

Appendix 1.2. Documentation of Changes in Analytical Methods and Data Processing Due to the Chemical Speciation Network (CSN) Contractor Changes in 2015

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This appendix includes a description of changes that occurred to the CSN that affects all sites and modules for filters collected November 2015 and later. This data advisory and other CSN documentation is available at <https://aqrc.ucdavis.edu/csn-documentation>.

1.2.1. OVERVIEW

During the first 15 years of the Chemical Speciation Network (CSN), RTI International (Research Triangle Park, NC) held the contract to perform filter shipping, handling, laboratory analysis, and data reporting, with the carbon analysis subcontracted to Desert Research Institute (DRI; Reno, NV) beginning in 2007. In November 2015, the laboratory analysis and data processing portion of the Environmental Protection Agency's (EPA) CSN contract was awarded to University of California, Davis (UCD; Davis, CA), with the ions and carbon analysis subcontracted to DRI. The filter shipping and handling was awarded separately to Wood PLC (Wood; Tallahassee, FL). Several data processing and analytical procedures changed corresponding with the change in CSN contractors in November 2015 or soon thereafter (Table 1.2.1).

This data advisory covers the following changes:

1. laboratory measurements;
2. filter blank corrections;
3. updated Method Detection Limit (MDL) calculations;
4. reporting of negative values;
5. PTFE filter sample deposit area; and
6. reporting chloride data.

Table 1.2.1 Summary of changes, ordered by effective sample date for each data stream.

| Data Stream | Type of Change | Effective Sample Date | See Section |
|-------------|---------------------------|-----------------------|-------------|
| Elements | Laboratory change | 2015-11-20 | 1.2.2.1 |
| Elements | Sample deposit area | 2016-01-01 | 1.2.6 |
| Elements | Blank correction | 2017-02-01 | 1.2.3.3 |
| Ions | Laboratory change | 2015-11-20 | 1.2.2.2 |
| Ions | Blank correction | 2016-01-01 | 1.2.3.1 |
| Ions | Reporting chloride | 2017-02-01 | 1.2.7 |
| Ions | Laboratory change | 2018-10-01 | 1.2.2.2 |
| Carbon | Blank correction | 2015-11-20 | 1.2.3.2 |
| Carbon | Laboratory change | 2016-01-01 | 1.2.2.3 |
| Carbon | Laboratory change | 2018-10-01 | 1.2.2.3 |
| All | MDL calculation | 2015-11-20 | 1.2.4 |
| All | Reporting negative values | 2015-11-20 | 1.2.5 |

| | | | |
|-----|-----------------|------------|-------|
| All | MDL calculation | 2017-01-01 | 1.2.4 |
|-----|-----------------|------------|-------|

1.2.2. LABORATORY CHANGES

1.2.2.1 Element measurements

Beginning with PTFE filter samples collected November 20, 2015, CSN elemental analysis is performed by UCD using PANalytical Epsilon 5 energy dispersive X-ray fluorescence analyzers.

1.2.2.2 Ion measurements

Beginning with nylon filter samples collected November 20, 2015, ions were analyzed by DRI using the Thermo Scientific Dionex ICS-5000+ Ion Chromatography System. Starting with nylon filter samples collected October 1, 2018, CSN ion analysis is performed by RTI International using Thermo Scientific Dionex Ion Chromatography Systems and Thermo Scientific Dionex Aquion Ion Chromatography Systems.

1.2.2.3 Carbon measurements

Beginning with quartz filter samples collected January 1, 2016, DRI transitioned from using the DRI Model 2001 to the DRI Model 2015 TOA analyzers. See data advisory “Carbon Analyzer Signal Integration Threshold Modified” available at <https://www.epa.gov/amtic/chemical-speciation-network-data-reporting-and-validation> for more details. Starting with quartz filter samples collected October 1, 2018, CSN carbon analysis is performed using Sunset Laboratory model 5L analyzers at UCD. Both labs use the IMPROVE_A TOR protocol. For more details see data advisory “Carbon Analyzer Change” at <https://www.epa.gov/amtic/chemical-speciation-network-data-reporting-and-validation>.

1.2.3. FILTER BLANK CORRECTIONS FOR IONS, CARBON, AND ELEMENTS

Concentration data for ions and carbon are now reported with blank corrections, also referred to as artifact corrections, to account for filter media content and positive sampling artifacts. Measurements are not corrected for negative artifacts. Prior to November 20, 2015, only elements were corrected (RTI International QAPP, 2014).

1.2.3.1 Ions blank correction

Blank correction of ion data began with samples collected in January 2016; ion measurements are corrected for each species using a median value of all nylon field blanks from the corresponding sample month. The ratio of corrected-to-uncorrected ion data for valid 2016–2020 ions data above the MDL is shown in Figure 1.2.1. The blank correction magnitudes are species specific; the corrected-to-uncorrected ratio for nearly all of the ammonium, nitrate, potassium ion, and sulfate measurements are above 0.95. Chloride and sodium ion are more often subject to a larger blank correction.

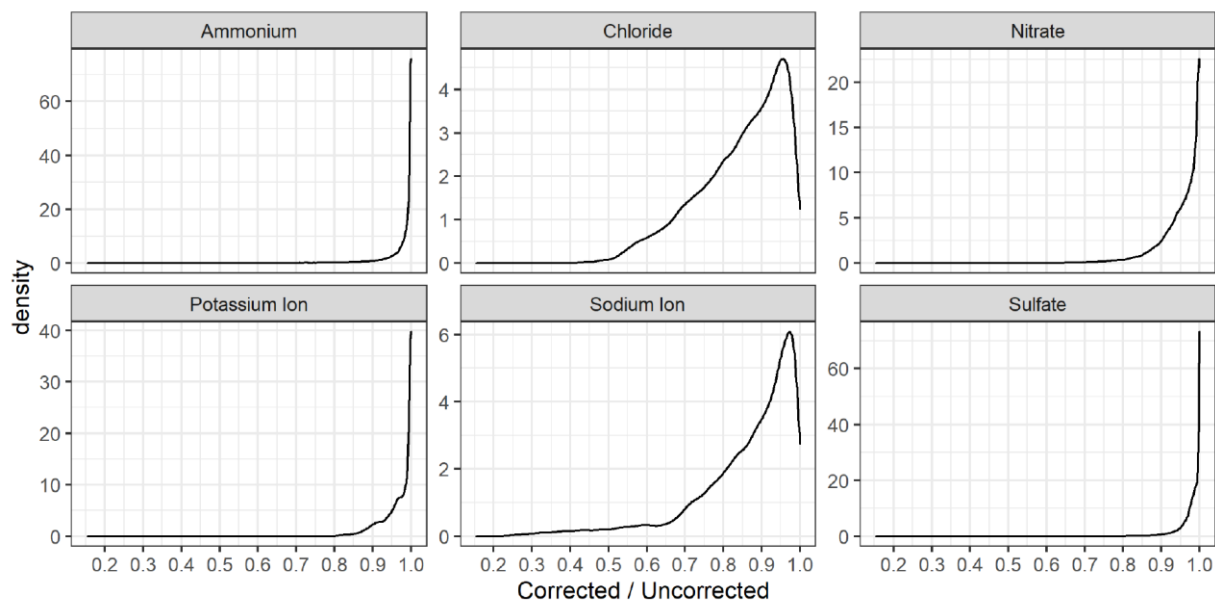


Figure 1.2.1. Density of corrected-to-uncorrected concentration ratios for each of the ion species for all valid 2016-2020 ions data above their respective MDLs.

1.2.3.2 Carbon blank correction

Blank correction of carbon sample data began with filters collected in November 2015 to be harmonized with the Interagency Monitoring of Protected Visual Environments (IMPROVE) network (see memorandum available at <https://www.regulations.gov/document/EPA-HQ-OAR-2007-0492-0364> and the presentation “Recent Changes to the IMPROVE and CSN Organic Carbon Artifact Adjustment Method” available at <https://www.epa.gov/amtic/chemical-speciation-2016-naamc>). During sample collection, the pre-fired quartz-fiber sampling media required for thermal evolution analysis adsorb and retain some amount of organic species from the vapor phase, which the subsequent analysis conflates with the particulate carbon concentration. Each reported thermal subfraction is corrected for this artifact by using the corresponding median value from all quartz field blanks during the sample month. For all valid 2016–2020 data above the MDL the ratio of corrected over uncorrected data ranges from 0.57 to 1.0, with a mode of about 0.95 (Figure 1.2.2). The blank correction has negligible effect on elemental carbon as zero elemental carbon is measured on most blanks, and an occasional small effect on pyrolyzed carbon (OPTR and OPTT). Note that, unlike elements and ions, both corrected and uncorrected carbon data are reported to EPA’s Air Quality System (AQS) (Table 1.2.2). The uncorrected carbon data continue to be reported as they have been previously and the corrected carbon data are reported as new parameters for CSN.

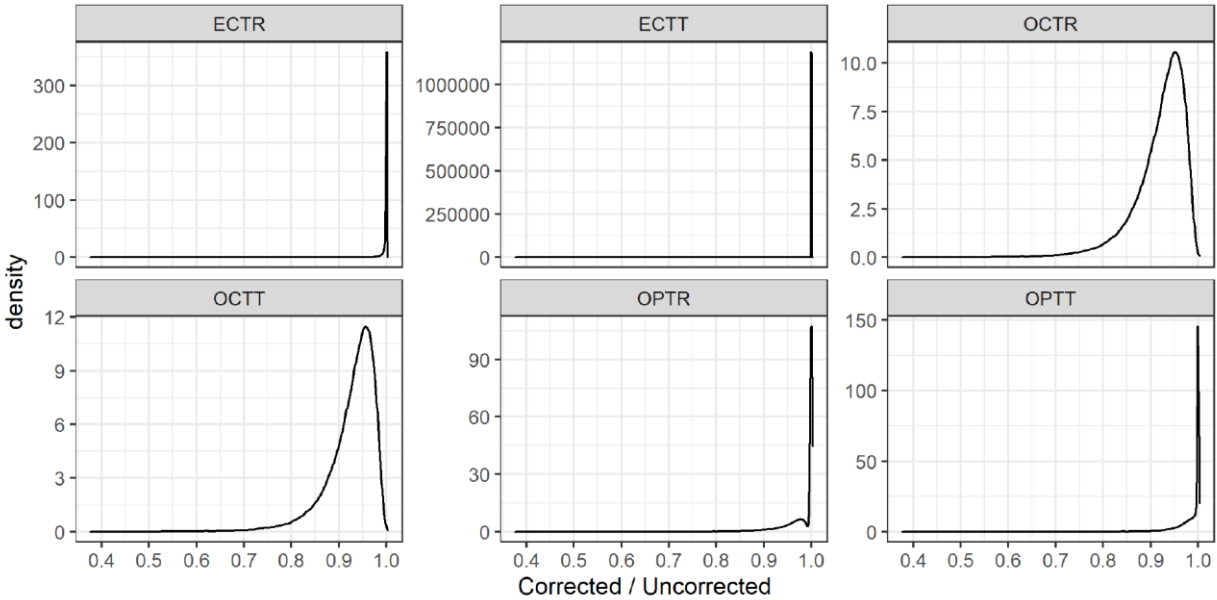


Figure 1.2.2. Density of corrected to uncorrected concentration ratios for all valid 2016-2020 carbon data above their respective MDLs.

Table 1.2.2. AQS names and codes for reported unadjusted and corrected carbon parameters.

| AQS Parameter Name | AQS Parameter Code |
|----------------------------|--------------------|
| EC1 PM2.5 LC | 88329 |
| EC1 CSN Unadj. PM2.5 LC | 88383 |
| EC2 PM2.5 LC | 88330 |
| EC2 CSN Unadj. PM2.5 LC | 88384 |
| EC3 PM2.5 LC | 88331 |
| EC3 CSN Unadj. PM2.5 LC | 88385 |
| EC PM2.5 LC TOR | 88321 |
| EC CSN Unadj. PM2.5 LC TOR | 88380 |
| EC PM2.5 LC TOT | 88381 |
| EC CSN Unadj. PM2.5 LC TOT | 88357 |
| OC1 PM2.5 LC | 88324 |
| OC1 CSN Unadj. PM2.5 LC | 88374 |
| OC2 PM2.5 LC | 88325 |
| OC2 CSN Unadj. PM2.5 LC | 88375 |
| OC3 PM2.5 LC | 88326 |
| OC3 CSN Unadj. PM2.5 LC | 88376 |
| OC4 PM2.5 LC | 88327 |
| OC4 CSN Unadj. PM2.5 LC | 88377 |
| OC PM2.5 LC TOR | 88320 |
| OC CSN Unadj. PM2.5 LC TOR | 88370 |
| OC PM2.5 LC TOT | 88382 |
| OC CSN Unadj. PM2.5 LC TOT | 88355 |
| OP PM2.5 LC TOR | 88328 |
| OP CSN Unadj. PM2.5 LC TOR | 88378 |

| AQS Parameter Name | AQS Parameter Code |
|----------------------------|---------------------------|
| OP PM2.5 LC TOT | 88379 |
| OP CSN Unadj. PM2.5 LC TOT | 88388 |

1.2.3.3 Elements blank correction

For PTFE filters collected prior to November 20, 2015, elemental data were corrected for filter lot-specific background levels (RTI International QAPP, 2014). For PTFE filters collected between November 20, 2015 and January 31, 2017, elemental measurements were corrected for each species using the laboratory filter blank median areal density from each manufacturer filter lot. Beginning with Teflon filter samples collected February 2017, the elemental blank correction was changed to use the median of field blanks to be in harmony with the blank correction used for other filter types.

1.2.4. UPDATED METHOD DETECTION LIMIT (MDL) CALCULATIONS

Prior to November 20, 2015, MDLs were typically calculated as three times the standard deviation of seven or more replicate measurements of a reagent blank, matrix blank, or low-level calibration standard (RTI International QAPP, 2014). This approach only characterized detection limits of the analytical methods in the laboratory, independent of contamination or other artifacts associated with sampling in the field. Since March 2017, MDLs are based on the observed concentration distributions of field blanks calculated and delivered for each species every month. The new approach attempts to characterize the detection limits of the overall network measurement system in the field as well as in the laboratory.

Between November 2015 and February 2017, the number of field blanks collected per month was highly variable. During this period of sometimes-limited number of field blanks, MDLs for elemental species were calculated as three times the standard deviation of lab blanks and were recalculated for each PTFE manufacturer filter lot. MDLs for ion and carbon species were calculated monthly as three times the standard deviation of field blanks using 50 field blanks for each filter type collected both during and closest to the sampling month. Field blank allocations were then increased, beginning with PTFE and nylon filter samples from March 2017 and quartz filter samples from May 2017, to collect approximately one field blank per filter type at each site per month.

More frequent field blank collection allows for more robust blank correction and MDL calculation methods. There are occasional cases of field blanks with unexpected heavy loadings; though there is often insufficient evidence to invalidate, these filters may have been collected with flow thus are not representative of true field blanks. To address occasional instances of heavily loaded field blanks, which produce standard deviations unrepresentative of the network’s analytical capabilities, the MDL calculation for CSN species was updated beginning with February 2017 filters. With field blank collection frequency increased, the percentile calculation method has been employed across all filter types (equation 1.2.1):

$$\text{MDL} = 95^{\text{th}} \text{ percentile} - \text{median} \quad (1.2.1)$$

determined from field blanks for each filter type using 50 field blanks collected during or closest to the sampling month. This method is more robust to outliers and makes the reported MDL values more consistent month-to-month.

Figure 1.2.3 compares the median reported MDLs for each species for three time periods: (1) prior to November 2015, (2) the initial calculation method used following the contract transition (November 2015 through January 2017), and (3) the harmonized percentile-based calculation method (beginning February 2017). For most species, the reported MDL increased beginning November 2015, with the largest changes observed for sodium, magnesium, sulfate, and organic carbon, and smaller or negligible changes observed for sulfur, potassium, and elemental carbon. For most species there was a small change in the reported MDL during the February 2017 calculation method update, except for sodium ion and potassium ion which had lower reported MDLs. These are likely more representative of the detection limits of the network than previous calculated MDLs.

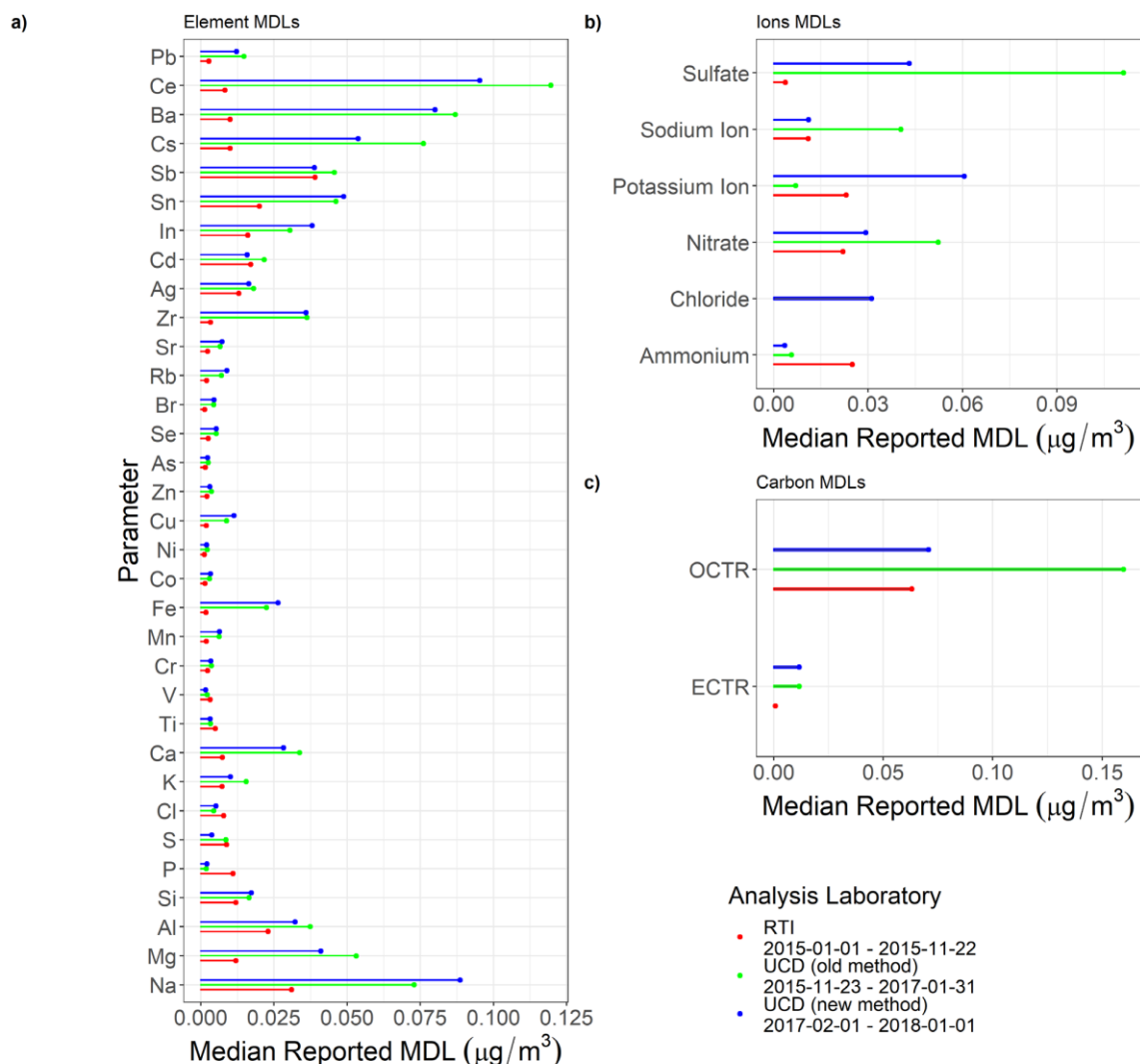


Figure 1.2.3. Median MDLs for a) elements, b) ions, and c) carbon species for three time periods with different MDL calculation methods: (1) January 1, 2015 through November 22, 2015, where RTI

International was the contractor, red points; (2) November 23, 2015 through January 31, 2017, where UCD was the contractor and the standard deviation method was used for MDL calculation, green points; and, (3) February 1, 2017 through January 1, 2018, where UCD was the contractor and the percentile method was used for MDL calculation, blue points.

1.2.5. NEGATIVE VALUES REPORTED

As sample filters are exposed to particles during manufacturing, shipping, and handling, the total amount of a species collected on a filter is a combination of both contamination and the aerosol sample. To estimate the true value of the collected sample in the field, blank corrections are performed, with some resulting measurement values being below zero. Censoring data by eliminating it or through data substitution can bias statistics.

For filter samples collected from CSN's inception in 2000 to November 2015, when RTI International held the laboratory analysis and data validation portion of the contract, data were reported without negative values; negative values were replaced with zeros and data flagged with a '9 – Negative value detected – zero reported' qualifier code. Beginning with filters collected from November 20, 2015, when UCD was awarded the analysis and validation contract, negative values are reported without substitution or flagging.

1.2.6. PTFE FILTER SAMPLE DEPOSIT AREA CHANGE

For samples collected from January 1, 2016, onwards, the sample deposit area estimation was increased from 11.3 cm² to 11.86 cm² to correspond with the EPA Code of Federal Regulations (US CFR). The filter sample deposit area is used in calculations for species concentrations as follows (equation 1.2.2):

$$\text{Concentration} = ((\text{Areal Density} \times \text{Sample Deposit Area}) - \text{Artifact}) / \text{Sample Volume} \quad (1.2.2)$$

This change in sample deposit area results in a 4.96% (11.86/11.3) increase in elemental concentrations reported.

1.2.7. REPORTING CHLORIDE DATA

Prior to UCD operation of CSN, chloride, which is collected on nylon filters and analyzed using IC, was not reported. 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 laboratory. Following resolution of the issue, chloride data were reported to AQS beginning with data from samples collected during February 2017. For more details, see the UC Davis Chemical Speciation Network 2016 Annual Data Quality Report (available at <https://www.epa.gov/amtic/chemical-speciation-network-data-reporting-and-validation>).

1.2.8. SUMMARY OF CHANGES AND ASSOCIATED IMPACTS

Analytical methods and data processing changes corresponding with the November 2015 contractor change led to an increase in reported elemental concentrations and a decrease in reported ions concentrations due to a change in assumed sample deposit area and implementation of blank corrections. Updates to the MDL calculation methods had minimal changes to reported

values but are now less susceptible to data outliers and more representative of the analytical capabilities. Further, the inclusion of negative values has reduced data biases.

REFERENCES

RTI International, Quality Assurance Project Plan (QAPP). Chemical Speciation of PM_{2.5} Filter Samples, available upon request from the EPA, 2014.

US CFR. Code of Federal Regulations Title 40: Protection of Environment, Part 50 – National Primary and Secondary Ambient Air Quality Standards, Appendix L to Part 50 – Reference Method for the Determination of Fine Particulate Matter as PM_{2.5} in the Atmosphere, Figures L-27 to L-29, available at <https://www.ecfr.gov/current/title-40/chapter-I/subchapter-C/part-50#Appendix-L-to-Part-50>, (last accessed September 17, 2021).