
NK-21-01	0.2	0.26	13%	June 2009			x	
NK-31-01	0.57	0.54	3%	June 2009			x	
NW-11-01	0.41	0.47	7%	May 2009				
NW-11-02	0.42	0.45	3%	May 2009				
NW-11-01	0.58	0.52	5%	June 2009			x	
NW-11-01	0.66	0.73	5%	June 2010			x	
RC-01-01	0.49	0.6	10%	June 2009			x	

Sample Name	Cation Sum (meq/L)	Anion Sum (meq/L)	Charge balance error	Date collected	Alkalinity < 5MRL	Sulfate < 5MRL	Chloride < 5MRL	Notes on cations
SK-01-01	0.37	0.42	6%	May 2009				
SK-01-02	0.37	0.42	6%	May 2009				
SK-01-01	0.32	0.52	24%	June 2009			x	
SK-01-02	0.33	0.34	1%	June 2009			x	
SK-02-01	0.34	0.4	8%	June 2010			x	
SK-11-01	0.31	0.33	3%	May 2009				
SK-11-02	0.31	0.33	3%	May 2009				
SK-12-01	0.34	0.35	1%	June 2009			x	
SK-12-01	0.43	0.62	18%	June 2010			x	
SK-12-02	0.44	0.55	11%	June 2010			x	
SK-21-01	0.18	0.27	20%	May 2009				
SK-21-02	0.18	0.19	3%	May 2009	x			
SK-21-01	0.43	0.48	5%	June 2009			x	
SK-31-01	0.48	0.55	7%	June 2009			x	
SK-31-01	0.74	1.25	26%	June 2010			x	
SK-41-01	0.33	0.38	7%	June 2010			x	
SK-51-01	0.81	0.9	5%	June 2010			x	
SY-01-01	0.39	0.53	15%	June 2009			x	
SY-02-01	0.35	0.4	7%	June 2010			x	
SY-11-01	0.07	0.05	17%	May 2009	x	x		Na < 5MRL
SY-11-02	0.07	0.05	17%	May 2009	x	x		Na<5MRL; Ca, Mg low
SY-11-01	0.06	0.09	20%	June 2009	x	x	x	Na<5MRL; Ca, Mg low
SY-11-02	0.06	0.07	8%	June 2009	x	x	x	Na < 5MRL
UT-01-01	0.43	0.56	13%	May 2009				
UT-01-02	0.43	0.39	5%	May 2009				
UT-01-01	0.76	0.72	3%	June 2009			x	
UT-01-01	0.94	0.95	1%	June 2010			x	
UT-02-01	0.38	0.41	4%	May 2009				
UT-02-02	0.38	0.41	4%	May 2009				
UT-02-01	0.49	0.49	0%	June 2009			x	
UT-02-01	0.68	0.75	5%	June 2010			x	
UT-03-01	0.66	0.72	4%	June 2010			x	
UT-03-02	0.67	0.72	4%	June 2010			x	
UT-11-02	0.4	0.46	7%	May 2009				
UT-11-01	0.42	0.46	5%	May 2009				
UT-11-01	0.35	0.46	14%	June 2009			x	
UT-11-01	0.55	0.58	3%	June 2010			x	
UT-12-01	0.56	0.69	10%	June 2010			x	
UT-21-01	0.42	0.44	2%	June 2009			x	
UT-31-01	0.44	0.54	10%	June 2009			x	
UT-41-01	0.95	1.1	7%	June 2010			x	
UT-41-02	0.95	1	3%	June 2010			x	

Table 20. Dissolved metals in greater concentration than total metals, 2009-2010. The table lists sets of analyses for which the dissolved concentration of the analyte is greater than the total concentration. Sets where the difference is within the filter limits and/or concentrations are less than MRL are not included.

3825	LT-11-01	05/02/2009	ug/L	Calcium	50	9	3400	1%
	LT-11-01	05/02/2009	ug/L	Calcium, Dissolved	50	9	3470	
	LT-11-02	05/02/2009	ug/L	Calcium	50	9	3430	2%
	LT-11-02	05/02/2009	ug/L	Calcium, Dissolved	50	9	3570	
	NW-11-02	05/01/2009	ug/L	Calcium	50	9	5160	2%
	NW-11-02	05/01/2009	ug/L	Calcium, Dissolved	50	9	5370	
	SK-01-01	05/01/2009	ug/L	Calcium	50	9	4290	1%
	SK-01-01	05/01/2009	ug/L	Calcium, Dissolved	50	9	4400	
	SK-01-02	05/01/2009	ug/L	Calcium	50	9	4350	1%
	SK-01-02	05/01/2009	ug/L	Calcium, Dissolved	50	9	4410	
	SK-01-03	05/01/2009	ug/L	Calcium	50	9	4330	1%
	SK-01-03	05/01/2009	ug/L	Calcium, Dissolved	50	9	4380	
	UT-11-01	05/01/2009	ug/L	Calcium	50	9	4720	2%
	UT-11-01	05/01/2009	ug/L	Calcium, Dissolved	50	9	4910	
	LT-11-02	05/02/2009	ug/L	Magnesium	20	0.7	584	4%
	LT-11-02	05/02/2009	ug/L	Magnesium, Dissolved	20	0.7	636	
	UT-11-01	05/01/2009	ug/L	Magnesium	20	0.7	1060	1%
	UT-11-01	05/01/2009	ug/L	Magnesium, Dissolved	20	0.7	1080	
	SY-11-01	05/02/2009	ug/L	Manganese	0.05	0.01	28.6	3%
	SY-11-01	05/02/2009	ug/L	Manganese, Dissolved	0.05	0.01	30.1	
	SY-11-02	05/02/2009	ug/L	Manganese	0.05	0.01	28.3	3%
	SY-11-02	05/02/2009	ug/L	Manganese, Dissolved	0.05	0.01	30.3	
SY-11-03	05/02/2009	ug/L	Manganese	0.05	0.01	29	4%	
SY-11-03	05/02/2009	ug/L	Manganese, Dissolved	0.05	0.01	31.2		
NW-11-02	05/01/2009	ug/L	Sodium	100	20	1480	2%	
NW-11-02	05/01/2009	ug/L	Sodium, Dissolved	100	20	1550		
KC-01-01	05/02/2009	ug/L	Zinc	0.5	0.08	5.45	32%	
KC-01-01	05/02/2009	ug/L	Zinc, Dissolved	0.5	0.08	10.5		

Lab code	Sample	Date Collected	Units	Component	MRL	MDL	Result	RPD
3897	UT01-01	05/03/2009	ug/L	Calcium	50	30	4200	2%
	UT01-01	05/03/2009	ug/L	Calcium, Dissolved	50	30	4410	
	NK-11-01	05/03/2009	ug/L	Calcium	50	30	3810	1%
	NK-11-01	05/03/2009	ug/L	Calcium, Dissolved	50	30	3850	
	NK-21-01	05/03/2009	ug/L	Calcium	50	30	2420	2%
	NK-21-01	05/03/2009	ug/L	Calcium, Dissolved	50	30	2530	
	NK-21-02	05/03/2009	ug/L	Calcium	50	30	2410	2%
	NK-21-02	05/03/2009	ug/L	Calcium, Dissolved	50	30	2530	
	NK-21-02	05/03/2009	ug/L	Magnesium	20	2	502	2%
	NK-21-02	05/03/2009	ug/L	Magnesium, Dissolved	20	2	521	
	UT01-01	05/03/2009	ug/L	Magnesium	20	2	1420	3%
	UT01-01	05/03/2009	ug/L	Magnesium, Dissolved	20	2	1500	
NK-11-01	05/03/2009	ug/L	Potassium	400	100	862	abs difference is <MRL	
NK-11-01	05/03/2009	ug/L	Potassium, Dissolved	400	100	909		
NK-21-01	05/03/2009	ug/L	Sodium	200	70	1270	2%	
NK-21-01	05/03/2009	ug/L	Sodium, Dissolved	200	70	1320		
NK-21-02	05/03/2009	ug/L	Sodium	200	70	1230	4%	
NK-21-02	05/03/2009	ug/L	Sodium, Dissolved	200	70	1320		
5121	SK01-04	06/06/2009	ug/L	Zinc	0.5	0.2	2.7	11%
	SK01-04	06/06/2009	ug/L	Zinc, Dissolved	0.5	0.2	3.4	
	CH11-01	06/05/2009	ug/L	Zinc	0.5	0.2	0.7	55%
CH11-01	06/05/2009	ug/L	Zinc, Dissolved	0.5	0.2	2.4		
5175	SY11-04	06/07/2009	ug/L	Iron	20	3	24.7	5%
	SY11-04	06/07/2009	ug/L	Iron, Dissolved	20	3	27.2	
5914	NK-11-01	06/07/2010	ug/L	Manganese, Dissolved	0.05		9.58	5%
	NK-11-01	06/07/2010	ug/L	Manganese, Total	0.05	0.3	8.74	

4.0 Discussion

Sample collection methods were designed to minimize contamination at the remote sampling sites. To maintain the cleanest possible sampling equipment, sampling was conducted using clean hands technique and through application of a peristaltic pump and tubing (with in-line filter for dissolved fractions) to pump stream water directly into pre-preserved sample bottles covered by a clear plastic sheeting forming a "tent"; tubing and filters were replaced at every site.

Baseline surface water was expected to have low concentrations of most analytes, and be easily impacted by contaminants. Quality controls in both the lab and the field were used to assess whether concentrations in field samples represented the "true" condition of the surface water.

4.1 Lab Quality Control

Lab quality control was quite high. Lab accuracy as measured by recovery of introduced spikes (LCS and MS) were all within acceptable limits, and lab precision as measured by duplicate aliquots (DUP) and duplicate spikes of field samples (DMS) was high. Where split aliquots had measurements that differed by more than 20%, the field sample concentrations were generally found to be quite low, within 5 times the MRL. Method blanks run by the lab for quality control also indicated that lab procedures met all standards, with the exception that gross alpha and gross beta occasionally exceeded method reporting limits slightly.

4.2 Quality Control for Field Methods

Field samples indicated that no systemic contamination of samples occurred. Nearly all analytes, including low level mercury, were within acceptable ranges. There are two issues to mention: one set of trip blanks (May 2009) and one set of equipment blanks (June 2010) did have analytes above detection limit. Additionally, there was a general issue with zinc in 2009.

4.2.1 Trip Blanks

Triplicate trip blanks were carried in the field in sample coolers during each sample trip in 2009. A single trip blank was carried during each of two days during the 2010 sampling trip. In 2009, blanks were analyzed for total metals and dissolved organic carbon. In 2010, trip blanks were analyzed for all elements that samples were analyzed for.

- The set of trip blanks carried on May 2, 2009 had aluminum, copper, dissolved organic carbon, calcium, manganese, and zinc all above MRL, and zinc significantly so. The lab was notified, and the lab manager determined that the wrong lab water had been sent out. Therefore, the exceedances were not an indication of contamination in the field.
- One trip blank carried on June 8, 2009 also had a small exceedance in total zinc (detected at 0.70 ug/L; MRL at 0.50 ug/L). No other trip blanks exceeded MRL in any analyte.
- In 2010, there appears to have been a mix-up at the lab, with a trip blank carried on June 8 found to have non-detect concentrations of total metals but detected concentrations of dissolved metals for four of nine analytes; the samples were sealed bottles that had not

been opened and analysis of dissolved metals had not been requested. The data for dissolved metals was excluded from analysis.

- After exclusion of the dissolved metals, in 2010, only pH and alkalinity were detected above MRL. This does not represent contamination.

4.2.2 *Equipment Blanks*

There were no issues with equipment blanks in 2009. However, in 2010, several analytes were detected above MRL, and seven analytes (of 96 analyses) were detected above 5 MRL. These included cations (two detections of calcium, one detection of magnesium) and metals (two detections of total copper, three of total manganese). In 2010, the three equipment blanks were collected at a single point in time, sequentially. The first sample had the highest concentrations. All concentrations were the same or lower in the second sample; some analytes dropped below detection limit in the third sample while two (total aluminum and total manganese) remained at the level of the second sample and two (calcium and magnesium) were actually slightly higher in the third sample than the second, although significantly lower than the first sample concentration.

In 2010, the set of three equipment blanks was collected sequentially at one point in time. Lab water is pumped through the equipment, with and without filters, to determine if equipment is a source of contamination to samples. Water from sealed bottles provided by CAS labs was utilized initially as water was pumped through the equipment and collected, but when that ran out, a sealed bottle of water from TTT labs, available at the Nondalton Environmental office, was utilized. The sharp difference in analyte concentrations between the initial collection of pumped water and final collection indicates that the CAS lab water was the source of the elevated analytes, rather than the equipment.

This issue occurred in 2009 with trip blanks, in which the lab provided the wrong water, resulting in elevated aluminum, copper, manganese, zinc, calcium, and dissolved organic carbon. The elements with the greatest exceedances in the June 2010 equipment blank sets were copper, manganese, calcium, and magnesium; aluminum, iron, lead, and zinc were also detected. The overlap of analytes from the trip blanks with lab water issues also suggests that lab water, rather than equipment, was the source of the elevated analytes.

The concentrations of calcium and magnesium in equipment blanks were low compared to actual water samples, and unlikely to affect the results; and copper in surface water was commonly in concentrations much lower than observed in the equipment blanks, indicating that systemic contamination from equipment handling was not an issue.

4.2.3 *Zinc*

In 2009, lab duplicates, trip blanks, and equipment blanks all had zinc occasionally detected at greater than acceptable concentrations.

- Total zinc fell outside the acceptable range in one sample in trip blanks in 2009; no other analytes were in exceedance.
- Equipment blanks had one exceedance in total manganese and one in total zinc in 2009.

- Lab duplicates in 2009 also had two exceedances, both for zinc.
- Dissolved zinc was observed in higher concentration than total zinc in three sets of samples.

This suggests that surface water zinc concentrations in May 2009 might be lower than concentrations measured by the lab, but that the issue appeared to have been resolved in June 2009 and June 2010. Surface water sites that show higher zinc in May 2009 than at other sample dates may be reflecting an issue not related to actual surface water conditions. However, this was also the only date in which sampling occurred during breakup, and metal concentrations were found to generally be higher at breakup; therefore it may be difficult to determine if a site with elevated zinc in May 2009 is reflecting concentrations elevated due to breakup or due to some issue not related to surface water. This may be best determined by examining the pattern of other metals at the site.

Field replicates (duplicates, triplicates, and quadruplicates) were also collected. No samples were rejected by the lab (completeness 100%). Zinc was the only analyte to have consistent variability. In May 2009, the variable zinc was strongly correlated with total suspended solids. Of eight sites with TSS above detection limit, seven had variable zinc; additionally one of the sites had variability in TDS. Zinc was less variable in June 2009 and June 2010 and was not correlated with TSS. Some variation is expected due to filter limitations: small particles able to pass through the 0.45 um filter; the filter LOD is 1 ug/L. Gloves containing talc and zinc-containing sunscreen were not used and are therefore not potential sources of contamination.

It is not likely that field methods contributed to the variability; methods were the same in June 2009, when little variation was observed, and there was no variation in June 2010.

4.2.4 Field Replicates

Field replicates (duplicates, triplicates, and quadruplicates) were also collected. No samples were rejected by the lab (completeness 100%). Issues with zinc in field replicates have been discussed. In addition to zinc, there was some variability in alkalinity at four sites in 2009, possibly due to the generally low concentrations of alkalinity in surface water. Other than zinc and alkalinity, variability was only observed at one to two sites for TDS, nitrate+nitrite, dissolved aluminum, total copper, total iron, and total lead. This indicates that concentrations in surface water generally did not vary much; when there was variation, it tended to be due to a single high or low concentration out of three or four replicates. This also indicates that the issues observed in equipment and trip blanks did not result in systemic issues in surface water analyte concentration results.

The overall conclusion is that most analytes are present in low concentrations, and field sample measurements represent a "true" condition of the natural stream water, with the exception that lab analysis may cause zinc to vary by about 1 ug/L, and variability of up to 6 ug/L may be observed in field replicates.

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