Chemical Speciation Network (CSN): Annual Quality Assurance Report

Air Quality Group | University of California, Davis | November 30, 2017

1. Introduction

The University of California Davis (UCD) Air Quality Group summarizes quality assurance (QA) parameters annually in this report as a contract deliverable for the Chemical Speciation Network (CSN) program (contract #EP-D-15-020). The primary objectives of this report are:

1. Provide the U.S. Environmental Protection Agency (EPA) and other potential users with graphical representations to illustrate key QA parameters for species measured within the network.
2. Identify and highlight observations of interest that may have short- or long-term impact on QA across the network or at particular sites.
3. Serve as a record and tool for ongoing UCD QA efforts.

The graphics shown in this report are a small subset of the many QA evaluations that UCD performs on a routine basis. They are selected to illustrate the nature and use of the QA tools, and provide a snapshot of the network's internal consistency and recent trends.

Each network site includes two samplers for the collection of particulate matter: (1) URG sampler (URG Corporation; Chapel Hill, NC) for collection of particulate matter on quartz filters; and (2) Met One SASS or SuperSASS (Met One Instruments, Inc; Grants Pass, OR) for collection of particulate matter on polytetrafluoroethylene (PTFE) filters and nylon filters. The following analyses are performed:

- PTFE filters: Analyzed at University of California Davis (UCD) using x-ray fluorescence (XRF) for a suite of 33 elements.
- Nylon filters: Analyzed at Desert Research Institute (DRI) using ion chromatography (IC) for a suite of six ions.
- Quartz filters: Analyzed at the Desert Research Institute (DRI) for organic and elemental carbon, including carbon fractions, using Thermal Optical Analysis (TOA).

Additional information and detail regarding analytical and validation procedures can be found in the standard operation procedure (SOP) documents and Quality Assurance Project Plan (QAPP) available at the EPA Ambient Monitoring Technology Information Center (AMTIC; https://www3.epa.gov/ttnamti1/specsop.html). Further information regarding data validation practices can be found in *Data Validation for the Chemical Speciation Network* guide, available from the EPA or UCD.

Unless otherwise noted, data included in this report cover the time period November 2015 through December 2016. CSN filters prior to November 2015 were collected and analyzed, and their data validated and delivered, by the previous contractor, Research Triangle Institute (RTI).

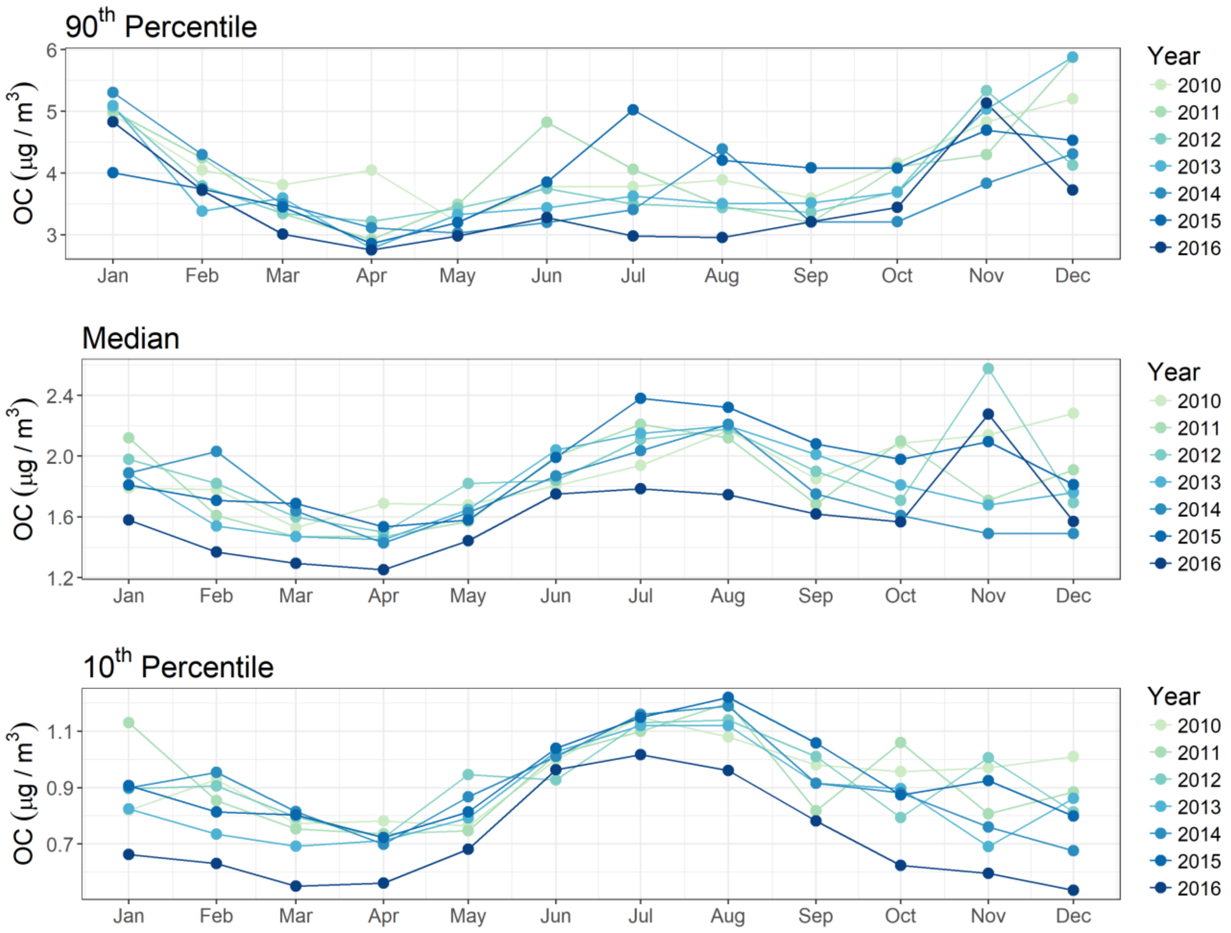
2. Concentration-Level QC Checks

2.1 Comparisons Across Years

Multi-year time series plots are used to examine large-scale trends and/or analytical problems. UCD is currently constructing a database backfilled to 2000 with CSN historical data. Comprehensive access to historical network data will provide context for validation and review of more recent data. The backfill is not yet complete and limited multi-year time series are available at this time.

Figures 1 and 2 show time series for the network-wide 90th percentile, median (50th percentile), and 10th percentile concentrations of organic carbon (OC) and elemental carbon (EC). The carbon fractions OC and EC are determined by DRI using thermal analysis with a correction for pyrolysis based on optical monitoring as it is heated. Measurements from 2005 through 2015 were made with DRI Model 2001 analyzers monitoring at the single wavelength 633 nm; starting with January 2016 samples, DRI switched to Model 2015 analyzers monitoring seven wavelengths centered at 635 nm. The 2016 data shown in Figures 1 and 2 are for the 635 nm measurements and should be comparable to the earlier data with some allowance for seasonal and annual variability. With the exception of November and December, the 2016 median OC values are lower than previous years. The 2016 10th percentile OC values are lower across all months. The 2016 EC median values align better with past years; however, the 10th percentile EC values are lower for 9 of 12 months.

Figure 1: Multi-year time series, organic carbon (OC).

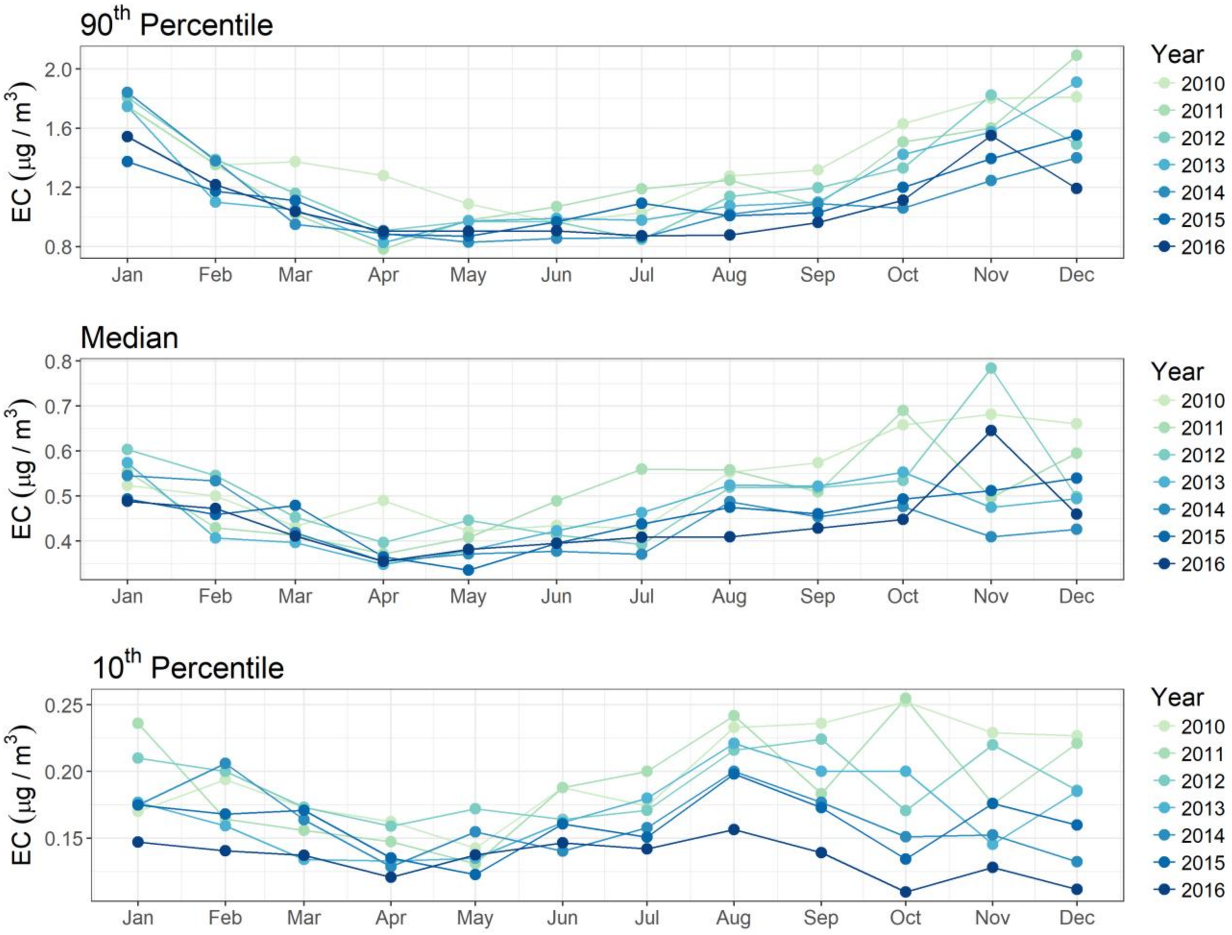


90th Percentile

Median

10th Percentile

Figure 2: Multi-year time series, elemental carbon (EC).



2.2 Comparisons Between Modules

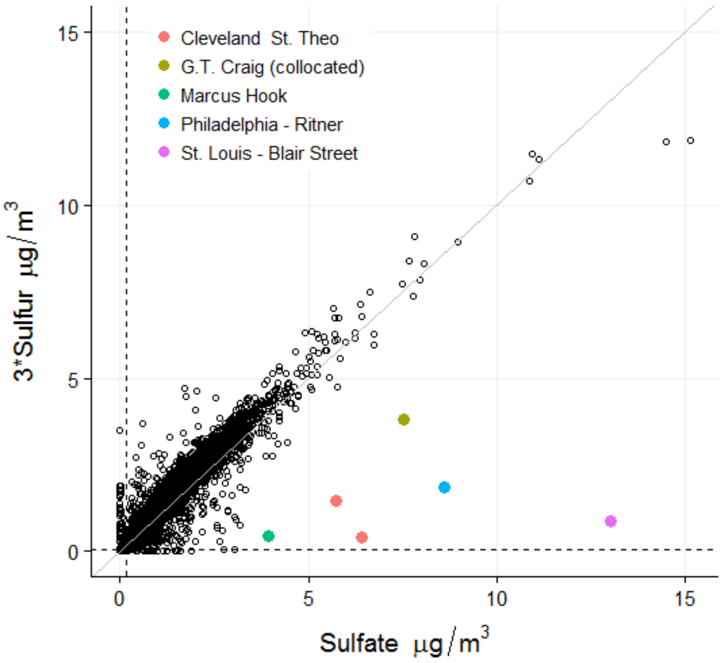
The following graphs compare two independent measures of aerosol properties that are expected to correlate. These graphs highlight cases where the two measurements do not correlate well, which can result from real atmospheric and anthropogenic events or analytical and sampling issues. As part of the data validation process, the highlighted cases are investigated.

2.2.1 Sulfur versus Sulfate

PTFE filters are analyzed for elemental sulfur using XRF, and nylon filters are analyzed for sulfate (SO_4) using IC. The molecular weight of SO_4 (96 g/mol) is three times the atomic weight of S (32 g/mol), so the concentration ratio (3×S)/SO_4 should be one if all particulate sulfur is present as water-soluble sulfate. In practice, real measurements routinely yield a ratio greater than one (Figure 3), suggesting the presence of some sulfur in a non-water soluble form of sulfate or in a chemical compound other than sulfate. However, instances are observed where $(3\times S)/SO_4$ ratios are lower than typically observed (Figure 3; colored points). Three of the six instances of low $(3\times S)/SO_4$ in Figure 3 are from the Cleveland St. Theo (AQS ID#39-035-0038-6) and G.T. Craig collocated (AQS ID#39-035-0060-6) sites, which are in close proximity and located in Cleveland, OH. This behavior may result from sampling artifacts on the nylon filter (resulting in higher SO_4 concentrations) associated with industrial processes, though is only seen on a few occasions during this time period.

The highest sulfur and corresponding sulfate measurements (3.96 µg/m^3 S and 15.16 µg/m^3 SO_4) in the network were on July 5, 2016 at the Riverside-Rubidoux site (AQS ID#06-065-8001-5). The collocated Riverside-Rubidoux sampler (AQS ID#06-065-8001-6) measured similarly high concentrations on the same day. Both samplers also measured elevated concentrations of potassium, aluminum, barium, copper, magnesium, titanium, and strontium on July 5, further evidence that the high S and SO_4 concentrations are related to Independence Day firework activity.

Figure 3: Scatter plot of (3xS) versus SO_4 for the CSN network, November 2015 through December 2016. MDLs indicated by dotted line.



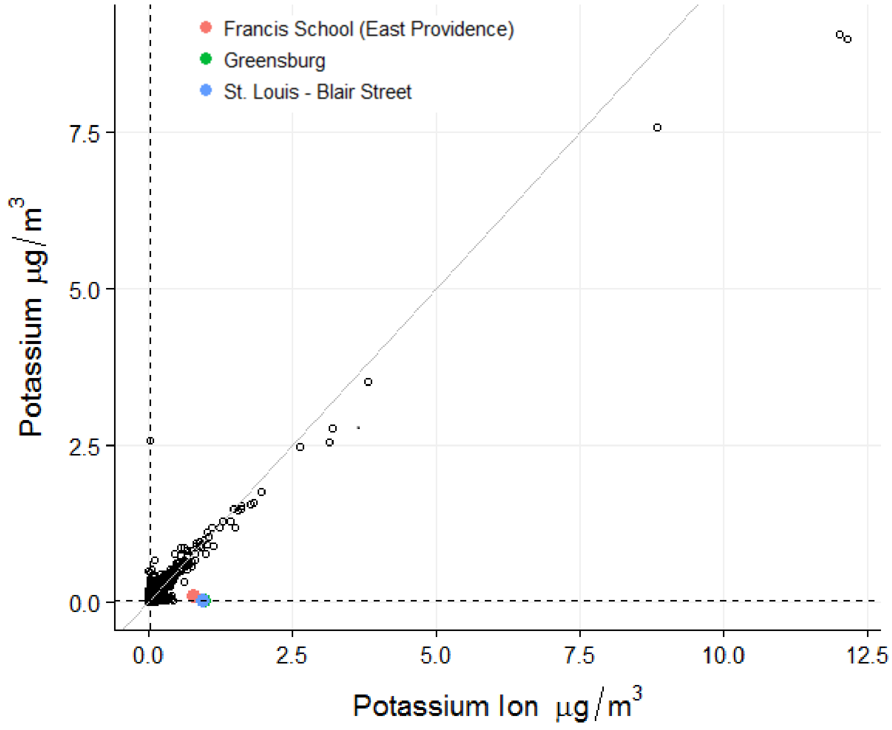
2.2.2 Potassium versus Potassium Ion

PTFE filters are analyzed for elemental potassium using XRF, and nylon filters are analyzed for potassium ion using IC. Similar to the S/SO_4 relationship, the potassium/potassium ion ratio can be used to identify outliers as well as atmospherically unusual events. In a scenario where all the particulate potassium is present as water-soluble potassium ion, the potassium/potassium ion ratio is expected to be near one. This expectation is generally met, with greater variability at low concentrations (Figure 4). A known exception to this expectation is for soil-borne potassium, which is not water soluble; high soil contributions are thus expected to result in ratios greater than one.

Notable outliers are observed (Figure 4; colored points), where the potassium/potassium ion ratio is lower than expected. Unlike the (3×S)/SO_4 outliers, these outliers correspond with different sites.

The highest potassium and corresponding potassium ion measurements (9.00 µg/m^3 potassium and 12.15 µg/m^3 potassium ion) in the network were on July 5, 2016 at the Riverside-Rubidoux site (AQS ID#06-065-8001-5) and the collocated Riverside-Rubidoux sampler (AQS ID#06-065-8001-6). As noted above in the discussion of S and SO_4, these high concentrations are likely from firework activity.

Figure 4: Scatter plot of potassium versus potassium ion for the CSN network, November 2015 through December 2016. MDLs indicated by dotted line.



2.2.3 PM2.5 vs. Reconstructed Mass (RCMN)

Gravimetric data are compared to RCMN, where the RCMN composite variable is estimated from chemical speciation measurements, to test many different aspects of overall data quality. The formulas used to estimate the mass contributions from various chemical species are detailed in *UCD CSN TI 801B, CSN Data Processing*. In the simple case where valid measurements are available for all needed variables, reconstructed mass is the following sum:

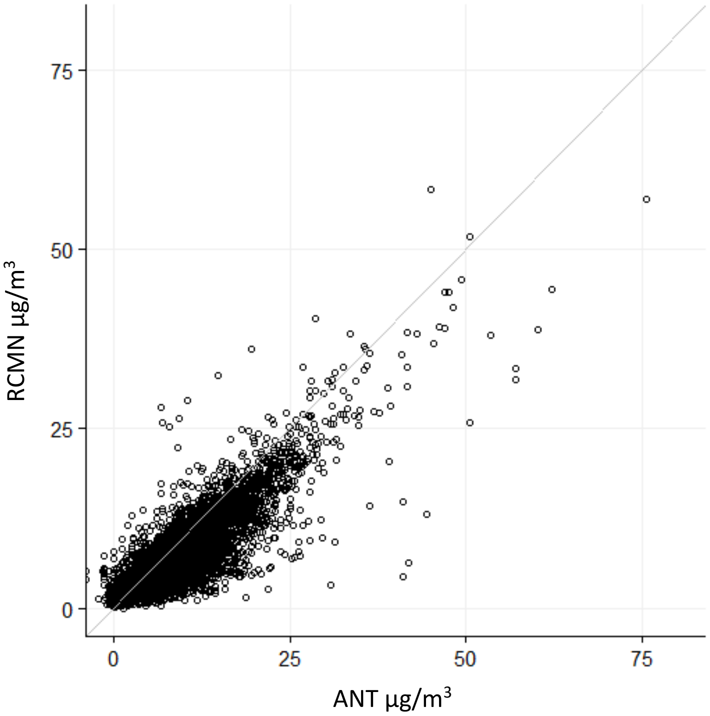
$$\begin{aligned} RCMN = {} & (4.125 \times S) + (1.29 \times NO_3^-) + (1.4 \times OC) + (EC) + \\ & (2.2 \times Al + 2.49 \times Si + 1.63 \times Ca + 2.42 \times Fe + 1.94 \times Ti) + (1.8 \times \text{chloride}) \end{aligned}$$

The parenthesized components represent the mass contributions from, in order, ammonium sulfate, ammonium nitrate, organic compounds, elemental carbon, soil, and sea salt.

As of April 2016, gravimetric analysis (i.e., weight before and after sample collection) was only performed for one site in the network (Douglas, GA, AQS ID#13-069-0002). Thus, for comparison purposes 24-hour average gravimetric PM2.5 mass data from AirNow Tech (ANT) is used as part of the validation process. The data provided by AirNow Tech is not final, so the data used here is a snapshot, downloaded at the time the plots were made.

If the RCMN completely captures and accurately estimates the different mass components, the RCMN/ANT ratio is expected to be near one. The gravimetric mass is likely to include some water associated with hygroscopic species, which is not accounted for by any of the chemical measurements. Conversely, some ammonium nitrate measured on the retentive nylon filter may volatilize from the inert PTFE filter during and after sampling. The RCMN and ANT masses generally correlate (Figure 5), but RCMN tends to underestimate ANT mass.

Figure 5: Scatter plot of RCMN versus ANT PM2.5 mass data, November 2015 through December 2016.



When considered for the entire network, the depressed RCMN/ANT ratio shows no seasonal pattern (Figure 6). Considered individually, sites across the network exhibit a range of RCMN/ANT ratio behavior including seasonality with high wintertime ratios relative to summer (Figure 7; San Jose, CA; AQS ID#06-085-0005), and low wintertime ratios relative to summer (Figure 8; Omaha, NE; AQS ID#31-055-0019). These patterns reflect the varying chemical composition at the sites by season. However, many sites exhibit no seasonal pattern and variable RCMN/ANT ratios.

Low RCMN/ANT ratios can result from an underestimate of variable(s) for derived RCMN. The organic mass estimate (1.4 × OC) is generally considered representative of a regime where organic matter is dominated by fresh motor vehicle emissions. However, there are many scenarios where a higher multiplier may be more appropriate. The IMPROVE (Interagency Monitoring of Protected Visual Environments) network uses a 1.8 multiplier for the organic mass estimate, which is thought to be more appropriate for a more aged air mass.

Figure 6: Network wide time series of RCMN/ANT ratios, November 2015 through December 2016.

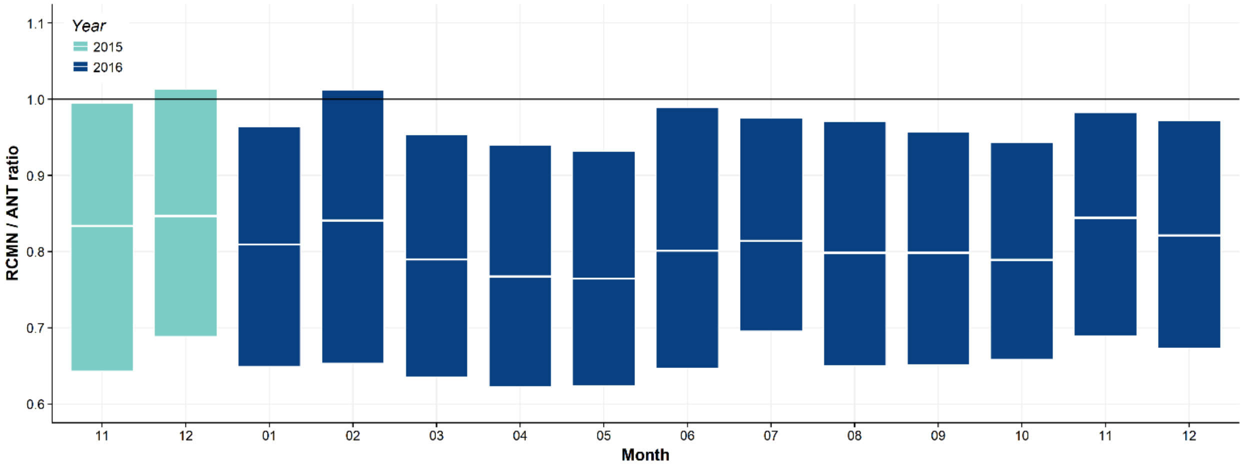


Figure 7: RCMN/ANT ratios at San Jose, CA site (AQS ID#06-085-0005), November 2015 through December 2016.

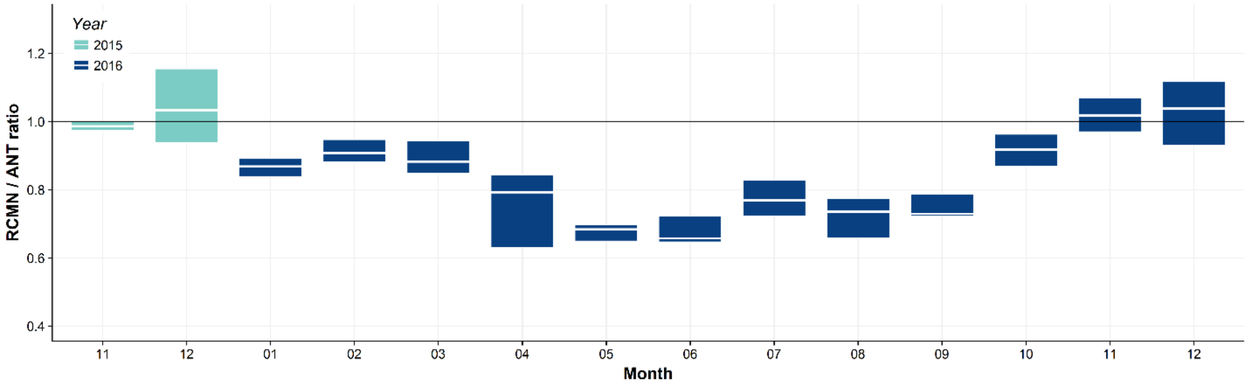
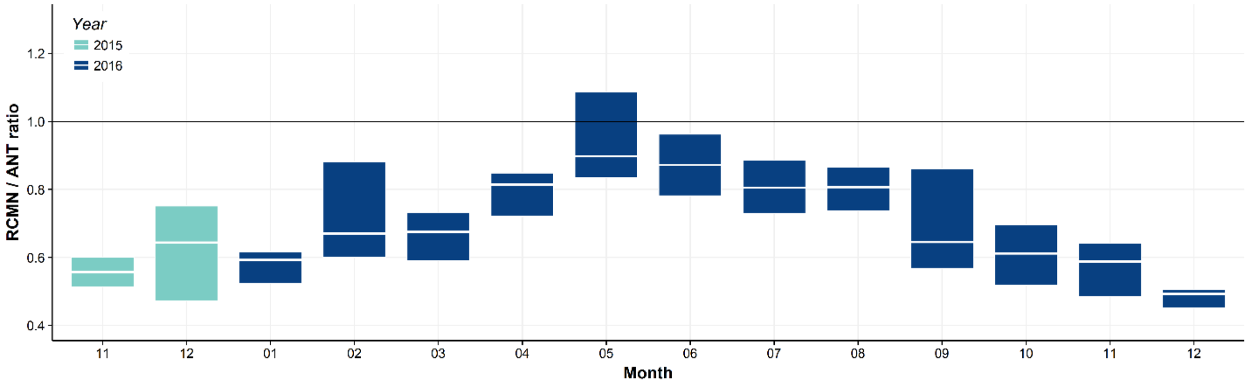


Figure 8: RCMN/ANT ratios at Omaha, NE site (AQS ID#31-055-0019), November 2015 through December 2016.



2.3 Comparisons Across Sites

Evaluating species data across the network by site allows for identification of site-specific and regional trends. Additionally, plots shown in this section can be used to identify outliers, which can be real atmospheric or anthropogenic events, or analytical outliers indicative of contamination.

Sulfur shows a distinct east/west gradient with lower concentrations primarily in the far western United States (Figure 9). However, there are several California sites where sulfur concentrations are higher than the other western sites (Figure 9; site code 06-XXX-XXX-Y).

Concentrations of nitrate (Figure 10) exhibit regional trends with elevated concentrations in the west, particularly California (site code 06-XXX-XXX-Y).

High vanadium concentrations are observed at several sites across the network (Figure 11). Highlighted area (1) includes five sites located along the Mississippi River (Davenport, IA, AQS ID# 19-163-0015; three sites in the St. Louis, MO area: AQS ID# 29-099-0019, AQS ID# 29-510-0085, and AQS ID# 17-119-0024; and, Baton Rouge, LA, AQS ID# 22-033-0009). Highlighted area (2) includes three sites in the Cleveland, OH area (two sites in Cleveland, OH: AQS ID# 39-035-0060 and AQS ID# 39-035-0038; and, Canton, OH: AQS ID# 39-151-0017). Network wide the highest concentrations of vanadium are observed at the Philadelphia, PA site (AQS ID# 42-101-0048; Figure 11, highlight 3).

Figure 9: Sulfur concentrations (μg/m^3) for the entire CSN network. Sites are ordered west to east on the x-axis, designated by XX-XXX-XXXX-Y, where XX-XXX-XXXX indicates AQS ID# and Y indicates site POC. Red points designate 2015 data, blue points designate 2016 data. Gray box and whisker indicate historical 90th percentile and 95th percentile, respectively.

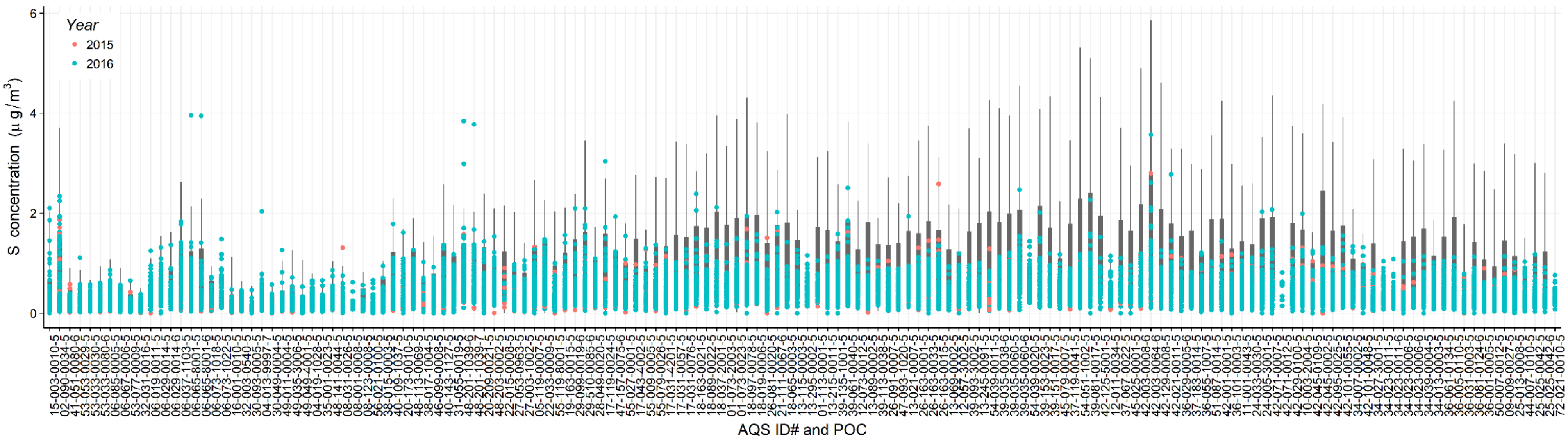


Figure 10: Nitrate concentrations (μg/m^3) for the entire CSN network. Sites are ordered west to east on the x-axis, designated by XX-XXX-XXXX-Y, where XX-XXX-XXXX indicates AQS ID# and Y indicates site POC. Red points designate 2015 data, blue points designate 2016 data. Gray box and whisker indicate historical 90th percentile and 95th percentile, respectively.

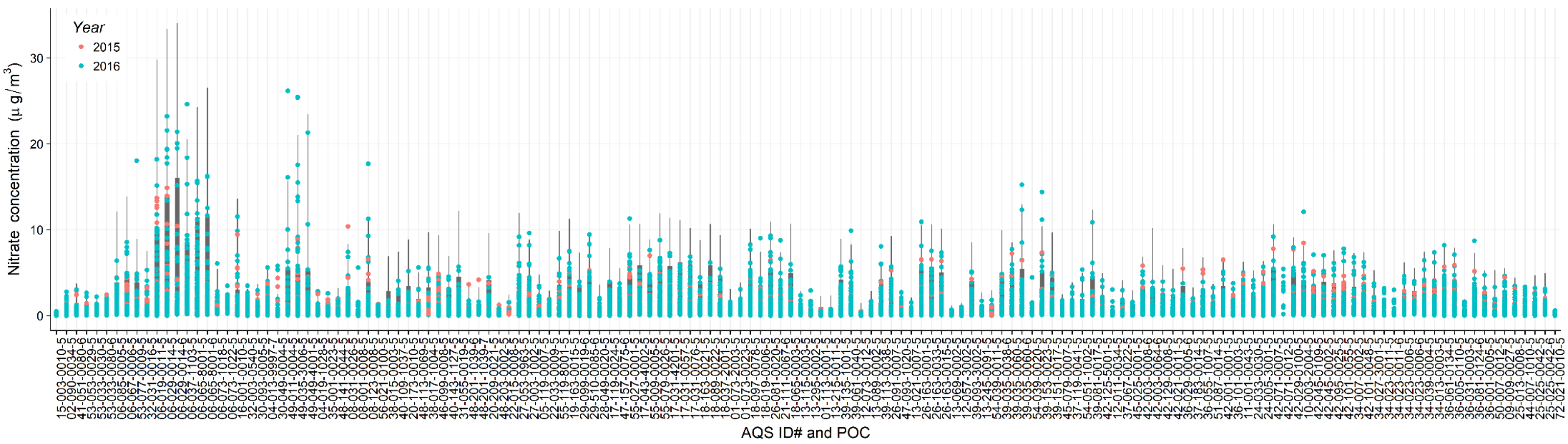
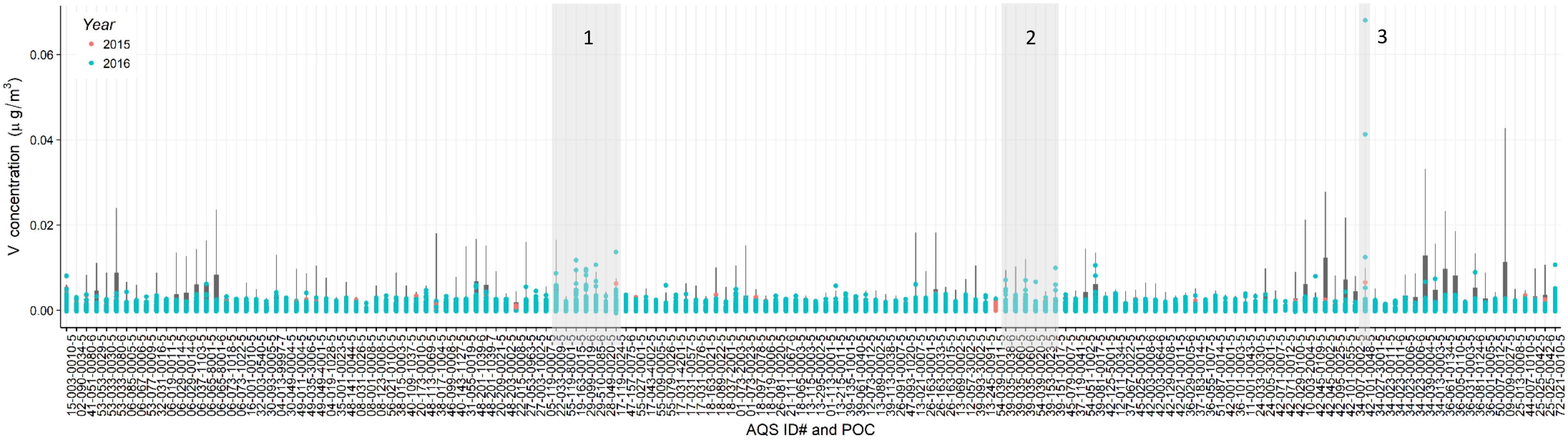


Figure 11: Vanadium concentrations (µg/m^3) for the entire CSN network. Sites are ordered west to east on the x-axis, designated by XX-XXX-XXXX-Y, where XX-XXX-XXXX indicates AQS ID# and Y indicates site POC. Red points designate 2015 data, blue points designate 2016 data. Highlighted sites indicate locations with observations of elevated vanadium. Gray box and whisker indicate historical 90th percentile and 95th percentile, respectively.



2.4 Comparisons between Collocated Samples

Several network sites are equipped with collocated samplers, where duplicate samples are collected on independent samplers and then analyzed using the same analytical protocols. Differences between the resulting data provide a measure of the total uncertainty associated with filter substrates, sampling and handling in the field, and laboratory analysis. This uncertainty is conventionally reported as collocated precision.

Collocated precision is calculated from the scaled relative differences (SRD) between the collocated sample pairs,

$$Scaled\ Relative\ Difference\ (SRD) = \frac{(\text{collocated} - \text{routine}) / \sqrt{2}}{(\text{collocated} + \text{routine}) / 2}$$

$$Collocated\ Precision\ (\%) = 100 \times \sqrt{\frac{1}{n}\sum_i SRD_i{}^2}$$

The scaled relative differences are ±√2 when one of the two measurements is zero, and vary between these limits at concentrations close to the detection limit. They generally decrease with increasing concentration, and are expected to converge to a distribution representative of multiplicative measurement error when the concentration is well above the detection limit (Figure 12, elements; Figure 13, ions; Figure 14, carbon). Note that this convergence is not observed for elements and carbon fractions that are rarely measured above the MDL.

For several species, outliers are observed for the G.T. Craig site (AQS ID# 39-035-0060; Figures 12, 13, and 14). The instances of poor agreement between the collocated samplers at G.T. Craig do not fall within a clear time period, rather are dispersed throughout the year.

Figure 12: Scaled relative difference for element measurements at sites with collocated samplers across the network (November 2015 through December 2016). Dotted vertical lines indicate the detection limits.

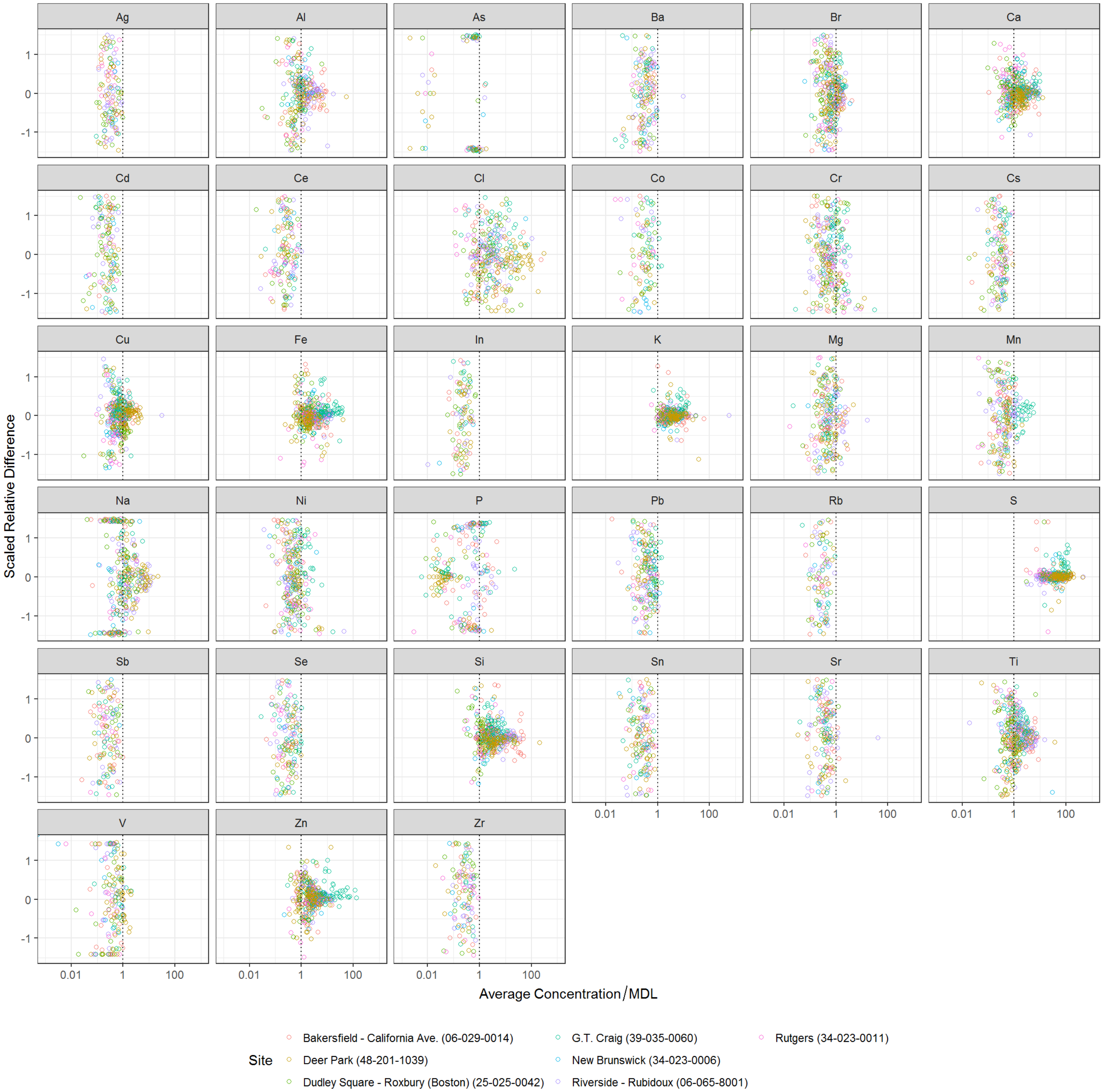


Figure 13: Scaled relative difference for ion measurements at sites with collocated samplers across the network (November 2015 through December 2016). Dotted vertical lines indicate the detection limits.

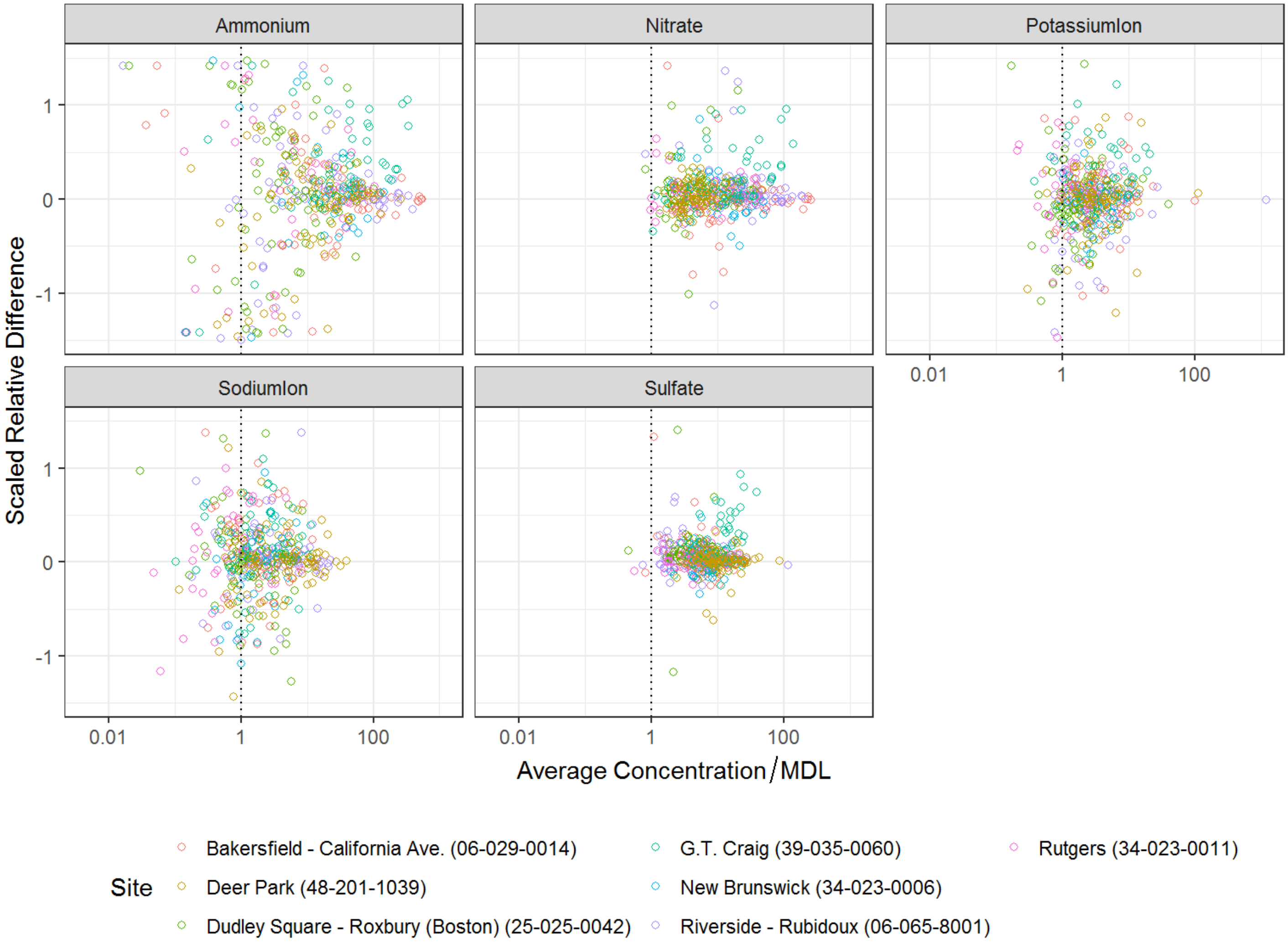
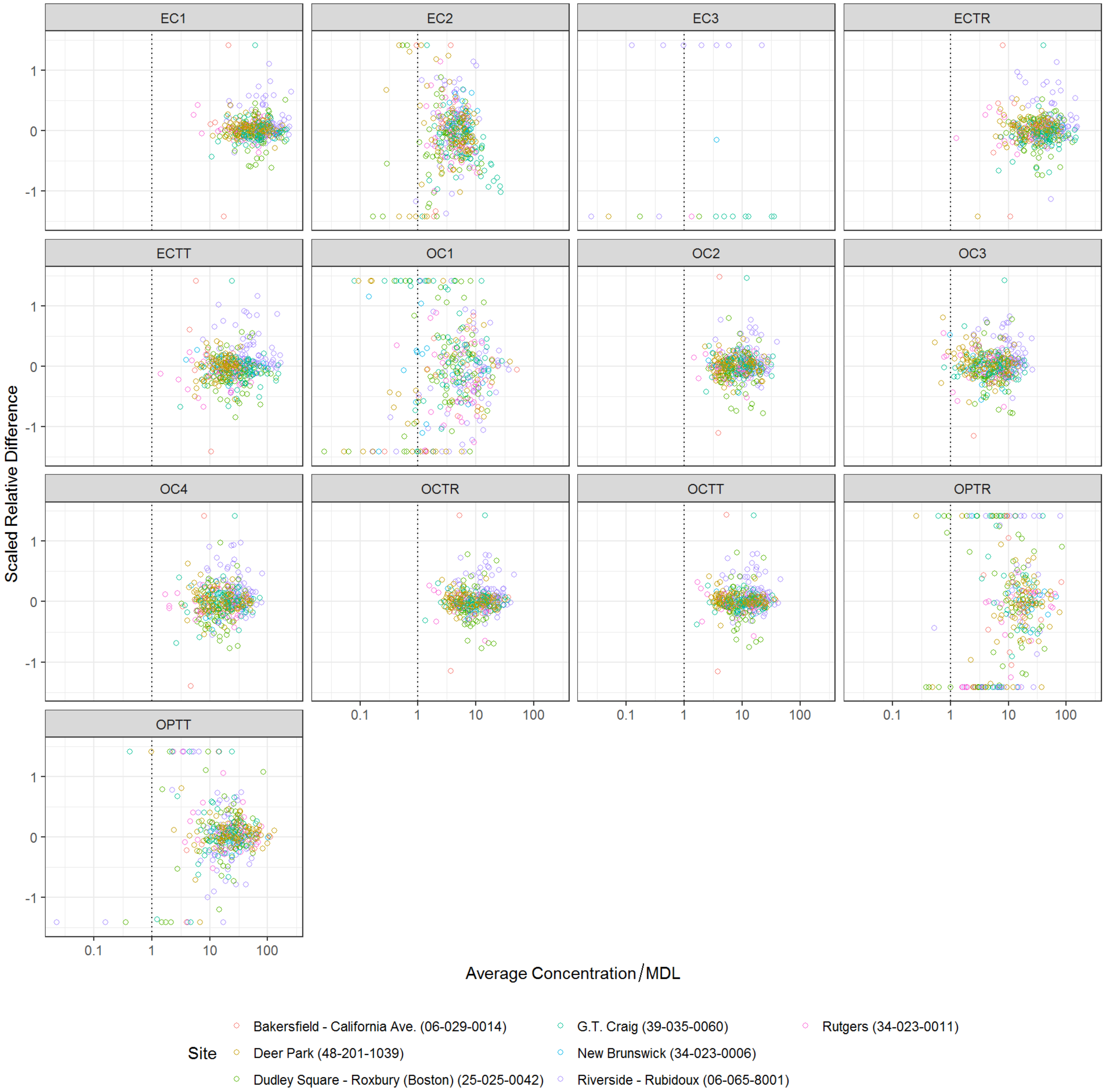


Figure 14: Scaled relative difference for carbon measurements at sites with collocated samplers across the network (November 2015 through December 2016). Dotted vertical lines indicate the detection limits.



Collocated precision is the standard deviation of SRDs from the subset of observations with concentrations at least three times the method detection limit (MDL). To minimize the effect of outlier SRDs associated with occasionally mismatched filter pairs, a robust estimate is used,

$$Collocated\ Precision\ (\%)\ = 100\ \times \frac{84th\ SRD\ percentile - 16th\ SRD\ percentile}{2}$$

Since many species are routinely measured at or below the MDL, there are numerous instances where there are no or few pairs of available data to calculate the collocated precision.

UCD CSN TI 801B, CSN Data Processing documents the calculation of collocated precision. Tables 1 (elements), 2 (ions), and 3 (carbon) compare the updated collocated precisions, calculated using data from November 2015 through December 2016, to the historical collocated precisions calculated from the 2009-2014 collocated data. The collocated precisions in Tables 1, 2, and 3 are calculated using the same method. These collocated precision estimates are used to calculate the uncertainties reported to AQS with each concentration and are updated annually.

Table 1: Collocated precision estimates for the elements.

Species	Collocated Precision (%) Nov 2015 – Dec 2016	Pairs	Collocated Precision (%) 2009 – 2014	Pairs
Na	---	38	16.4	1,270
Mg	---	2	24.5	365
Al	---	35	25.2	1,209
Si	15.3	178	15.2	3,897
P	---	6	17.3	93
S	6.6	331	6.2	5,530
Cl	31.4	104	34.2	1,740
K	7.4	199	10.6	4,825
Ca	16.1	91	16.8	4,067
Ti	---	46	17.4	697
V	---	0	12.8	499
Cr	---	1	38.9	83
Mn	---	4	15.4	623
Fe	12.2	167	17	5,520
Co	---	0	---	10
Ni	---	1	17.8	400
Cu	---	11	26.9	2,313
Zn	11.5	125	12.3	3,144
As	---	0	18.8	155
Se	---	0	---	43
Br	---	1	15	1,610
Rb	---	0	---	0

Sr	---	1	---	58
Zr	---	0	---	3
Ag	---	0	---	1
Cd	---	0	---	0
In	---	0	---	0
Sn	---	0	---	0
Sb	---	0	---	0
Cs	---	0	---	7
Ba	---	1	16.5	123
Ce	---	0	---	21
Pb	---	0	18.5	381

Table 2: Collocated precision estimates for the ions.

Species	**Collocated Precision (%) Nov 2015 – Dec 2016**	**Pairs**	**Collocated Precision (%) 2009 – 2014**	**Pairs**
Ammonium	29	222	7.1	5,466
Nitrate	12.6	257	7.6	5,767
Potassium Ion	17.7	213	12.6	2,072
Sodium Ion	19	130	24.7	3,562
Sulfate	9.8	279	4.9	5,680

Table 3: Collocated precision estimates for carbon fractions.

Species	**Collocated Precision (%) Nov 2015 – Dec 2016**	**Pairs**	**Collocated Precision (%) 2009 – 2014**	**Pairs**
Elemental Carbon (1)	12.5	274	12.9	1,948
Elemental Carbon (2)	28.6	189	36.8	992
Elemental Carbon (3)	---	1	---	4
Elemental Carbon (TR)	17.3	271	15.5	1955
Elemental Carbon (TT)	18.7	272	12.8	1,606
Organic Carbon (1)	35.9	110	32.9	1,039
Organic Carbon (2)	15.4	254	13.6	1,877
Organic Carbon (3)	17.8	194	17.8	1,860
Organic Carbon (4)	19.2	263	15.7	1,487
Organic Carbon (OCTR)	12.8	256	11.6	2,033
Organic Carbon (OCTT)	11.6	256	7.3	1,774
Organic Pyrolyzed (TR)	37.9	143	25.1	919
Organic Pyrolyzed (TT)	12.2	253	17.3	1,557

3. Analytical QC Checks

3.1 Replicate versus Routine

Analytical precision is evaluated by comparing data from replicate and routine analyses, where the replicate analysis is a second analysis performed on the same sample. Reliable laboratory measurements should be repeatable with good precision. Analytical precision for each species for the time period of interest is calculated as follows,

$$Scaled\ Relative\ Difference\ (SRD) = \frac{(\text{replicate} - \text{routine}) / \sqrt{2}}{(\text{replicate} + \text{routine}) / 2}$$

$$Analytical\ Precision\ (\%) = 100 \times \sqrt{\frac{1}{n}\sum_{i} {SRD_i}^2}$$

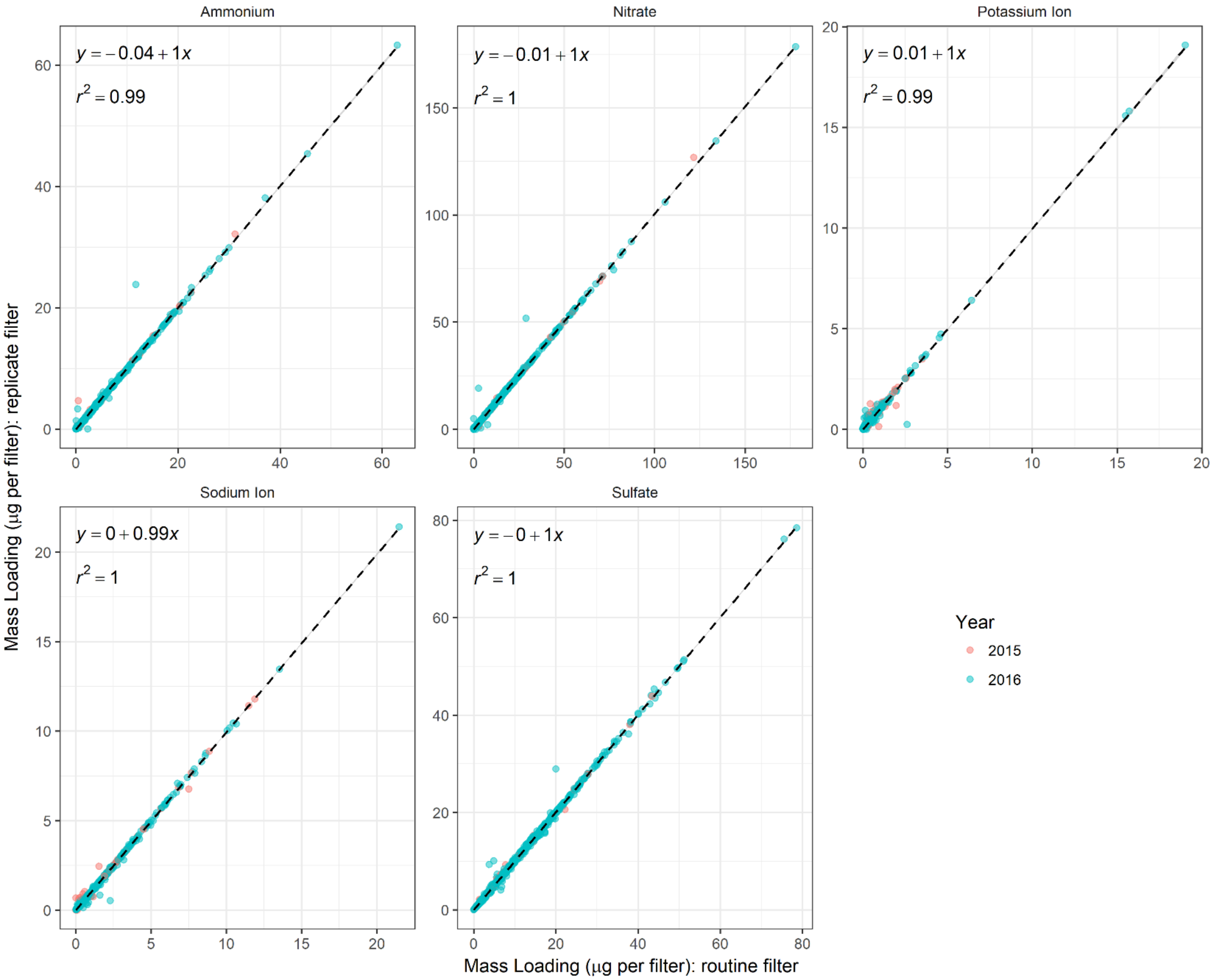
The replicate (Section 3.1) and collocated (Section 2.4) pairs both generate measures of uncertainty. Analytical precision includes only the uncertainties associated with the laboratory handling and analysis, whereas collocated precision also includes all the uncertainties associated with sample preparation, field handling, and sample collection. As such, analytical precision is expected to be lower than collocated precision.

Comparison of replicate and routine ion mass loading on nylon filters analyzed by IC show generally good agreement (Table 4, Figure 15). As expected, ions (Table 4) exhibit lower analytical precision than collocated precision (Table 2).

Table 4: Analytical precision, ions.

Species	Analytical precision (%) Nov. 2015 – Dec. 2016	Pairs
Ammonium	5.9	902
Nitrate	4.2	865
Potassium Ion	10.0	694
Sodium Ion	2.6	254
Sulfate	2.5	1,077

Figure 15: Comparison of ion mass loading form replicate and routine filters. Red points designate 2015 data, blue points designate 2016 data.

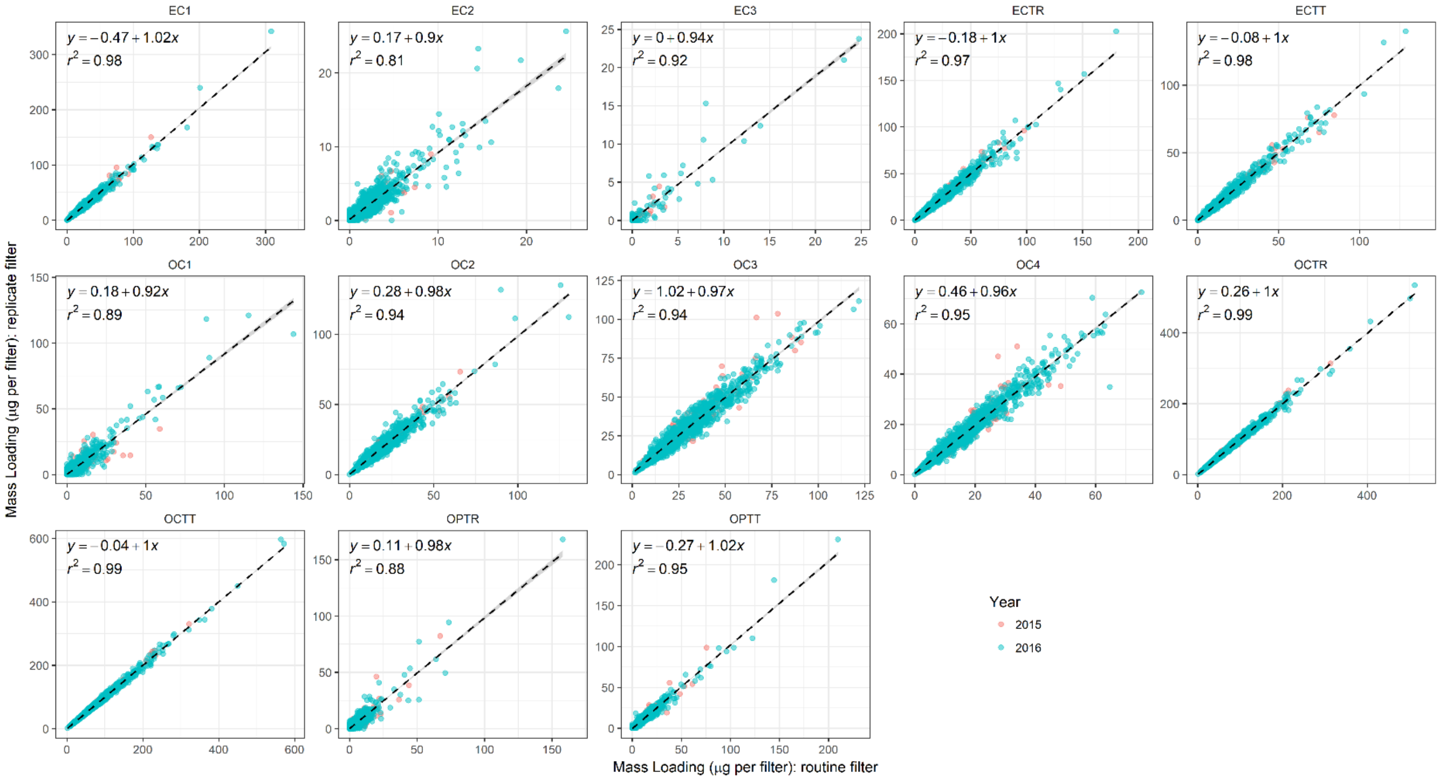


Comparison of replicate and routine carbon mass loadings on quartz filters analyzed by TOA generally show agreement (Table 5, Figure 16). As expected, the analytical precision (Table 5) is lower than collocated precision (Table 3), except OPTT (analytical precision = 13.7%, collocated precision = 12.2%). For OPTT, the difference between analytical and collocated precision comes from the different calculation methods used; the formula for analytical precision is not robust to outliers whereas the formula for collocated precision is.

Table 5: Analytical precision, carbon fractions by TOA.

Species (Ions)	Analytical Precision (%) Nov 2015 – Dec 2016	Pairs
Elemental Carbon (1)	7.5	1,665
Elemental Carbon (2)	21.3	1,221
Elemental Carbon (3)	38.3	66
Elemental Carbon (TR)	9.7	1,641
Elemental Carbon (TT)	10.1	1,609
Organic Carbon (1)	28.0	642
Organic Carbon (2)	11.0	1,525
Organic Carbon (3)	9.9	1,189
Organic Carbon (4)	10.2	1,591
Organic Carbon (TR)	4.0	1,553
Organic Carbon (TT)	3.6	1,572
Organic Pyrolyzed (TR)	28.3	996
Organic Pyrolyzed (TT)	13.7	1,540

Figure 16: Replicate versus routine carbon analyses. Red points designate 2015 data, blue points designate 2016 data.



Replicate XRF analyses are not performed on the routine CSN samples. Rather, long-term reanalysis are performed to assess both the short- and long-term stability of the XRF measurements as described in *CSN SOP 302, XRF Analysis*.

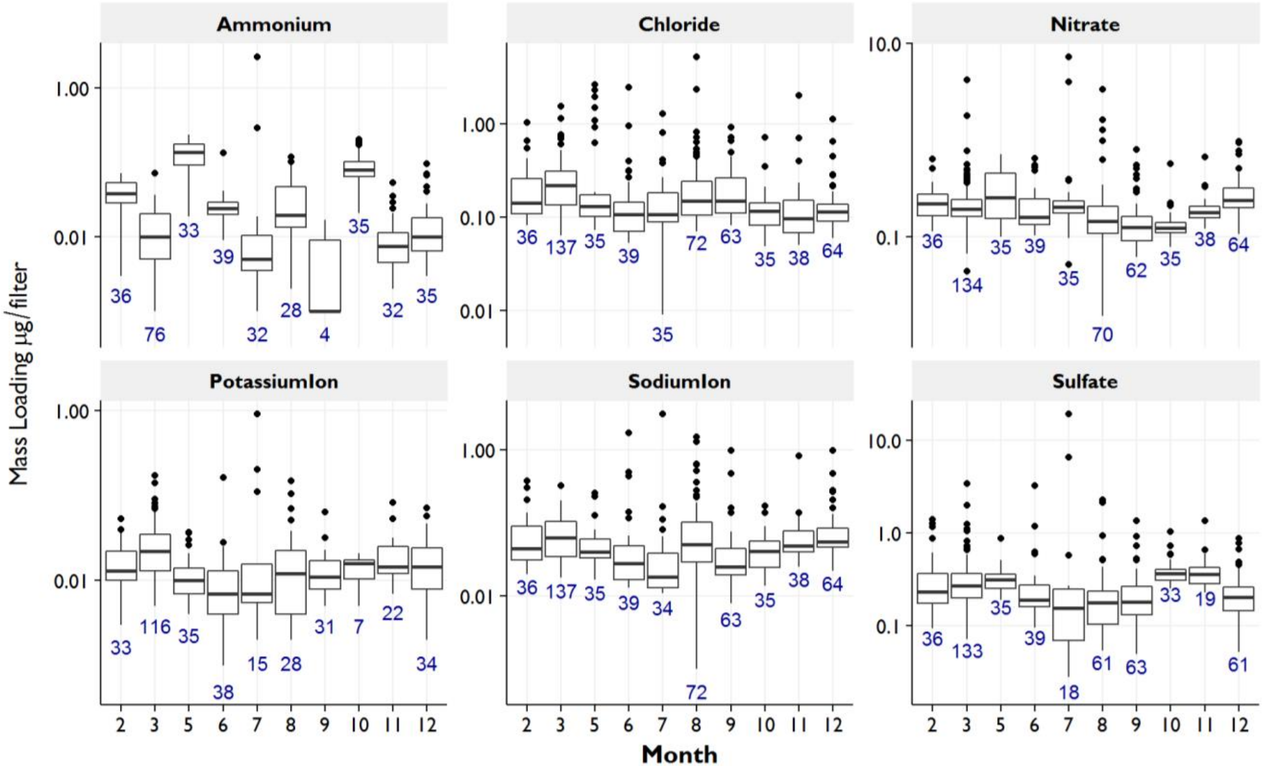
3.2 Blanks

Three types of blanks – lab blanks, field blanks, and trip blanks – are handled and analyzed in the laboratory using the same process as sampled filters. Lab blanks are only handled in a laboratory environment and have the least amount opportunity for mishandling and contamination. Field blanks are collected at sampling sites across the network by exposing filters to the same conditions and handling that a sampled filter experiences but without pulling air through the filter. Trip blanks receive highly variable treatment in the field, and are sample and field blank filters that were mishandled or incorrectly sampled (mistakes).

Field blanks are an integral part of the QC process, and analysis results allow for artifact correction of the sampled filters as part of the concentration calculation. Artifacts result from contamination in the filter material or handling and analysis.

There is some variability in field blank mass loadings by species and month, as shown in Figure 17 for ion species measured from nylon filters. Considering that field blanks capture artifacts from both field and laboratory processes, it is expected that field blank mass loadings are generally higher than field and trip blanks.

Figure 17: Nylon filter field blank mass loadings, 2016. Numbers shown on plot indicate count of samples with mass loading > 0.



3.2.1 Blank Correction

Blank correction for carbon and ions measurements was implemented from November 22, 2015 and January 1, 2016 onward, respectively. Blank correction is performed using a rolling median value from at least 50 quartz and nylon field blanks collected closest to the sample month.

3.2.2 Method Detection Limits

Method detection limits (MDL) are calculated and delivered for each species every month. A sufficient number of field and/or laboratory blanks must be available in order to calculate MDLs representative of the network. Initially, the number of field blanks collected network wide per month was highly variable, and the MDLs were calculated as follows:

- Elements: Calculated for each species as 3× standard deviation of lab blanks. Recalculated for each new lot of PTFE filters.
- Ions and carbon: Calculated monthly for each species as 3× standard deviation of field blanks, using 50 nylon (for ions) or quartz (for carbon) field blanks collected closest to the sampling month.

MDLs for data reported during the period of interest for this report (November 2015 through December 2016) are shown in Table 6. The percent of values reported above the MDL varies greatly among species.

Table 6: Average MDLs for all species, November 2015 through December 2016.

Species	**Average MDL, µg/m^3**	**% Above MDL**
Ag	0.019	1.4
Al	0.038	32.4
As	0.003	7.2
Ba	0.086	1.9
Br	0.005	17.7
Ca	0.027	65.1
Cd	0.024	0.7
Ce	0.116	0.9
Cl	0.005	42.9
Co	0.003	1.5
Cr	0.004	14.4
Cs	0.078	0.5
Cu	0.009	18.9
Fe	0.023	85.1
In	0.031	0.2
K	0.016	95.8
Mg	0.055	9.0
Mn	0.007	7.2
Na	0.070	27.3
Ni	0.002	11.1
P	0.002	9.9
Pb	0.015	4.7
Rb	0.008	1.1
S	0.009	99.4
Sb	0.047	1.1
Se	0.006	1.3
Si	0.015	90.3
Sn	0.046	0.9
Sr	0.007	2.7
Ti	0.003	45.8
V	0.002	5.5
Zn	0.004	78.0
Zr	0.037	0.9
Ammonium Ion	0.015	80.7
Chloride Ion	0.089	49.0
Nitrate Ion	0.095	89.7
Potassium Ion	0.008	90.5

Sodium Ion	0.043	53.2
Sulfate Ion	0.144	96.1
Elemental Carbon (1)	0.011	99.5
Elemental Carbon (2)	0.010	95.7
Elemental Carbon (3)	0.002	3.6
Elemental Carbon (TR)	0.017	99.1
Elemental Carbon (TT)	0.014	98.6
Organic Carbon (1)	0.024	60.6
Organic Carbon (2)	0.050	98.9
Organic Carbon (3)	0.151	94.8
Organic Carbon (4)	0.031	99.3
Organic Carbon (TR)	0.213	98.9
Organic Carbon (TT)	0.216	99.0
Organic Pyrolyzed (TR)	0.010	79.2
Organic Pyrolyzed (TT)	0.013	95.8

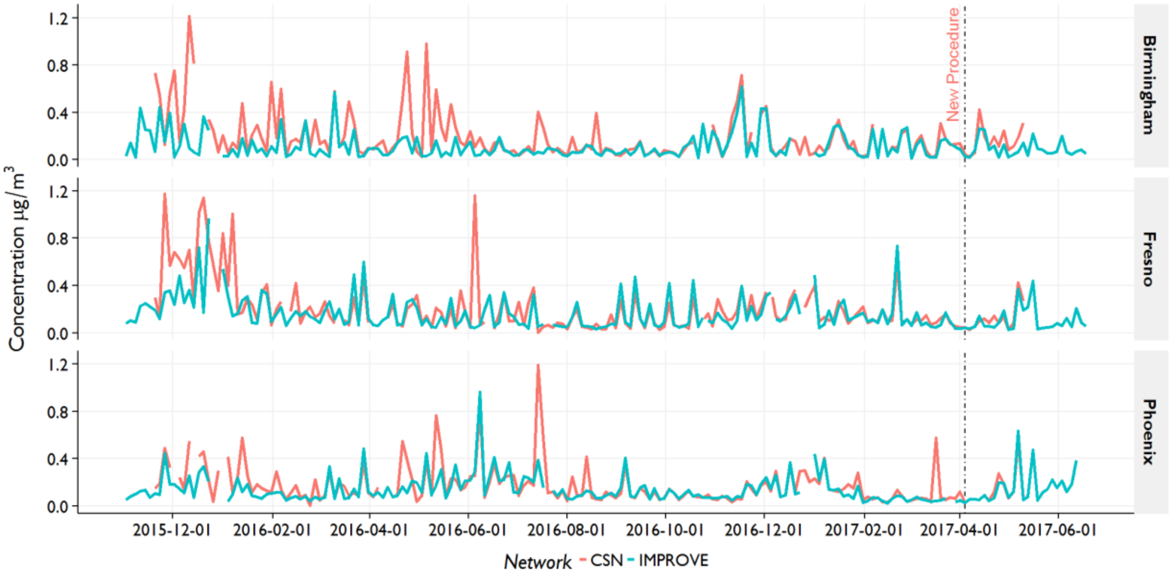
The method used for calculating MDLs has evolved as availability of field blanks has increased. Beginning in March 2017, field blank collection increased to one field blank per site per month, allowing for a more robust MDL calculation method. For data reported February 2017 onward, the MDL calculation is harmonized for all analysis pathways, calculated as 95th percentile minus median of field blanks, using 50 field blanks collected closest to the sampling month for each respective filter type. Future reports will include MDLs calculated using the updated method.

4. Reporting and Completeness

4.1 Chloride Contamination

Data reported November 2015 through December 2016 does not include chloride, which is collected on nylon filters and analyzed using IC. A chloride contamination issue was discovered in the network beginning in November 2015; the contamination was traced to cleaning wipes used in the filter handling lab. Shown in Figure 18, measurements at CSN sites collocated with IMPROVE network sites show high chloride attributed to contamination. The contamination issue appears to be resolved beginning August or September 2016, and the change in sample handling procedure effective April 2017 likely further reduced the chance of chloride contamination.

Figure 18: Chloride comparison as measured on filters collected from collocated CSN and IMPROVE network sites. The dotted line for 'New Procedure' designates a change in the CSN sample handling lab procedure.



4.2 Completeness

Completeness is evaluated network wide by filter type, and determined by the total number of valid samples relative to the total number of samples collected (Table 7). The completeness is comparable for PTFE and nylon filters which are both collected by the Met One SASS / Super SASS sampler; however, the number of invalid samples is higher for quartz filters, which are collected by the URG sampler.

Table 7: Network sample completeness by filter type, November 2015 through December 2016.

Filter Type	Total Number of Samples	Number of Valid Samples	Number of Invalid Samples	% Valid
PTFE	14,291	13,680	611	95.7
Nylon	14,288	13,671	617	95.7
Quartz	14,242	13,211	1,031	92.8

Across the network there were nine sites with sample completeness less than 75% for at least one filter type (Table 8). Seven of the nine cases had low completeness resulting from invalid quartz filters.

Table 8: Network sites with less than 75% sample completeness for at least one filter type, November 2015 through December 2016.

AQS ID #	Location	PTFE Completeness (%)	Nylon Completeness (%)	Quartz Completeness (%)
06-029-0014-6	Bakersfield, CA	93	93	32
48-113-0069-5	Hinton, TX	85	85	33
28-049-0020-5	Jackson, MS	98	98	51
20-209-0021-5	Kansas City, KS	91	91	58
37-067-0022-5	Winston-Salem, NC	92	91	67
45-079-0007-5	Parklane, SC	87	87	67
47-093-1020-5	Knoxville, TN	98	98	70
50-007-0012-5	Zampieri State, VT	73	79	96
06-073-1022-5	El Cajon, CA	74	76	90

Samples can be invalidated for a variety of reasons, as detailed in the *UCD CSN TI 801C, CSN Data Validation*, and the *Data Validation for the Chemical Speciation Network* guide. Null codes are applied to indicate reasons for invalidation (Table 9).

Table 9: SASS and URG sampler null codes applied, November 2015 through December 2016.

Null Code	SASS PTFE	SASS Nylon	URG Quartz	Null Code Description
AP	0	0	2	Vandalism
BK	0	0	10	Site computer/data logger down
AU	2	2	2	Monitoring Waived
AW	1	0	0	Wildlife Damage
AI	1	2	4	Insufficient Data (cannot calculate)
DA	2	2	3	Aberrant Data (Corrupt Files, Aberrant Chromatography, Spikes, Shifts)
BI	5	4	3	Lost or damaged in transit
BB	6	5	8	Unable to Reach Site
AK	6	4	6	Filter Leak
AM	21	2	4	Miscellaneous Void
AL	7	7	21	Voided by Operator
AJ	7	4	6	Filter Damage
SA	3	3	5	Storm Approaching
AQ	13	13	7	Collection Error
BE	10	10	14	Building/Site Repair
AR	19	19	17	Lab Error
BA	20	20	23	Maintenance/Routine Repairs
AG	14	16	23	Sample Time out of Limits
AS	23	23	26	Poor Quality Assurance Results
AH	32	36	83	Sample Flow Rate or CV out of Limits
AC	14	13	13	Construction/Repairs in Area
AB	43	41	50	Technician Unavailable
AO	20	17	15	Bad Weather

AV	53	51	54	Power Failure
AF	54	53	64	Scheduled but not Collected
BJ	64	57	49	Operator Error
AN	171	213	519	Machine Malfunction

4.3 Data Flagging Modifications

Data are flagged as part of the CSN data validation process as detailed in the *UCD CSN TI 801C, CSN Data Validation* and the *Data Validation for the Chemical Speciation Network* guide. Flags can be applied throughout the sampling, filter handling, and validation process, using automated checks or on a case-by-case basis. The use and application of flags evolves as problems are identified and remedied. The following flagging updates and modifications were made during the process of validating network data during the period of interest, November 2015 through December 2016.

4.3.1 Sample Flow and Volume Flags

The flow rate coefficient of variation (CV; calculated as the standard deviation of flow rates divided by the mean 24-hour flow rate) is used to evaluate flow rate stability, where a high flow CV may be indicative of sampler malfunction.

Upon heavy use of the AN and AH flags for flow CV out of limits (Table 9), UCD conducted an analysis to better understand the impact of expanding the acceptable range for the flow CV. Per direction from the EPA, the acceptable range for the SASS/Super Sass sampler was updated to include flow CV equal to or less than 5%; no changes were made to the range for the URG sampler (Table 10). Additionally, the SV flag was implemented for cases where the sample volume is outside of an acceptable range (Table 10). These changes became effective starting with August 2016 data.

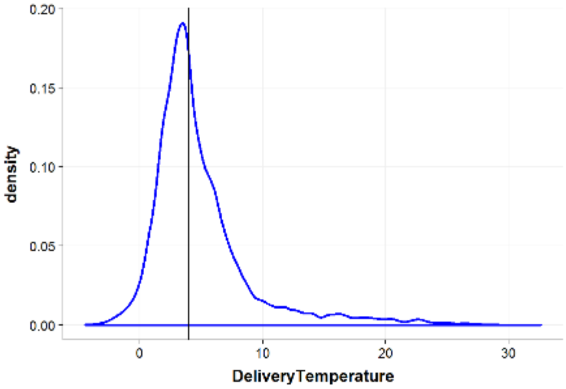
Table 10: Summary of AH and SV null flags. Flags are applied when data is outside of the specified range.

Flag	Definition	URG Acceptable Range	SASS/Super Sass Acceptable Range
AH	Sample flow rate, or CV out of limits	19.8 to 24.2 LPM (±10% of 22 LPM expected flow)	6.0 to 7.4 LPM (±10% of 6.7 LPM expected flow)
		0 to 2% flow CV	0 to 5% flow CV
SV	Sample volume out of limits	28.5 to 34.9 m^3 (±10% of 31.7 m^3 expected SV)	8.6 to 10.6 m^3 (±10% of 9.6 m^3 expected SV)

4.3.2 Transport Temperature Flag

Prevalence of the Transport Temperature (TT) qualifier flag across the network motivated investigation. Approximately, 43% of PTFE filters (typically also representative of other filter types) had the TT flag, indicating the filter temperature was above 4°C when received from the field by the sample handling lab. Evaluation of the overall distribution of the delivery temperature (Figure 19), suggested that most filters were received with temperature below 10°C. Communication with the EPA and the sample handling lab resulted in modification of shipping practices (change in number and type of ice packs), which resulted in a reduced number of TT flags.

Figure 19: Temperature distribution (°C) for samples received.



4.3.3 Ambient Pressure and Temperature Flags

The QP (pressure sensor questionable) and QT (temperature sensor questionable) flags are informational indicators of potential issues with the sensors, but are not thought to be indicative of issues that affect species concentrations.

The QP informational flag is applied when ambient pressure is outside of a designated range, which was initially defined as 710 to 810 mmHg when the flag was implemented beginning August 2016. Ambient pressure below 710 mmHg is often observed, particularly at high elevation sites, which resulted in heavy application of the QP informational flag. The median pressure for valid filters collected within the network was determined to be 665 mm Hg. The EPA revised the lower limit for the QP flag range (Table 11), with the change effective starting with December 2016 data.

The EPA implemented the QT (temperature sensor questionable) flag based on the sampler manufacturer guidelines (Table 11). This change became effective starting with the August 2016 data.

Table 11: Summary of QT and QP informational flags, where flags are applied when data is outside of the specified range.

Flag	Definition	Acceptable Range	Acceptable Range
QT	Temperature Sensor Questionable	-20 to 45 °C	-30 to 50 °C
QP	Pressure Sensor Questionable	600 to 810 mmHg	600 to 810 mmHg