analytical precision and recovery: In addition to the effects of water volumes and total sample weight, the RPDs between duplicate samples are due in part to the variability and accuracy that is inherent to the analytical methods that were used to measure the analytes of interest.[1] For example, EPA methods often include RPD performance criteria of up to 35% for duplicate analyses. EPA draft Method 200.7 (which was used to measure the concentration of metals during this study) includes RPD criteria ranging from 0.5 to 20%. In this study, analytical RPDs between duplicate analytical QC samples for dissolved metals and sulfate measurements that were above the laboratory's minimum detection limit (MDL) ranged from 0 to 109%, with 4.5 percent falling outside method prescribed analytical RPD of 20%. The highest RPDs were observed for datasets that included a majority of results that were below or near laboratory detection level, as indicated by the percentage of sample pairs with results falling below the laboratory MDL (see Table 4.6). Analytical recoveries in spiked samples run by the metals laboratory, ranged from 62 to 134%.

For each analyte measured by the metals laboratory, Table 4.6 lists (1) the percent of total sample pairs with results below the laboratory MDL, (2) the range of RPDs across analytical duplicate QC samples, (3) the pooled RPD across all analytical QC duplicates, and (4) the range of percent recovery in analytical spikes. To isolate the results of weathering as much as possible from the variability introduced by sample analysis, data results for the analytes listed in Table 6 and associated with quality control samples (i.e., analytical duplicates or analytical spikes) that fall above an RPD of 20 or outside a % recovery range of 75 to 125, were eliminated from the assessment presented in this report. The percentage of results eliminated based on analytical quality control also are included in Table 4.6.

Table 4.6: Relative Percent Differences (RPD) Between Analytical QC Duplicates

Analyte	%Total Pairs with results <MDL	Analytical RPDs (excluding results < MDL)	Pooled Analytical RPD	% Recovery Range	% of Column Results Eliminated based on analytical QC Failures
Fe	41	0 – 109	29	78 – 122	1.7
Mn	0	0 – 30.1	5.4	80 – 130	0.2
Al	80	0 – 30.3	10.3	81 – 112	0.2
Ca	0	0 – 7.5	2.2	65 – 128	0.4
Mg	0	0 – 7.9	2.3	80 – 133	0.2
Se	16	0 – 75.7	24.6	62 – 134	2.2
Zn	8	0 – 20.1	4.6	78 – 112	0.1
Na	0	0 – 37.8	7.8	75 – 115	0.4
K	0	0 – 15.4	4.8	80 – 110	0
SO_4	0	0 – 4.8	1.2	90 – 125	0

Only a subset of the laboratories measuring acidity, alkalinity, pH and conductivity reported laboratory detection limits and/or results of analytical quality control (QC) samples. All QC results reported for these analytes passed method-specified criteria; therefore, none of these data were eliminated based on association with failed QC results.

[1] EPA methods often include RPD performance criteria of up to 30% for duplicate analyses. EPA draft Method 200.7 (May 2001) includes RPD criteria ranging from 0.5 to 20%. EPA draft Method 1630 for measurement of methylmercury includes an RPD criterion of 35%.