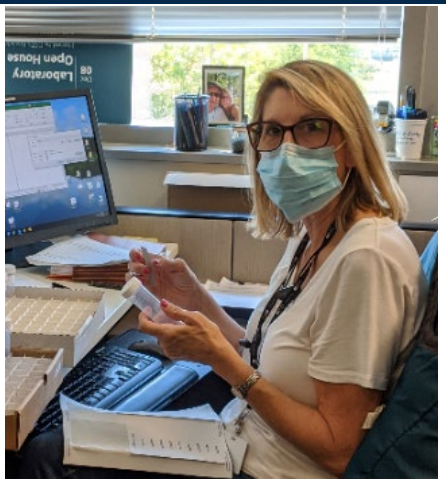
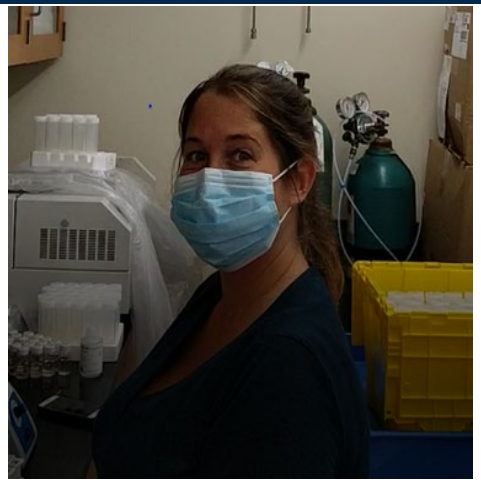
IMPROVE Steering Committee Meeting

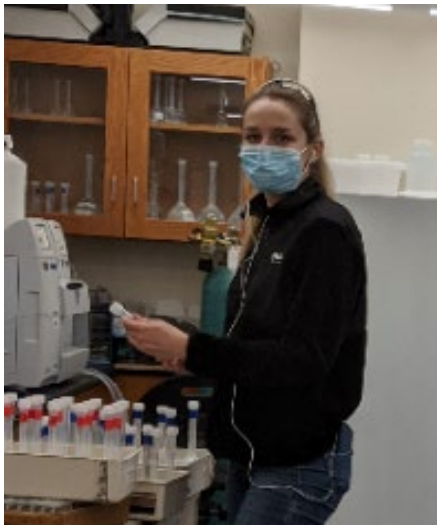
Virtual 2020

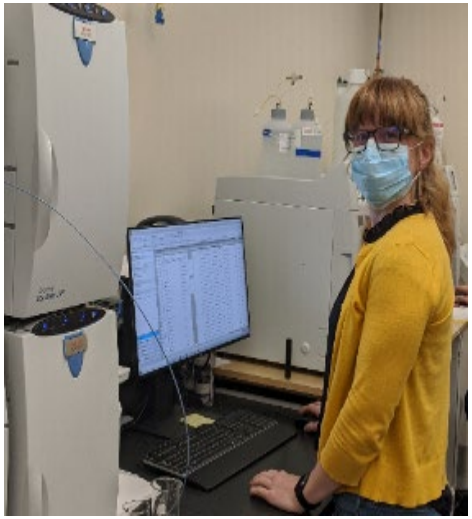
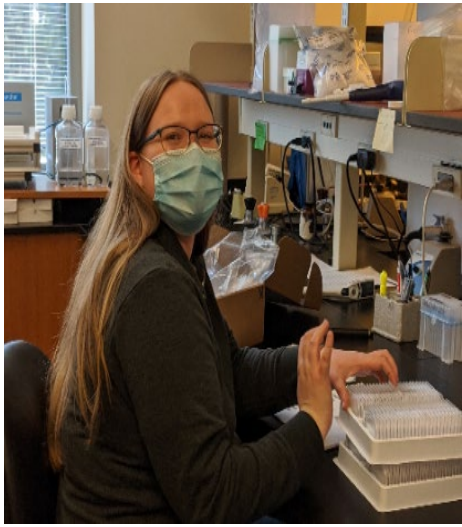
Tracy Dombek, Ions Report

RTI International





Minimum Detection Limits & Process

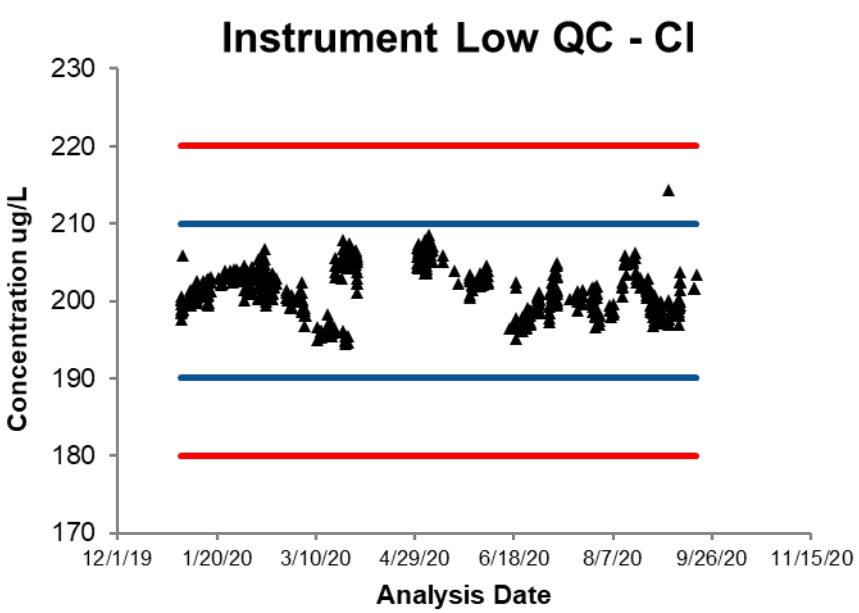
- Extract nylon filters in 20 mL of DI water.
- Calibrate systems daily using primary stock standards.
- Quality Controls using secondary source standards before and after every ten samples analyzed.
- Duplicates at a rate of 3 per batch of 50 samples.
- Perform matrix spikes at a rate of 2 per batch of 50 samples.
- Random reanalysis of 5% of the sample total.
- Re-extraction of filters to evaluate extraction efficiencies.

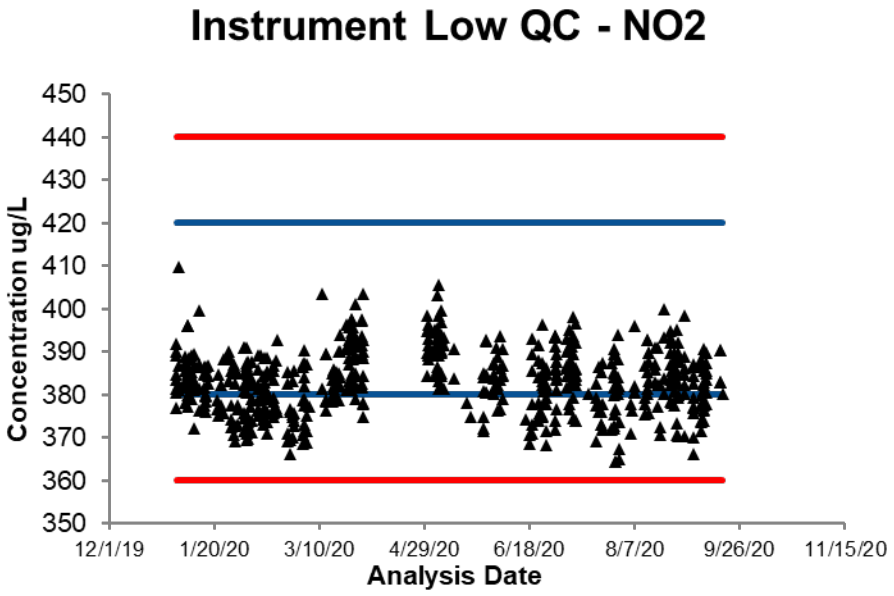
	Chloride	Nitrite	Nitrate	Sulfate
2020	0.005 ppm	0.010 ppm	0.008 ppm	0.011 ppm

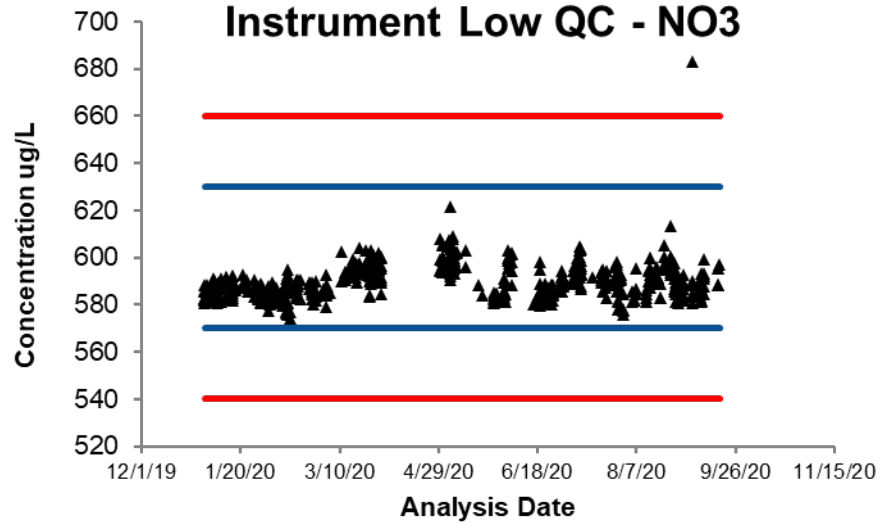
Quality Control Standards

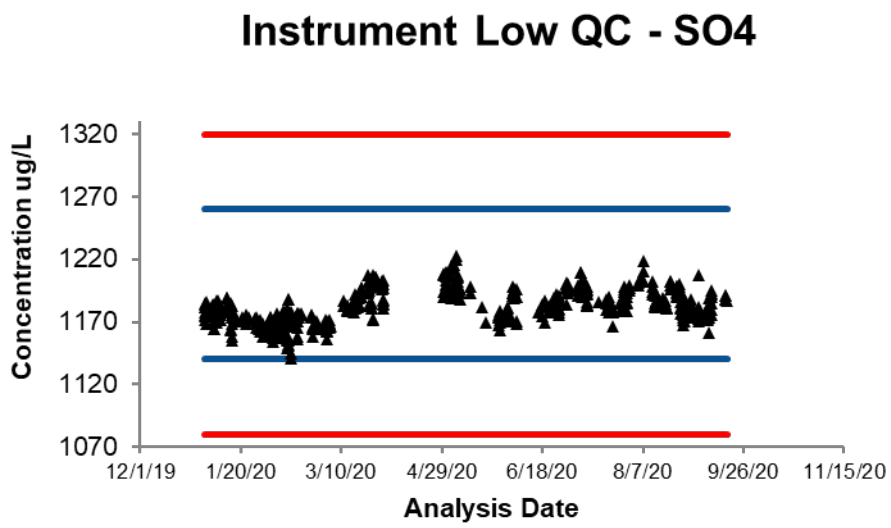
	Average Recovery Chloride	Average Recovery Nitrite	Average Recovery Nitrate	Average Recovery Sulfate
QC-Low n= 652	101%	95.9%	98.3%	98.6%
QC-Med n=1024	101%	97.8%	98.8%	98.9%
QC-Med-HI n=598	101%	99.3%	99.4%	99.2%
QC-High n-= 315	102%	101%	99.7%	100%

Instrument Control Charts

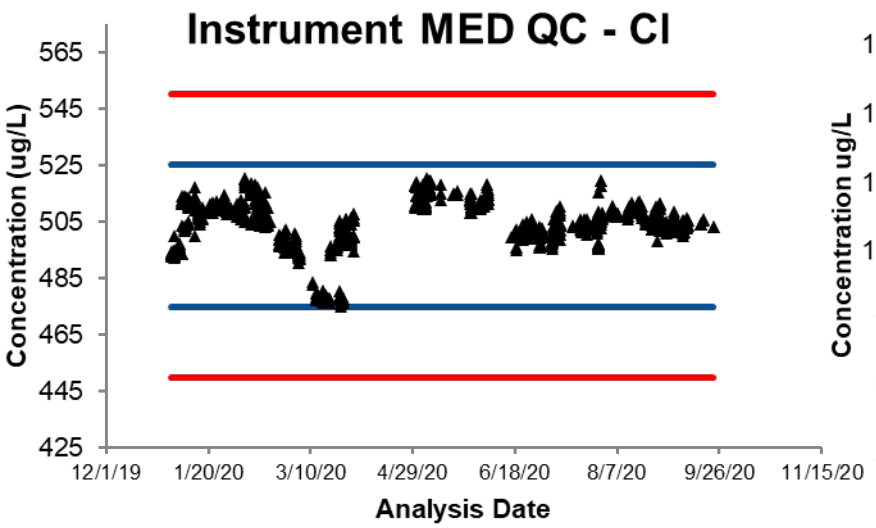


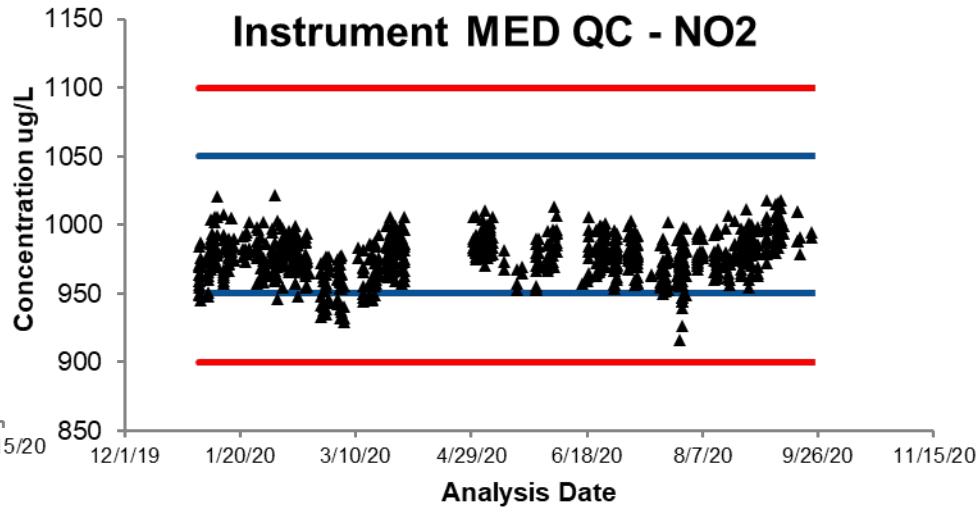


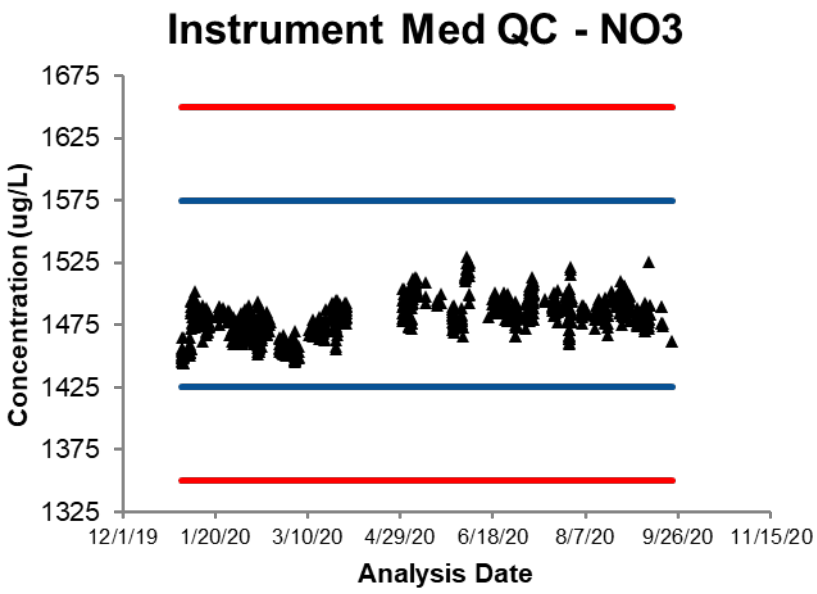


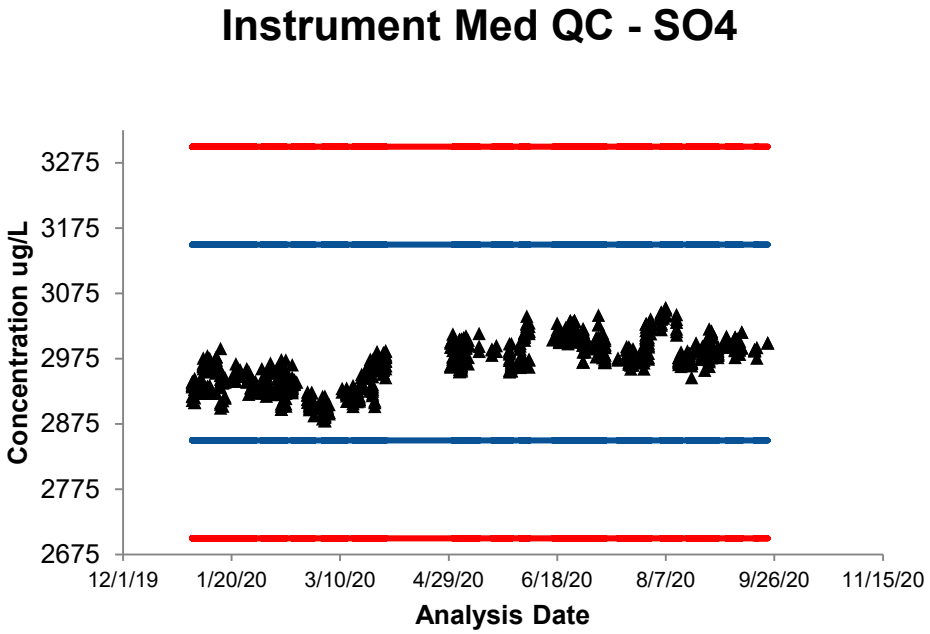


Instrument Control Charts

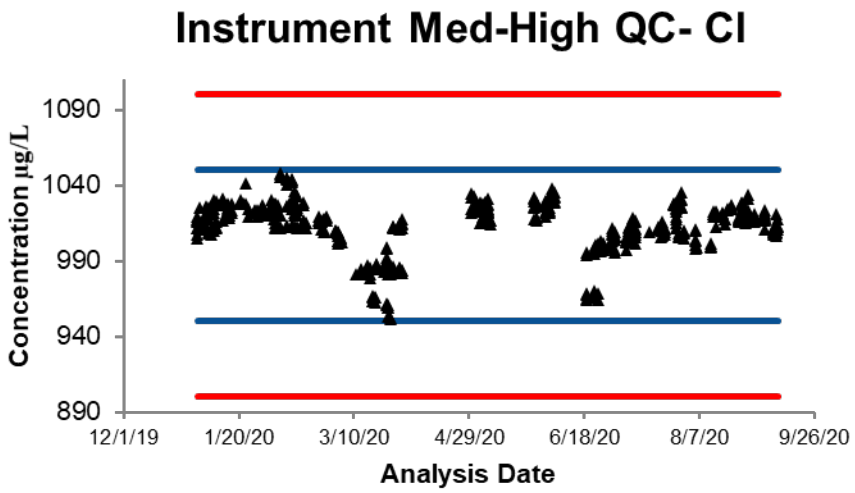


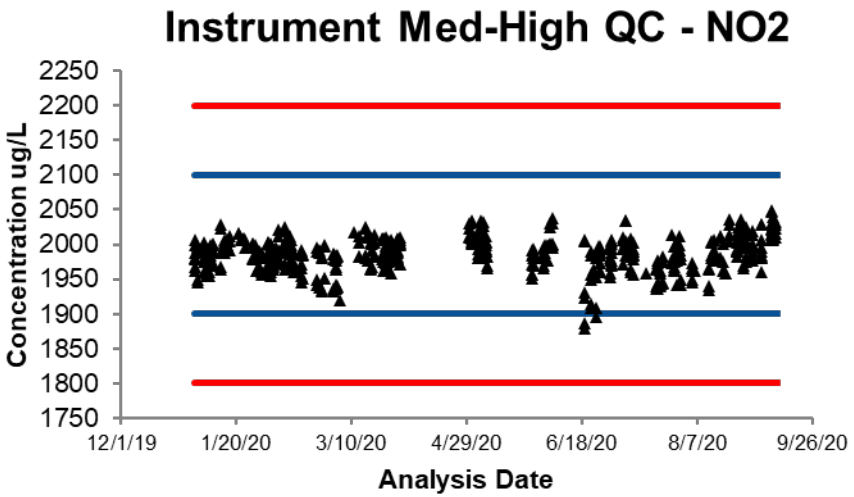


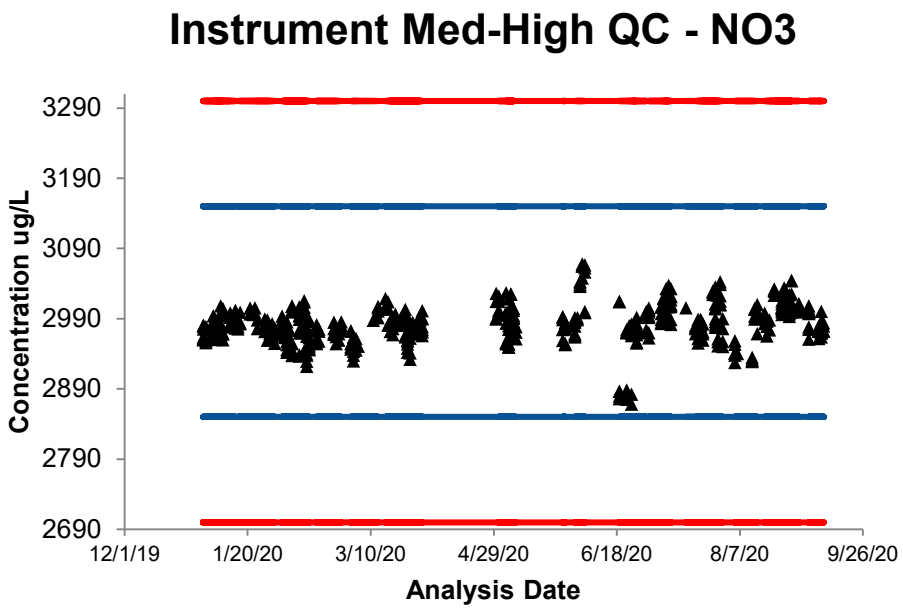


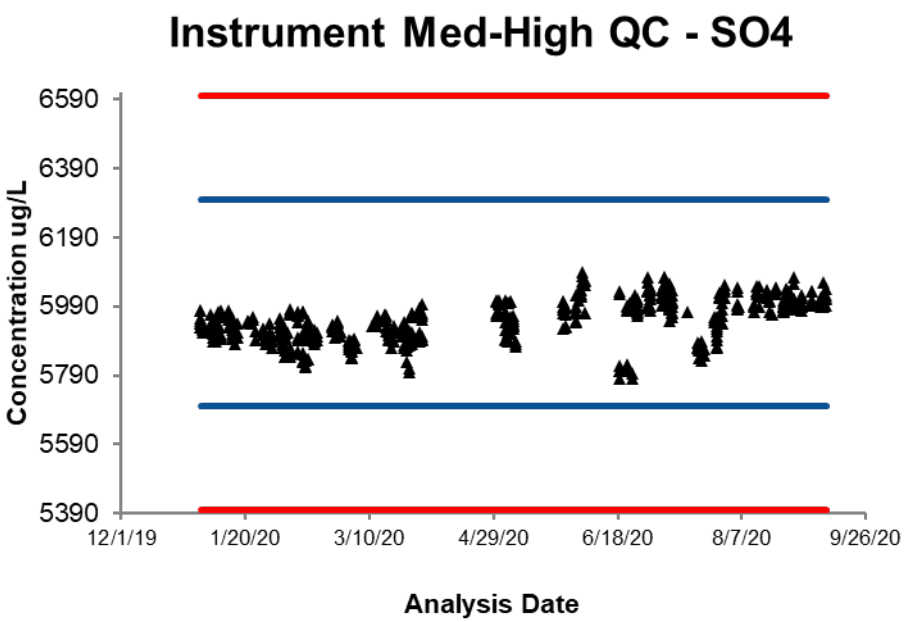


Instrument Control Charts

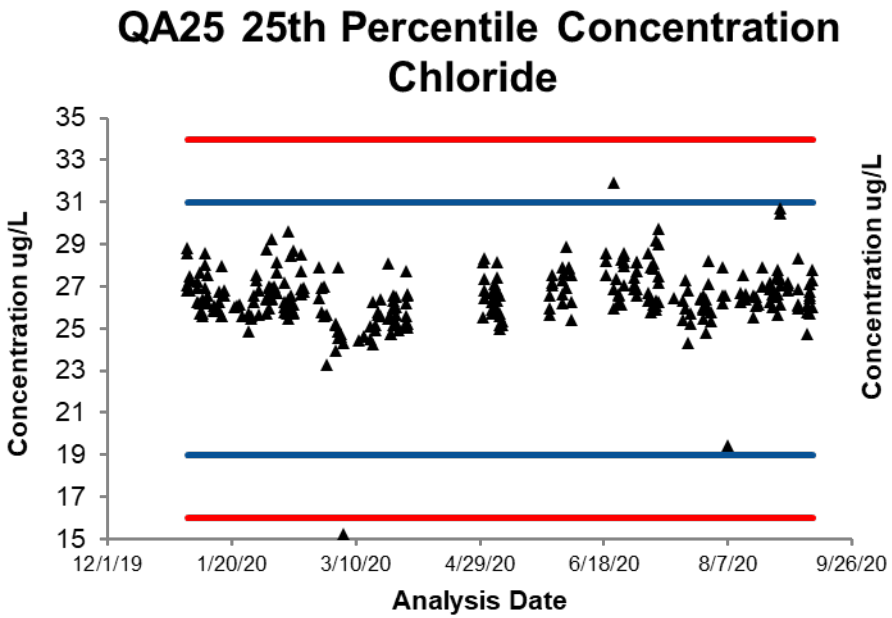


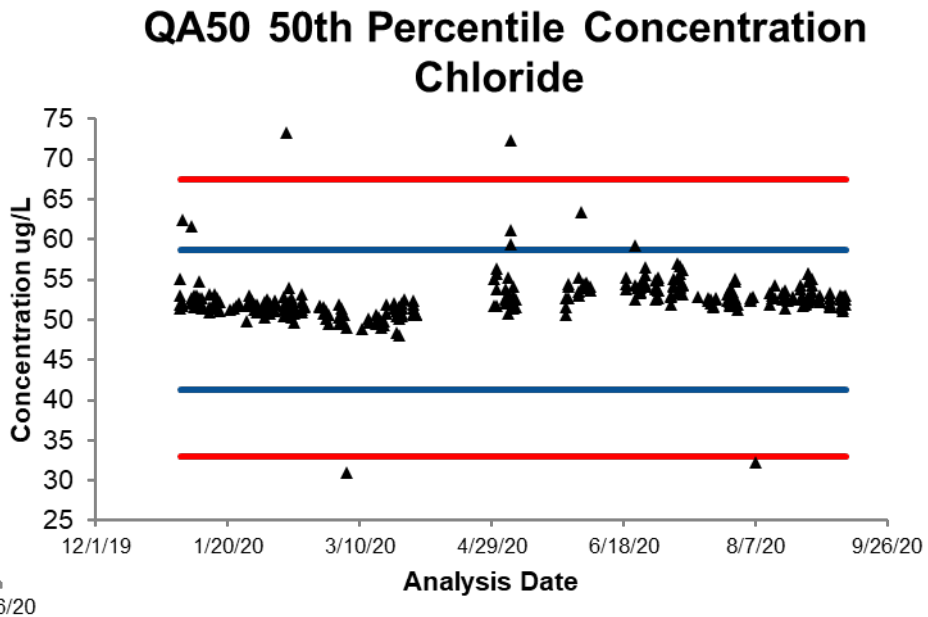






25th, 50th,& 75th Percentile Chloride



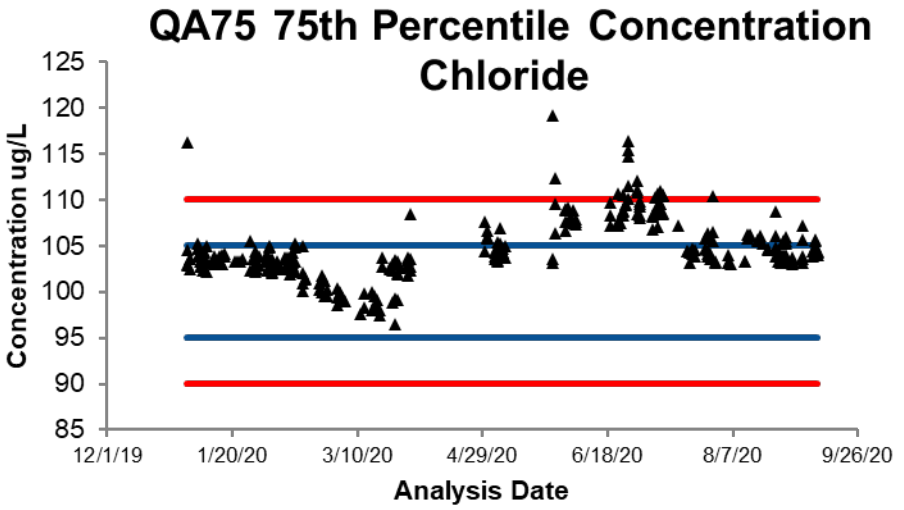


Approximate Air Concentrations

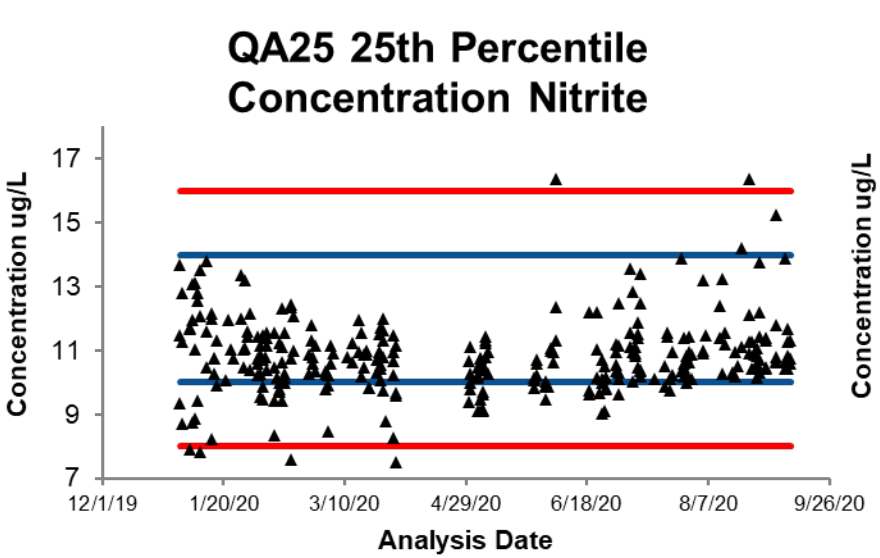
25th Chloride - 0.016 ug/m^3

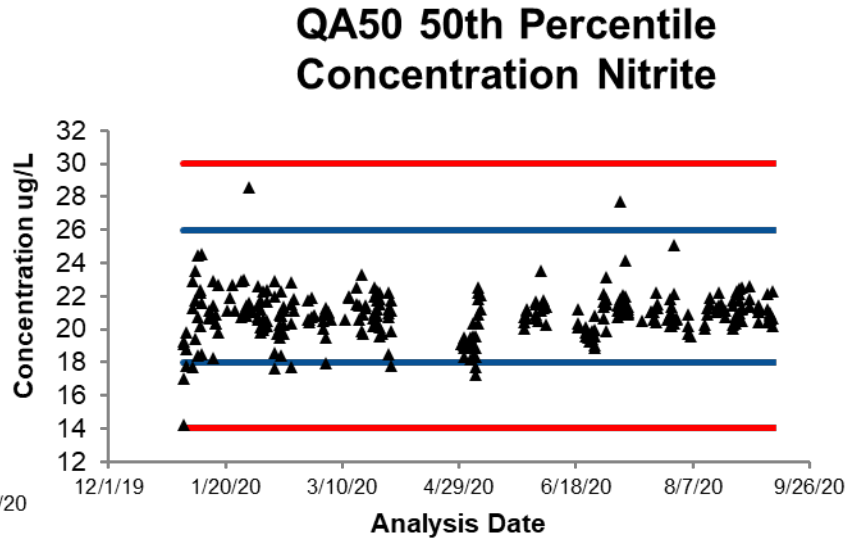
50th Chloride – 0.031 ug/m^3

75th Chloride - 0.061 ug/m^3



25th , 50th , & 75th Percentile Nitrite



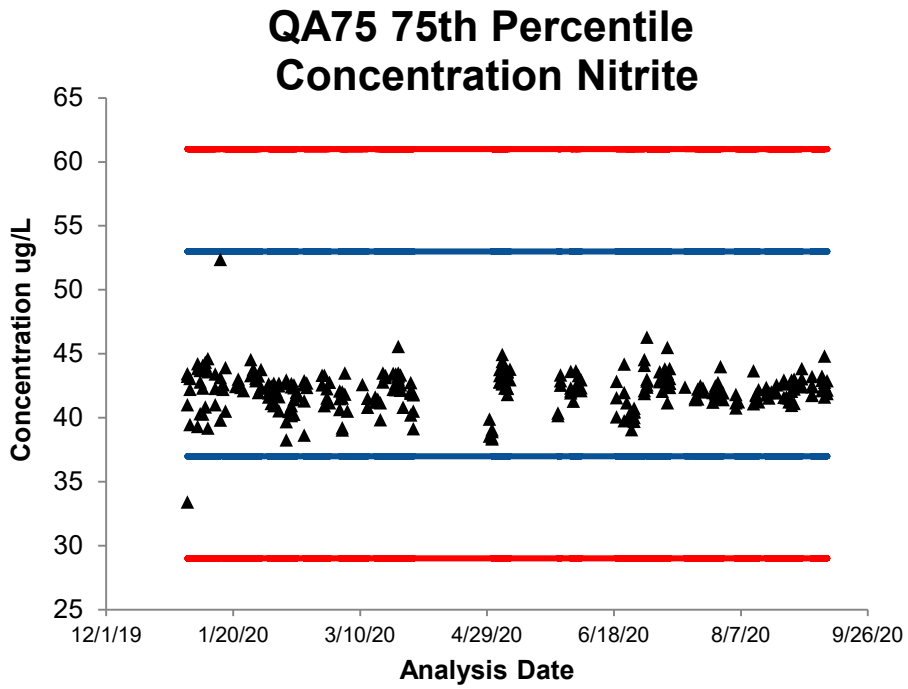


Approximate Air Concentration

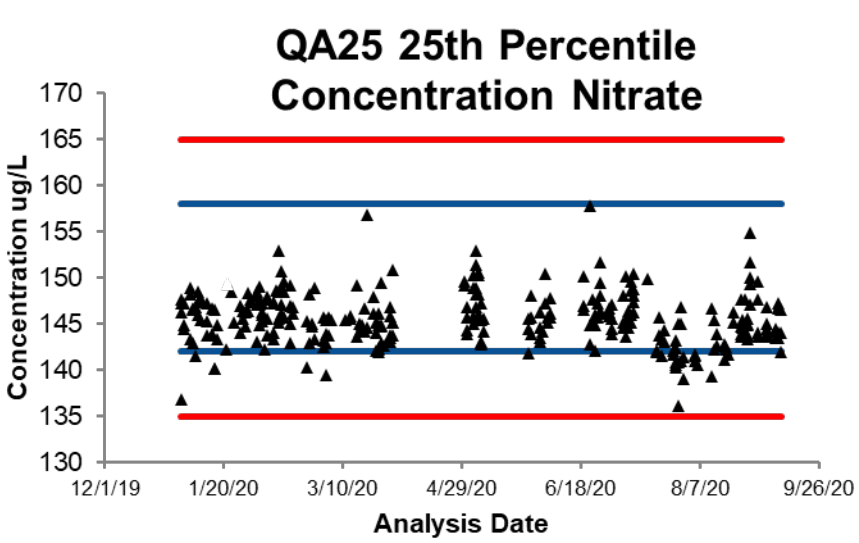
25th Nitrite – 0.007 ug/m3

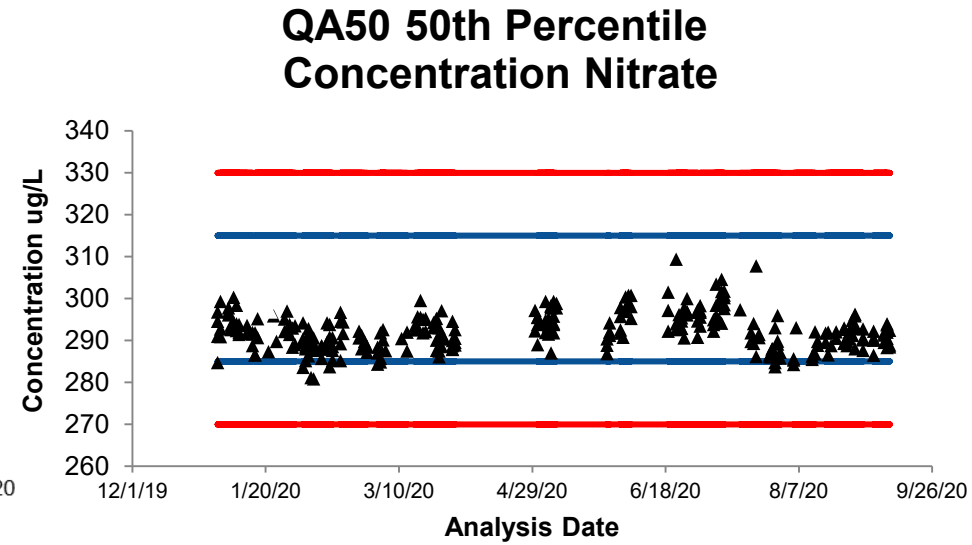
50th Nitrite – 0.013 ug/m3

75th Nitrite – 0.026 ug/m3



25th, 50th , & 75th Percentile Nitrate



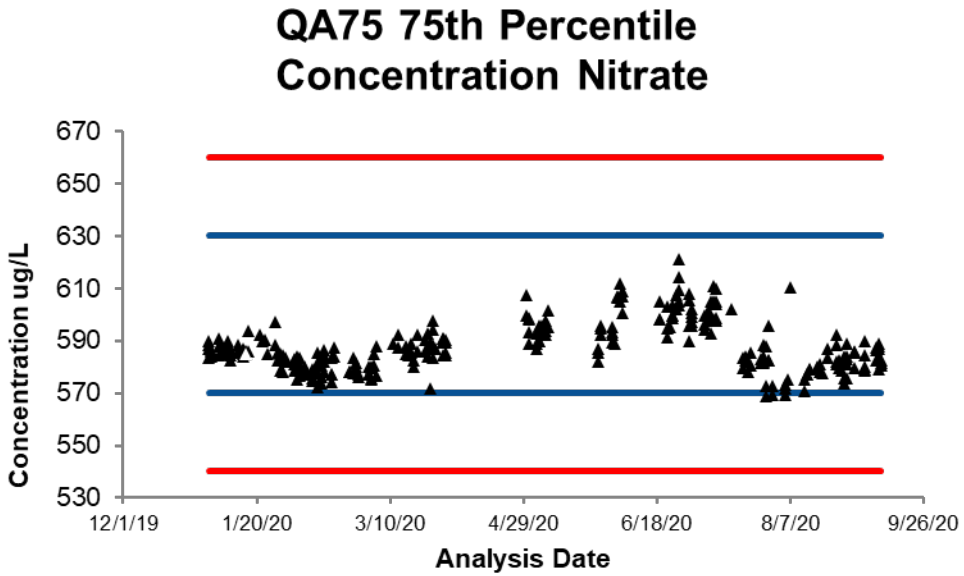


Approximate Air Concentration

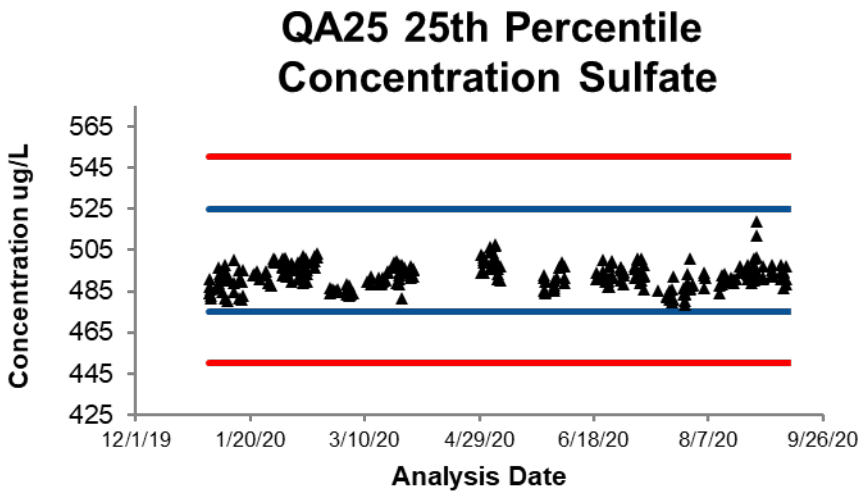
25th Nitrate – 0.092 ug/m^3

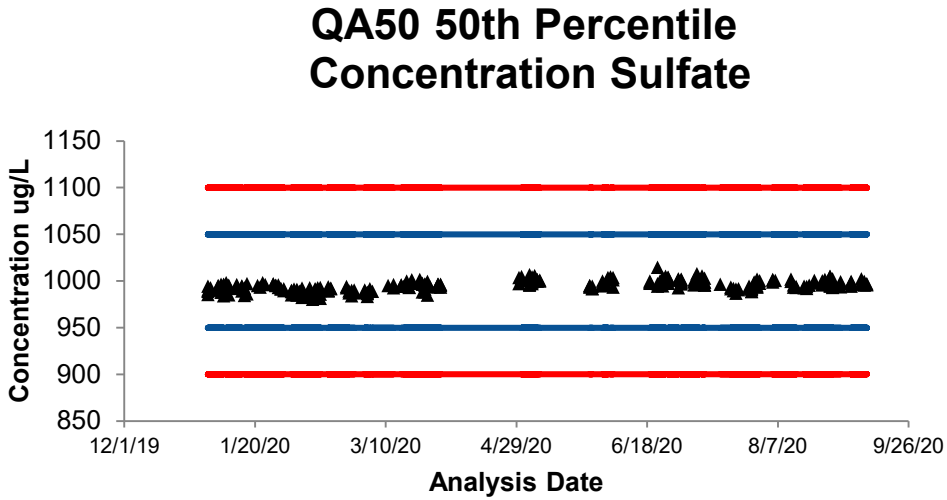
50th Nitrate – 0.18 ug/m^3

75th Nitrate – 0.36 ug/m^3



25th, 50th, & 75th Percentile Sulfate



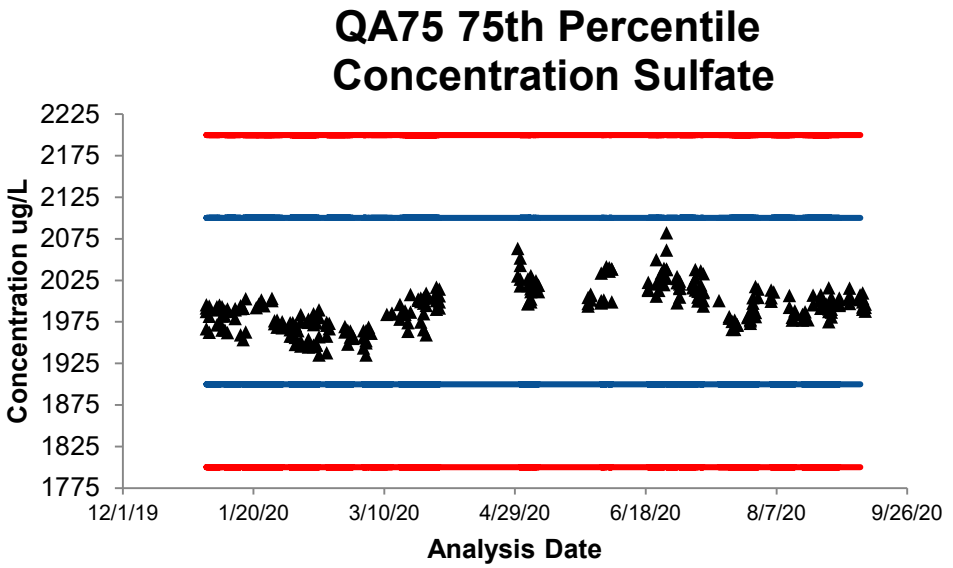


Approximate Air Concentration

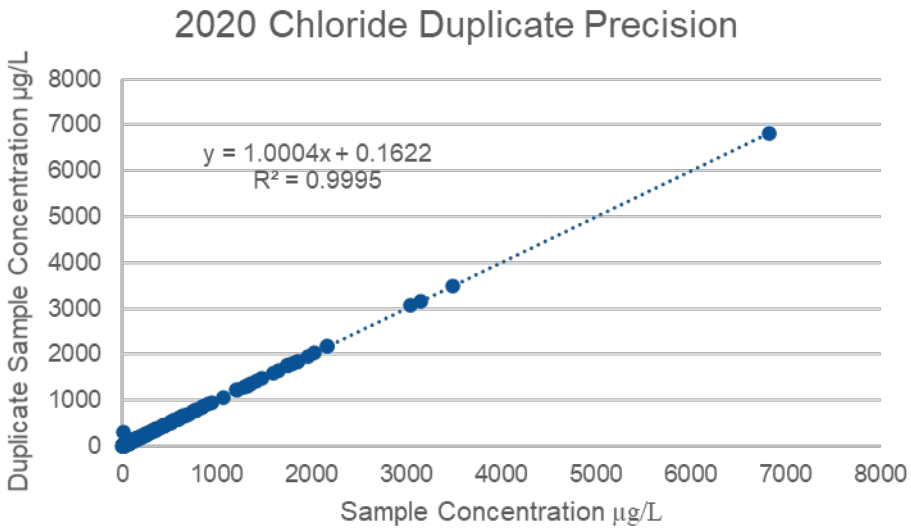
25th Sulfate – 0.30 ug/m3

50th Sulfate – 0.60 ug/m3

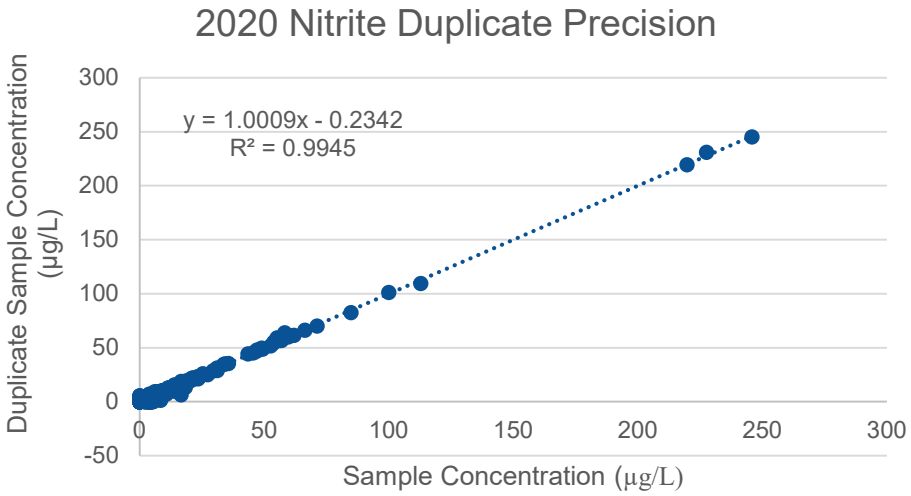
75th Sulfate – 1.2 ug/m3



Duplicate Precision

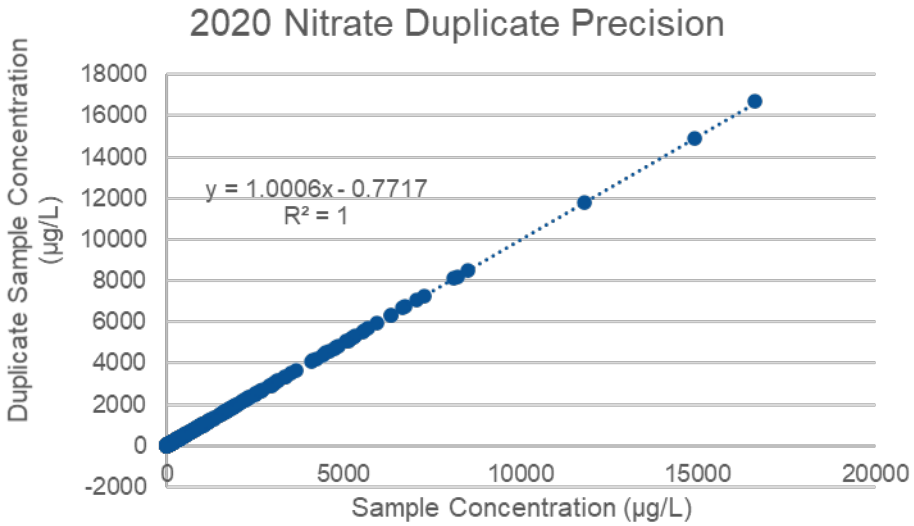


Chloride Percent Differences
Average = 0.44%
Median = 0%
Maximum = 41.0%
Minimum = -175.%
Count = 838
Failures 0.002%

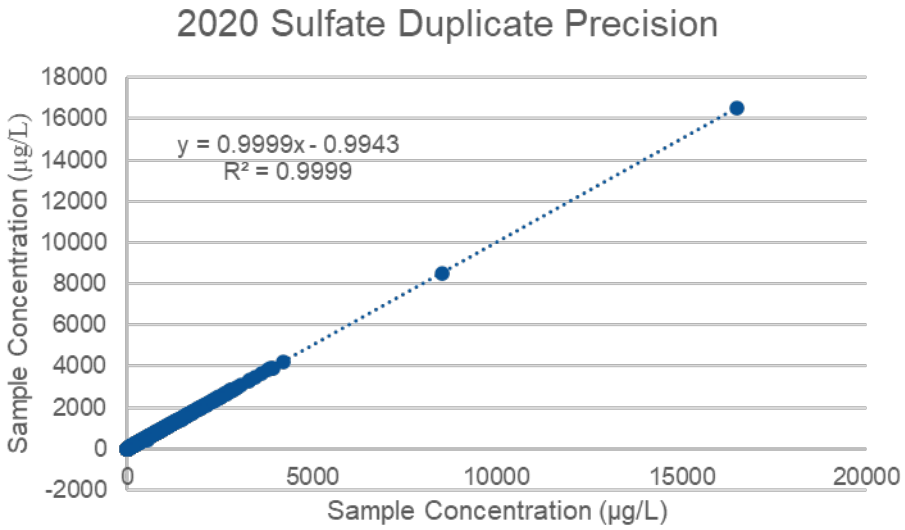


Nitrite Percent Differences
Average = 6.73%
Median = 0%
Maximum = 200%
Minimum = -200 %
Count = 838
Failures 0%

Duplicate Precision



Nitrate Percent Differences
Average = 0.32%
Median = 0.08%
Maximum = 200%
Minimum = -200 %
Count = 838
Failures 0.002%



Sulfate Percent Differences
Average = 1.50%
Median = 0.03%
Maximum = 200%
Minimum = -200%
Count = 838
Failures 0.002%

Reanalysis

	Chloride	Nitrite	Nitrate	Sulfate
2020 median RPD	-0.27%	0%	0.18%	0.19%
2020 Average RPD	-0.38%	2.98%	0.69%	-1.63%

- Roughly 5% of each batch of 400 NPS samples are reanalyzed after the original analysis.
- The Relative Percent Differences are calculated and verified against the DQO requirements.
- Any samples failing to meet DQO's are reanalyzed a third time to check.

Routine Filter Re-Extraction

- Extraction efficiencies were evaluated on nearly 370 samples.
- Efficiency is determined by dividing the result measured on the re-extracted filter by the sum of the original and re-extracted results.

Chloride	Nitrite	Nitrate	Sulfate
100%		100%	100%

Documentation of New Instruments

- RTI purchased 2 new Aquion systems and 3 new AS-AP autosamplers.
- Samples were analyzed on existing systems and on new systems and compared statistically for differences, we observed no statistically significant differences between results analyzed on existing systems and the new systems. The instruments will be referred to as Aquion A11, January 1, 2020 and Aquion A12, March 24, 2020.

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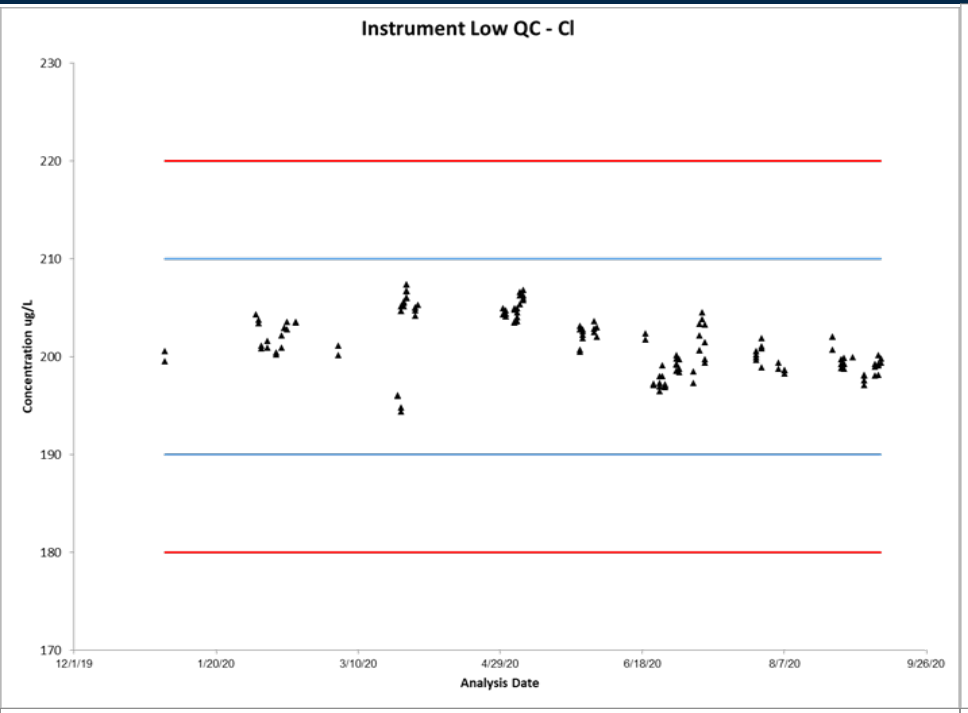
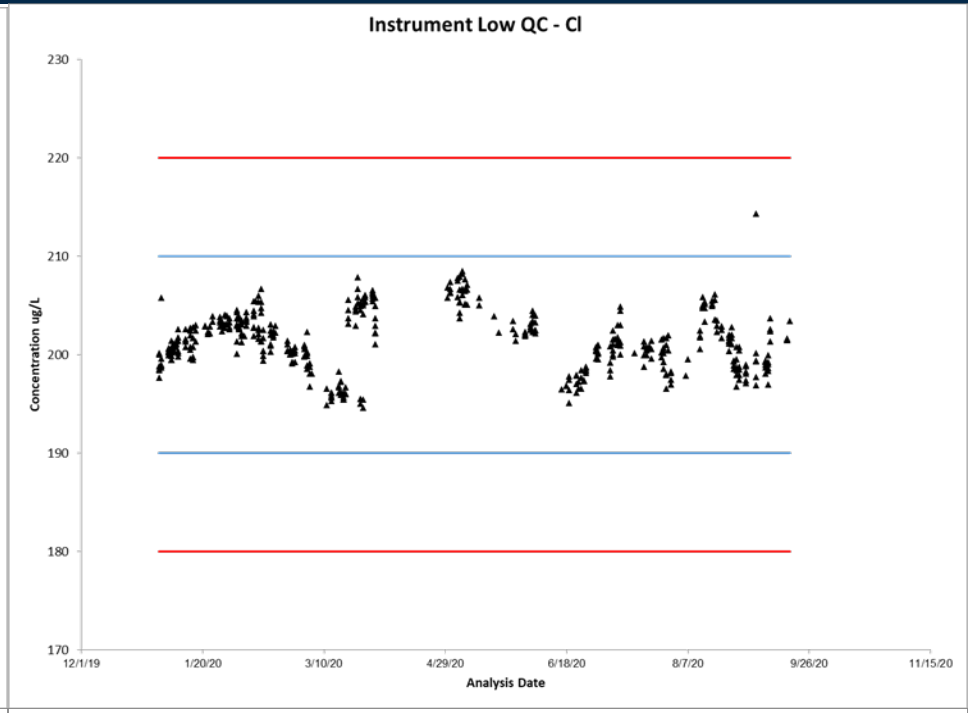
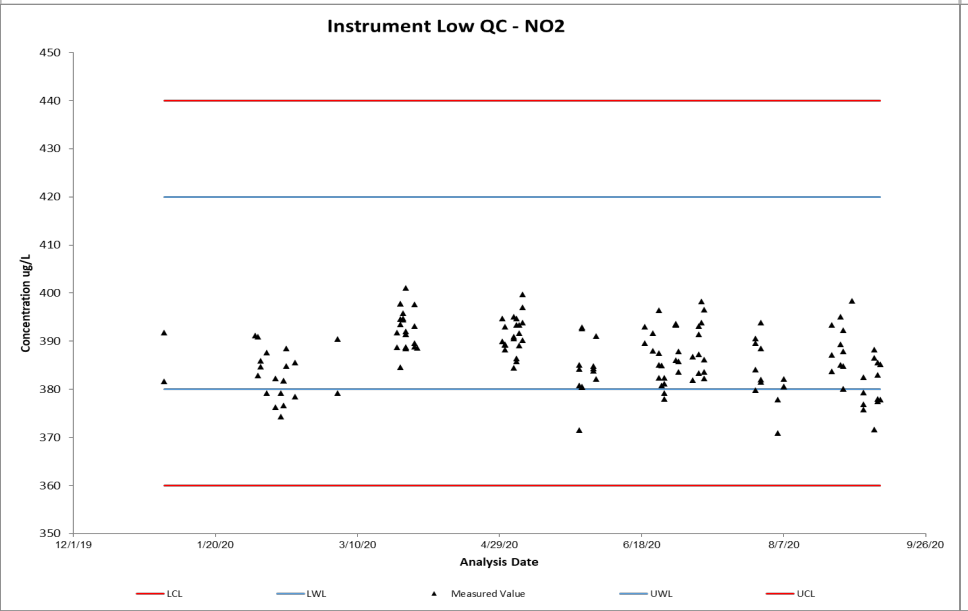
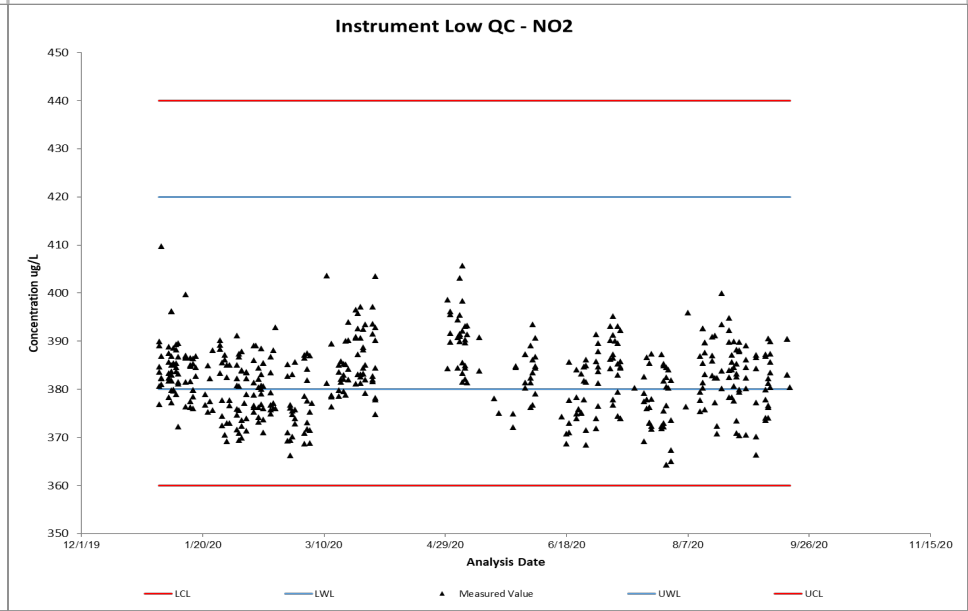
Control Chart New Systems Compared to Existing









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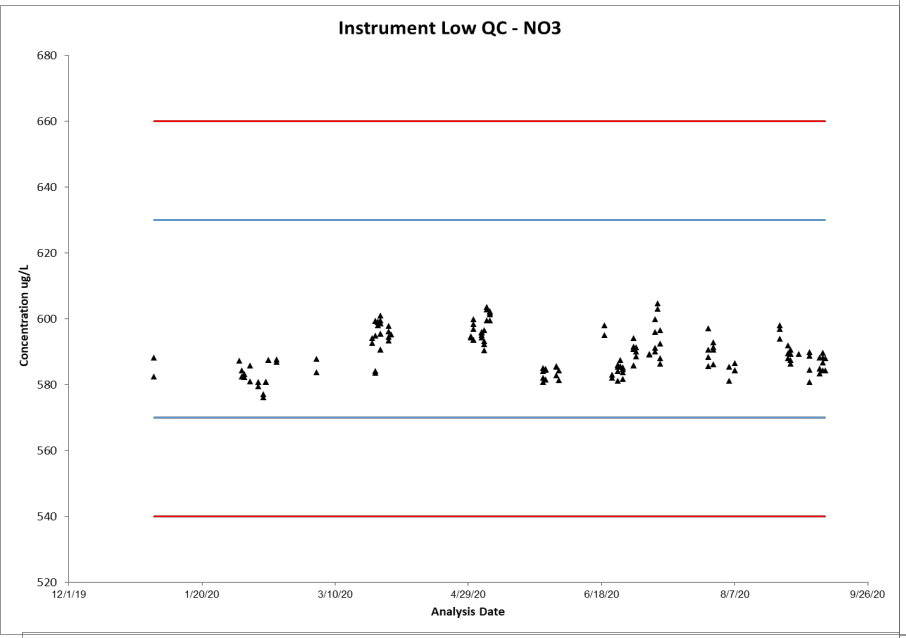
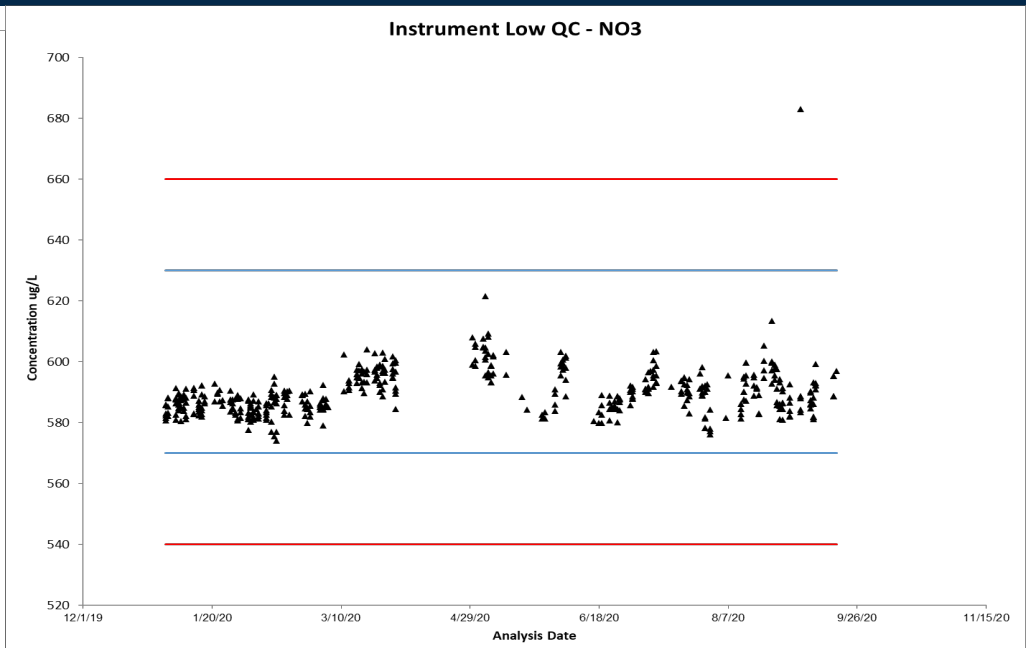
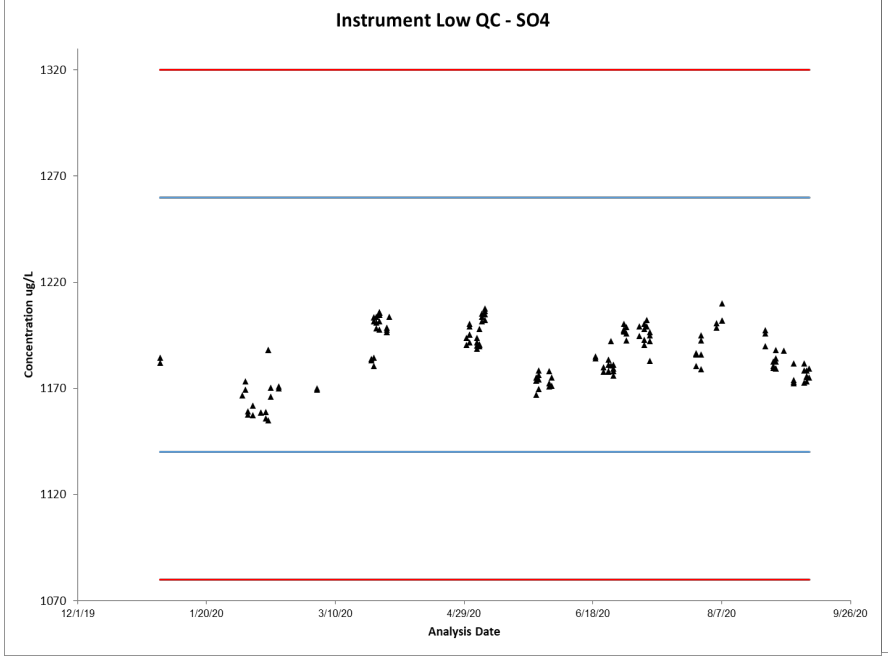
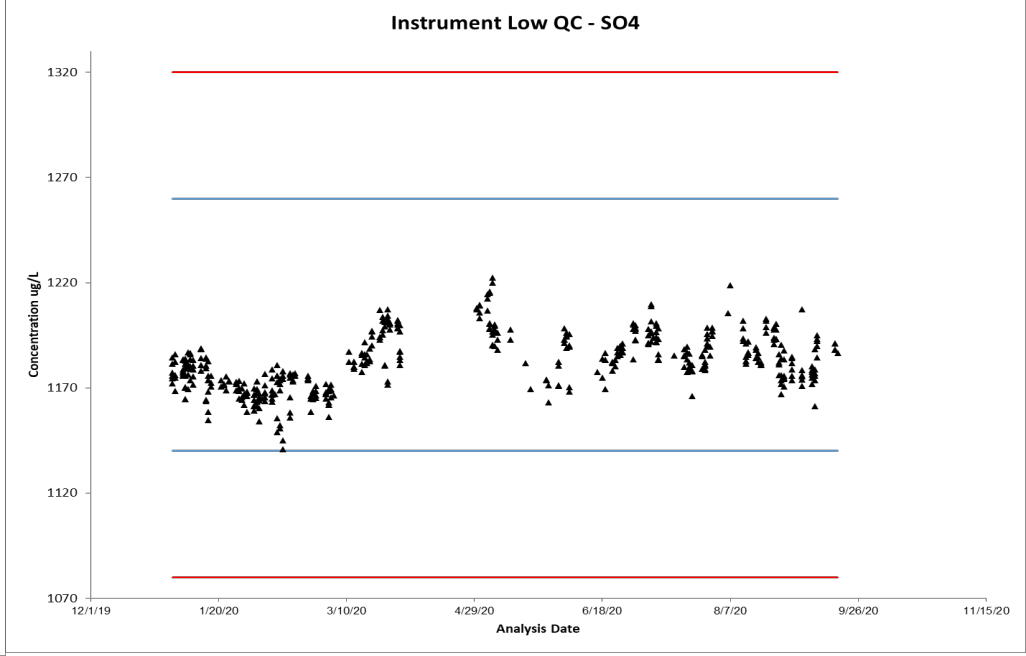
Control Chart New Systems Compared to Existing









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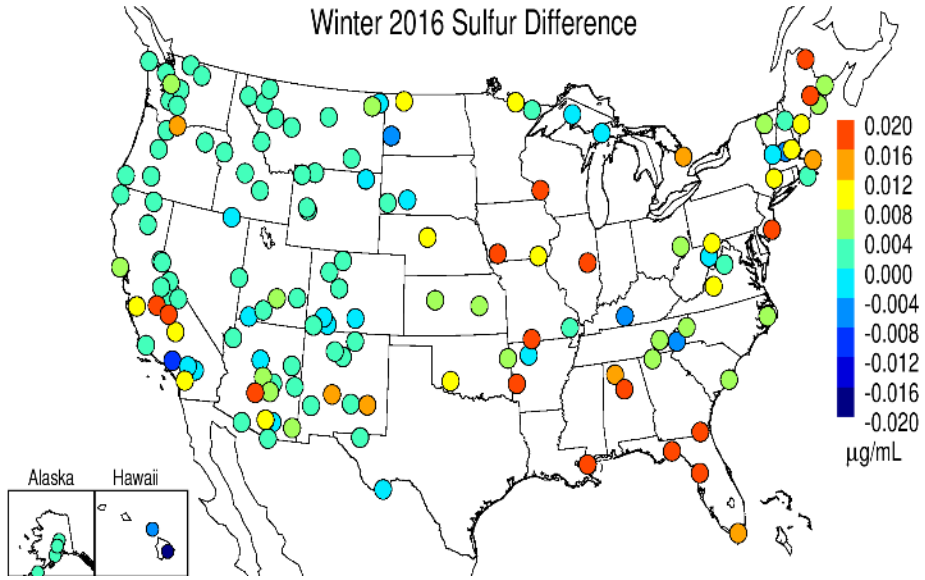
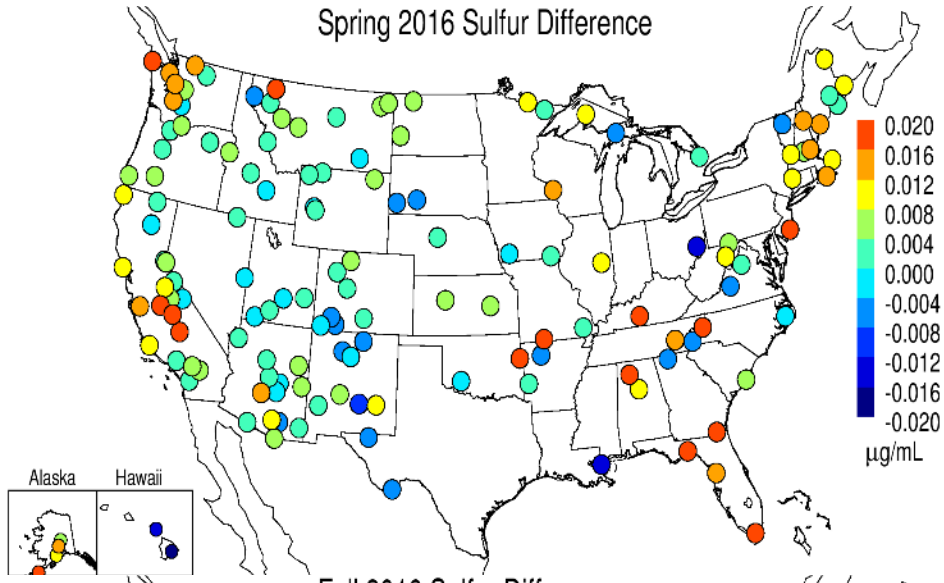
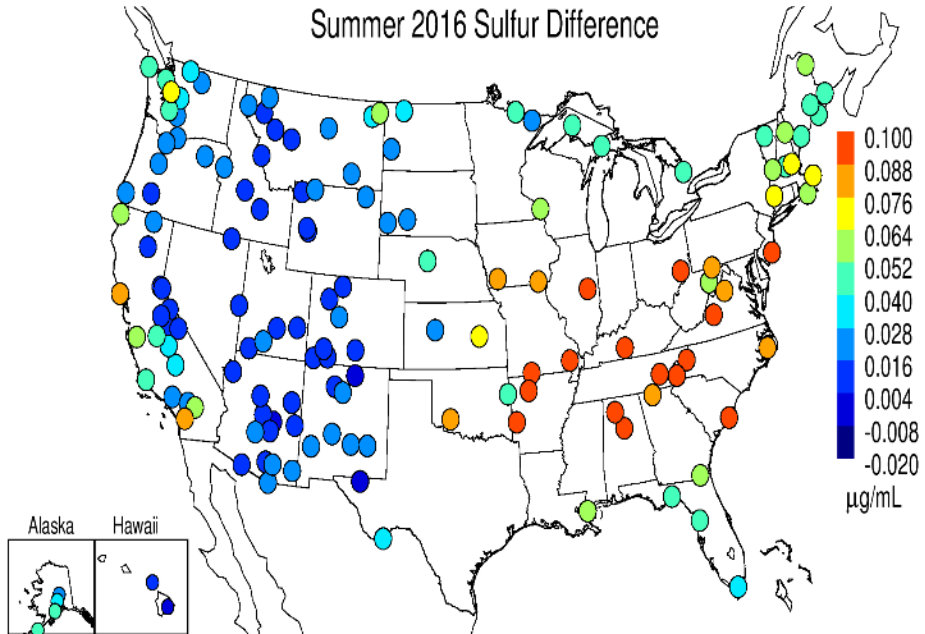
Method Development and Research

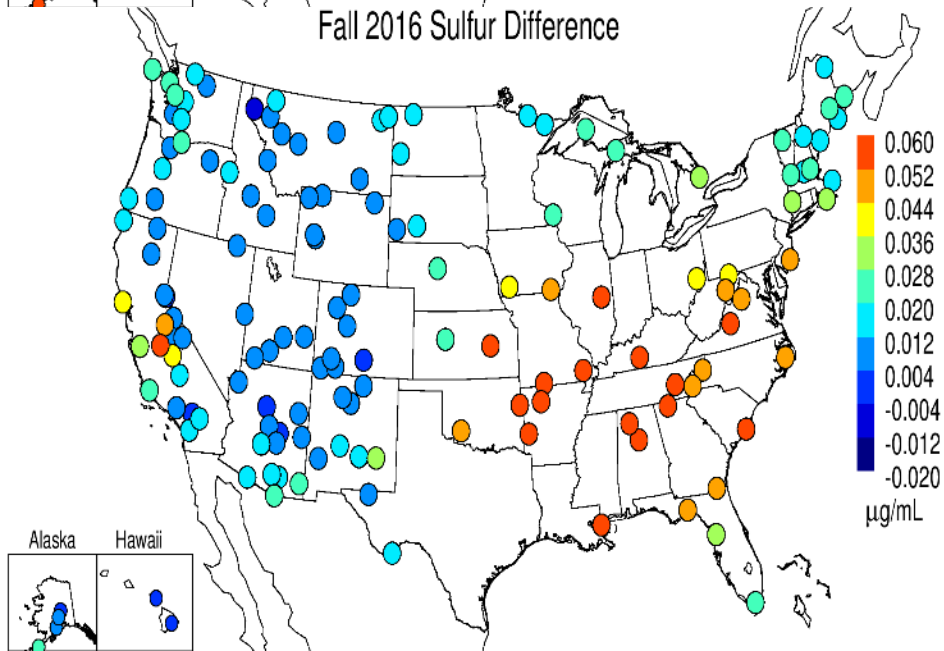
Last year, RTI contributed to our research efforts by providing $120K to support research and method development and purchasing three dual Ion Chromatography systems.

Evidence of water-soluble OS in IMPROVE Extracts

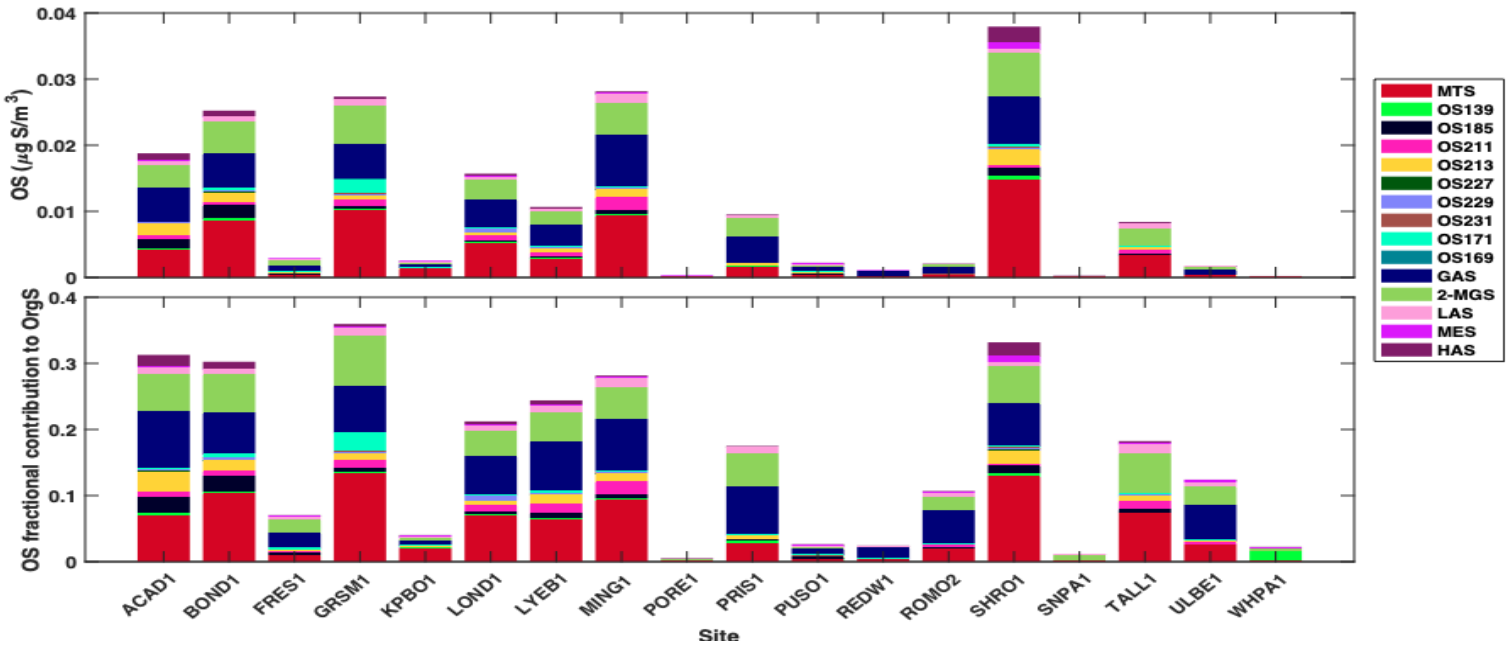








Characterization of Isoprene Derived OS

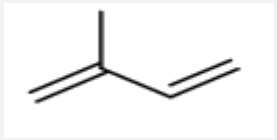
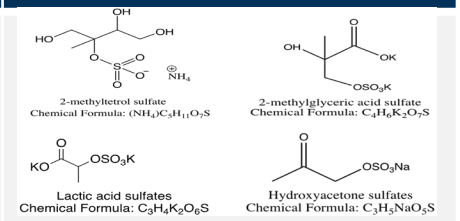
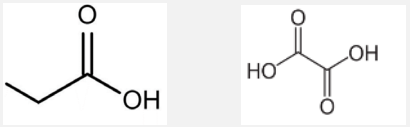
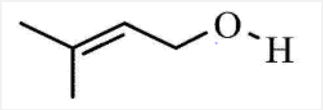
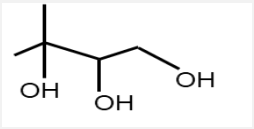
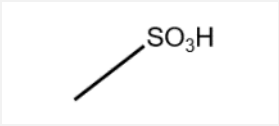
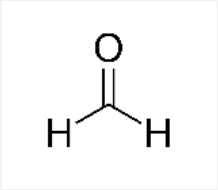
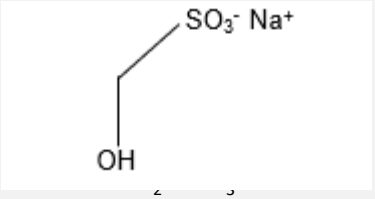


Characterization of Isoprene derived OS in IMPROVE composite samples collected during Jul/Aug of 2016. (HILIC/ESI-HR-QTOFMS).

This data confirms the presence of OS in IMPROVE samples and helps explain discrepancies between total S by XRF and SO_4^{2-} by IC.

2MTS was the most abundant OS detected, it is important to note that 2MGS was also abundant. This has been identified as forming from further oxidation of 2MTS in the particle phase.(Yuzhi Chen et al., 2020, ES&T Letters)

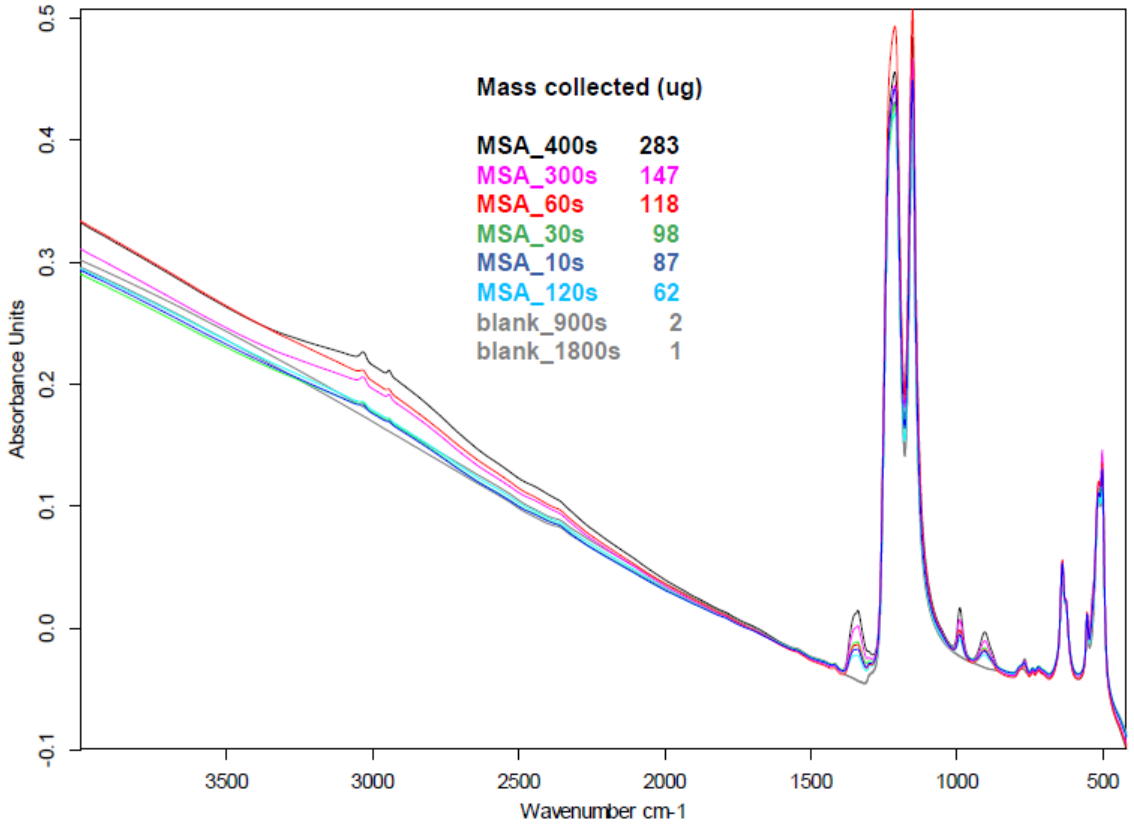
Targeted Analytes

Precursor	Chemical Structures	Source	Potential Tracers
Isoprene		Trees such as oaks, poplars, eucalyptus, legumes Shrubs Oceanic emissions Used to make synthetic rubber	
Monoterpenes		Trees- pines, barks heartwood, softwood of vegetables, fruits and herbs, used in perfumes cosmetics, cleaning products	 Carboxylic Acids
Methylbutenol		Several Pine Species	 Dihydroxyisopentanol (DHIP)
Dimethylsulfide		Oceans by phytoplankton, also bacterial transformation of dimethyl sulfoxide (DMSO) from waste disposed into sewers	 Methane Sulfonic Acid
Formaldehyde		Intermediate through oxidation of carbon compounds emitted by exhaust, forest fires	 Hydroxy Methane Sulfonate

Collaboration between RTI and UCDavis OS

- Evaluate measurement capabilities of organic sulfur compounds by IC and FT-IR
- MSA (methansulfonic acid)
  - Biogenic marine compound, unique tracer for marine source
  - Measure of marine biogenic impact of S compounds in the atmosphere
  - Biogenic S species increasingly important as anthropogenic S decreases
- HMS (Moch et al., 2020)
  - formed in extreme haze
  - observed in IMPROVE IC
- Atmospherically relevant organosulfates –
  - Methyl Sulfate
  - Lactic acid sulfate – observed in SE US by other methods
  - Methyl tetrol sulfate - observed in composite IMPROVE samples

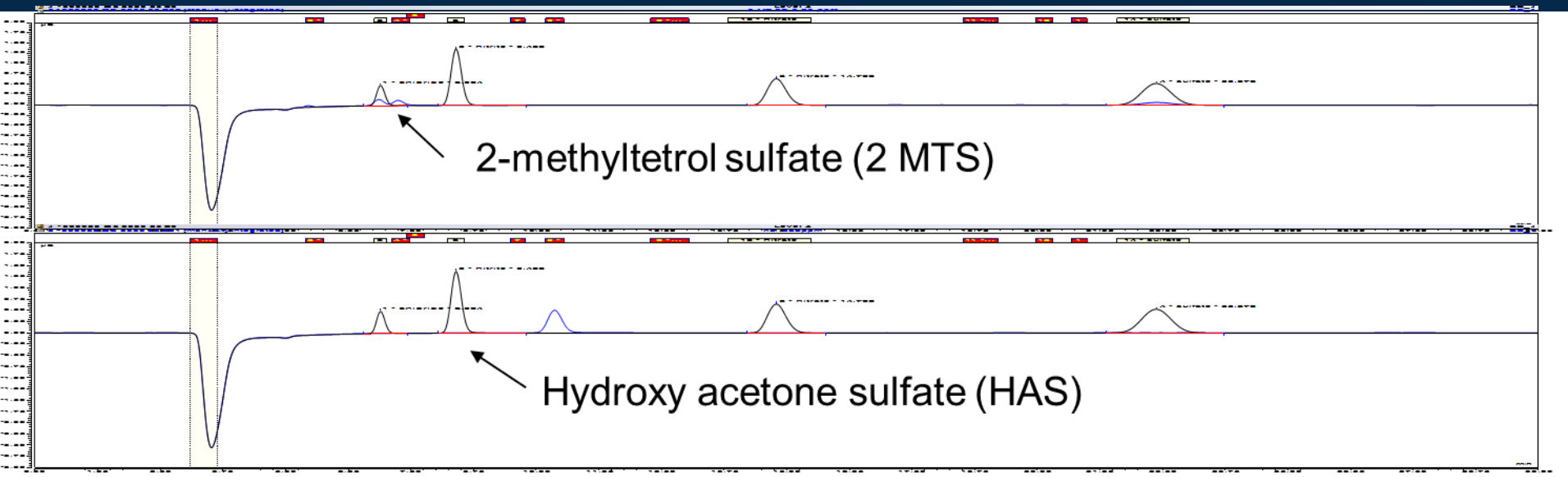
FTIR Spectra of laboratory generated MSA standards

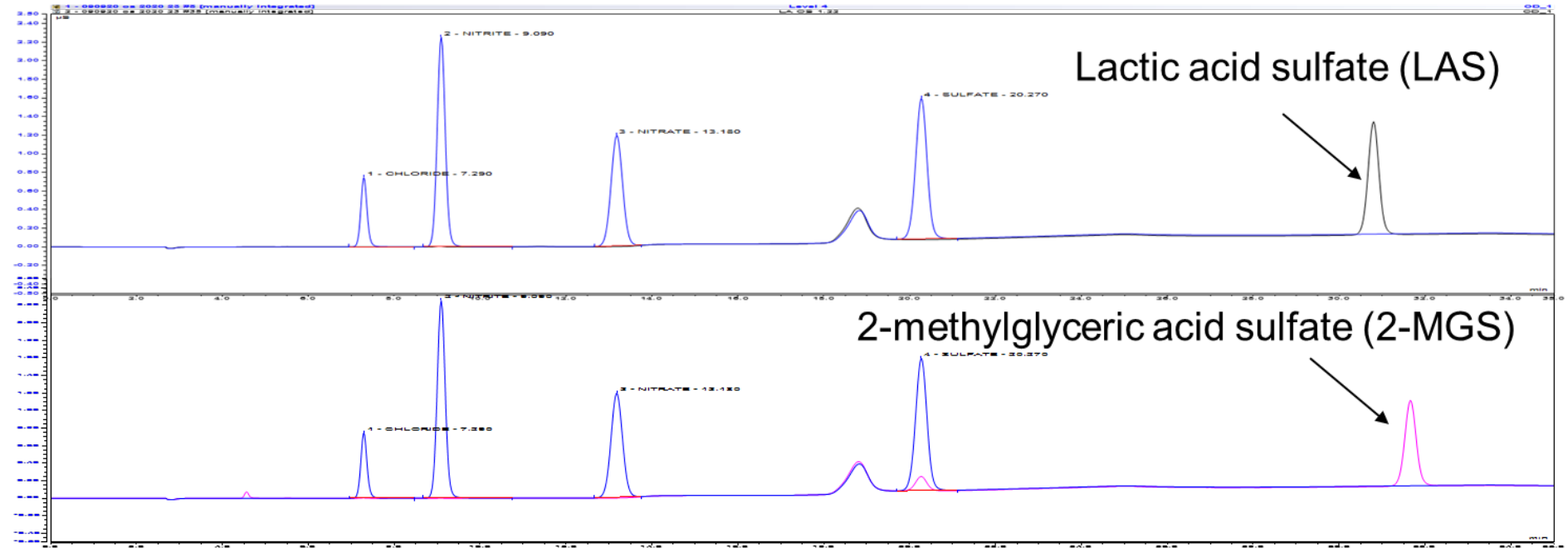


Research Goals for 2020

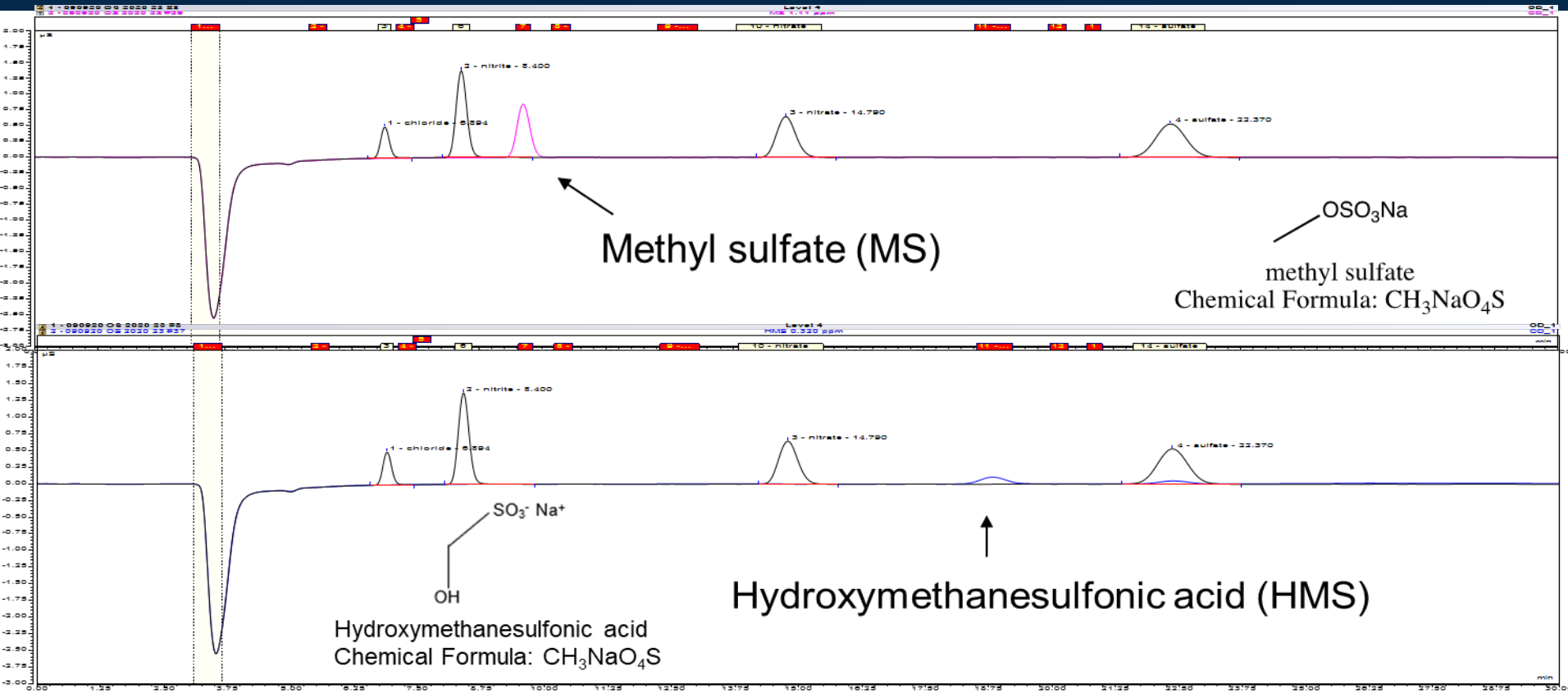
- Evaluate IMPROVE samples using our current IC Carb/Bicarb method and KOH method for detection of tracers.
- Continuing with analyses of targeted samples for total sulfur by ICP-OES. Dombek, T., E. Poitras, J. Hand, B. Schichtel, J.M. Harrington and K.E. Levine. 2020. Total sulfur analysis of fine particulate mass on nylon filters by ICP–OES. Journal of Environmental Quality 49: 762-768. doi:10.1002/jeq2.20066.
- Collaborate with Jason Surratt and his graduate student Yuzhi Chen at UNC to map out tracers of interest and evaluate methods between our laboratories.
- Collaborating with Ann Dillner at UC Davis to evaluate OS on Teflon and Nylon filters.

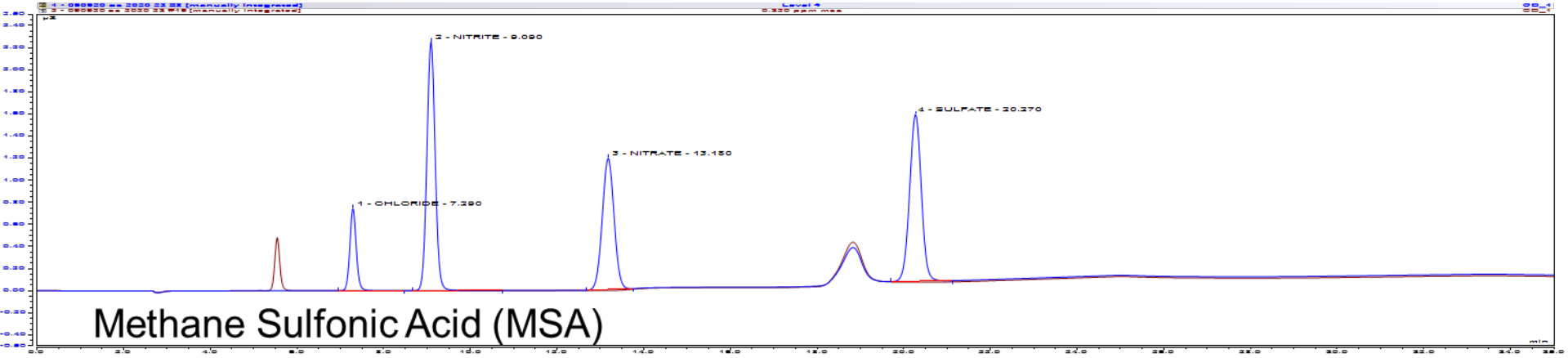
Isoprene Derived OS



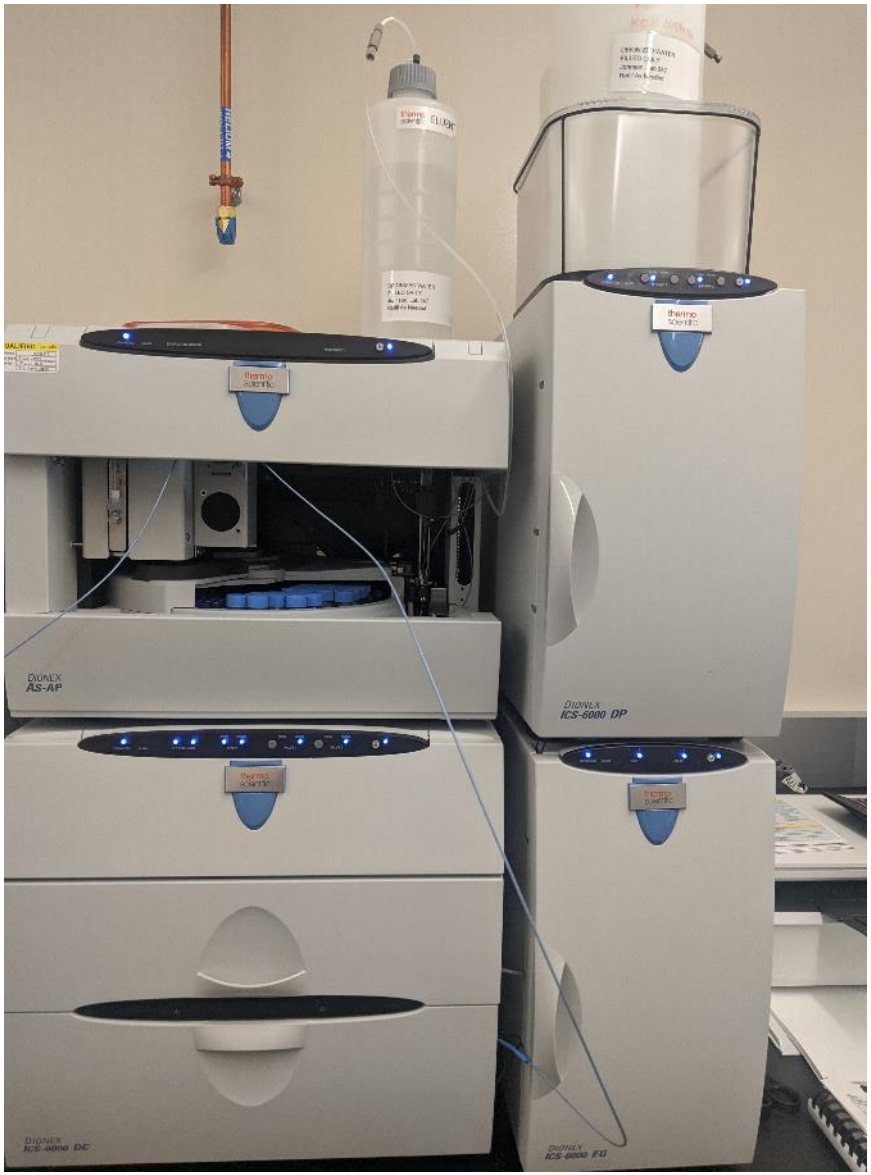


Other OS


2 - nitrite - 5.400
1 - chloride - 6.594
3 - nitrate - 14.790
4 - sulfate - 22.370
Methyl sulfate (MS)
OSO_3Na
methyl sulfate
Chemical Formula: CH_3NaO_4S
SO_3^- Na^+
OH
Hydroxymethanesulfonic acid
Chemical Formula: CH_3NaO_4S
Hydroxymethanesulfonic acid (HMS)

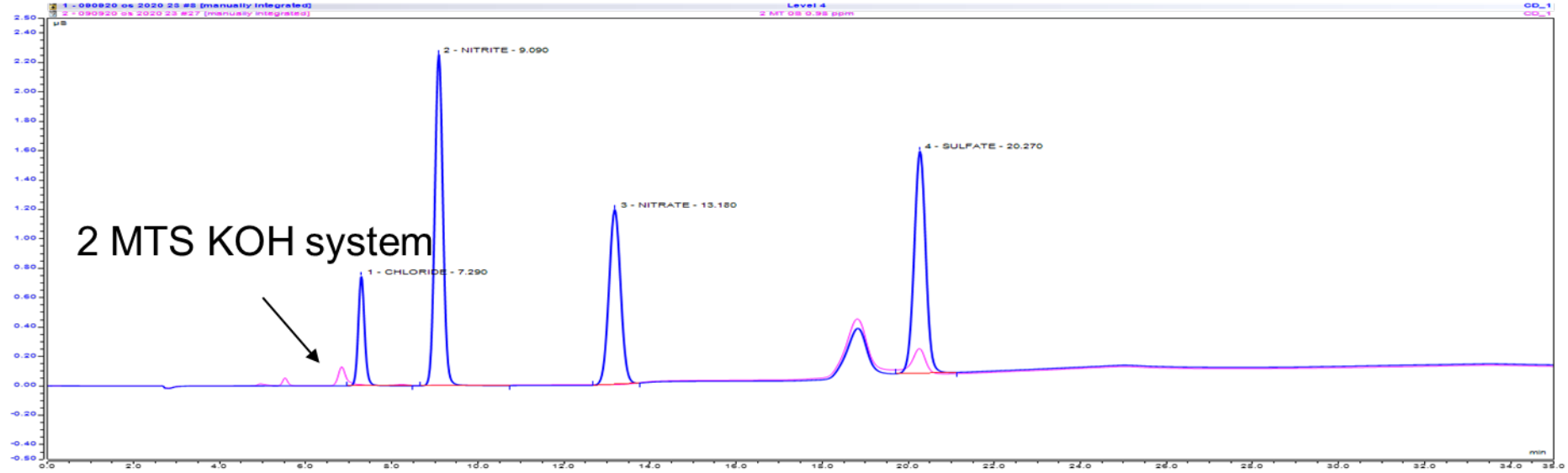

2 - NITRITE - 9.090
1 - CHLORIDE - 7.290
3 - NITRATE - 13.150
4 - SULFATE - 20.270
Methane Sulfonic Acid (MSA)

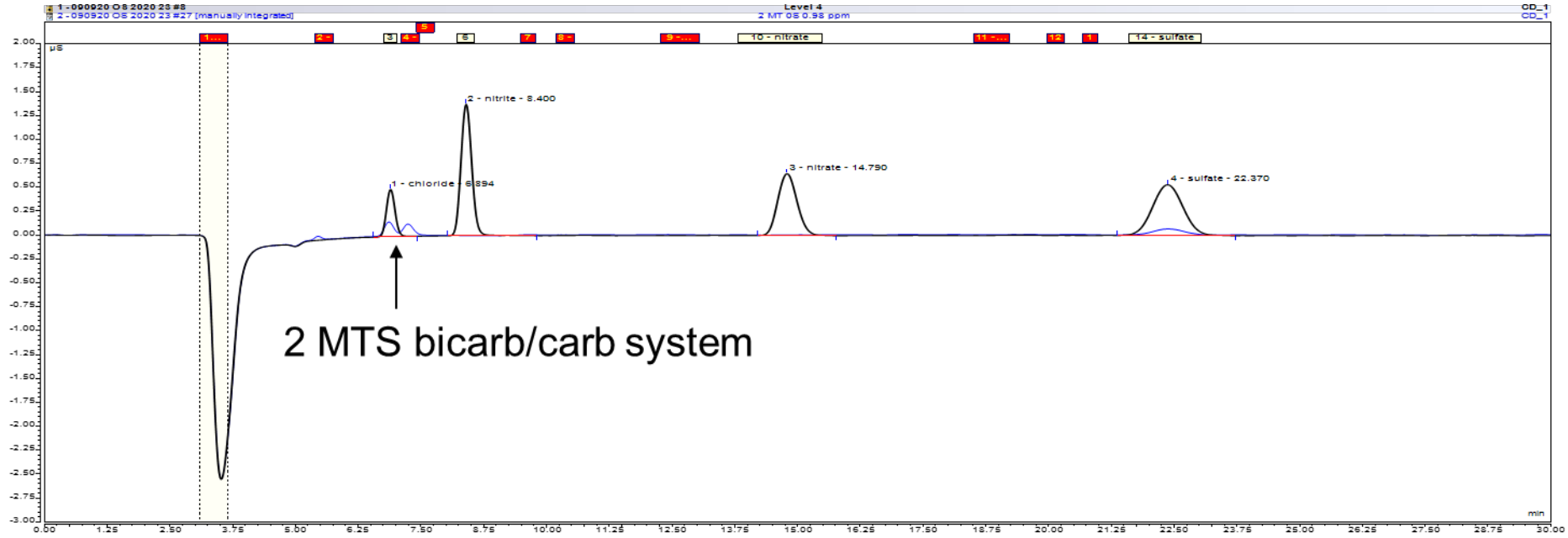
Method Development



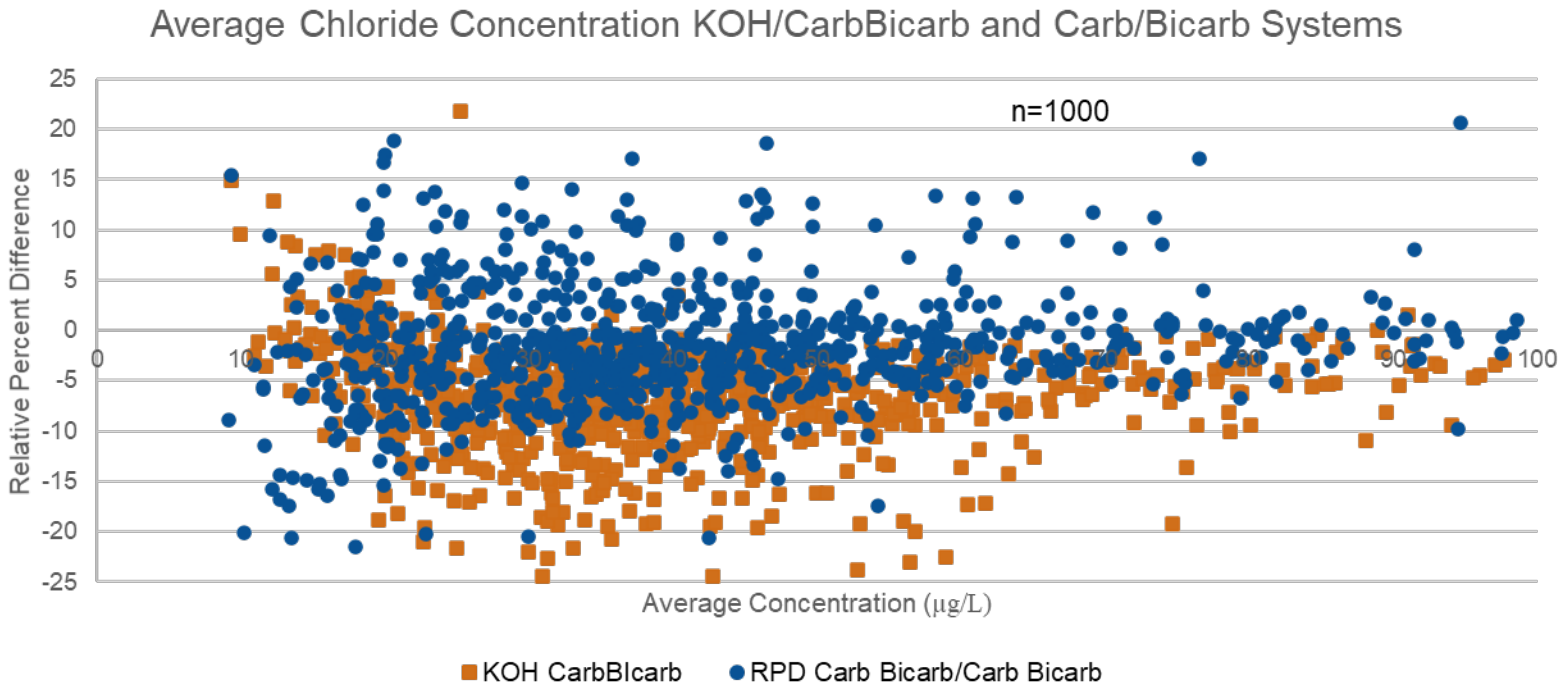
- Samples with that have evidence of the 2MTS peak are flagged for further analysis by DUAL IC Methods
- Dual IC system with 2 different methods, samples are analyzed by both methods.
- One system is set up with method using KOH as the eluent and the second system is set up to analyze samples with a method using a Na_2CO_3/$NaHCO_3$ (carb/bicarb) eluent.
- The carb/bicarb method is nearly identical to the traditional IC method used for IMPROVE analyses, with the exception that flow rate has been slowed to move MSA away from the water dip.

Resolving 2MTS and Chloride



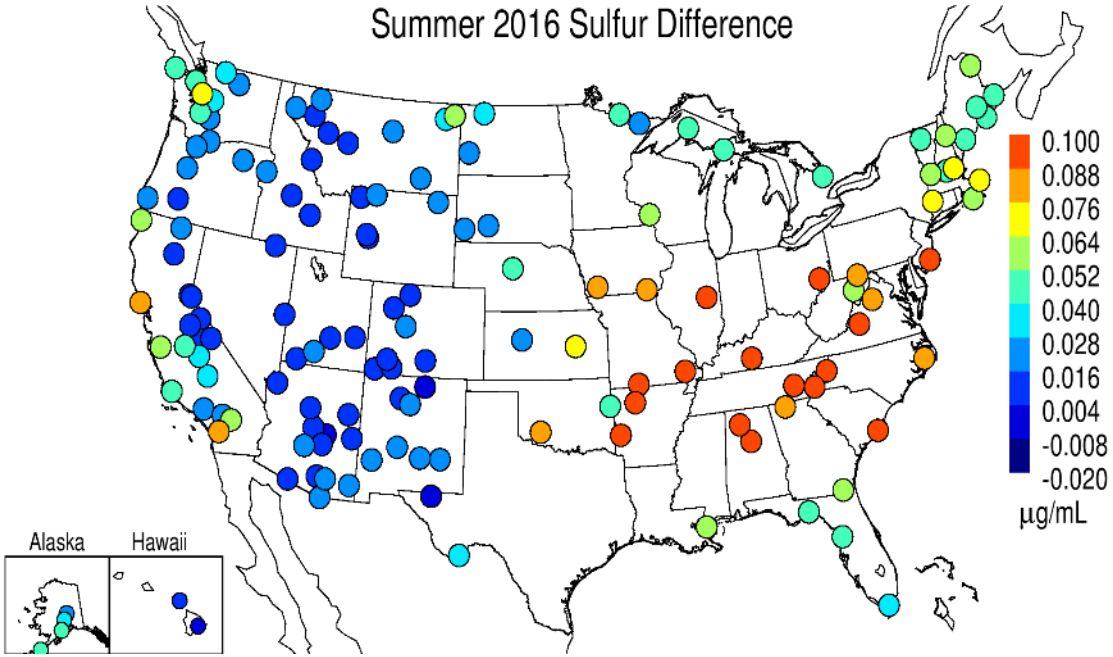


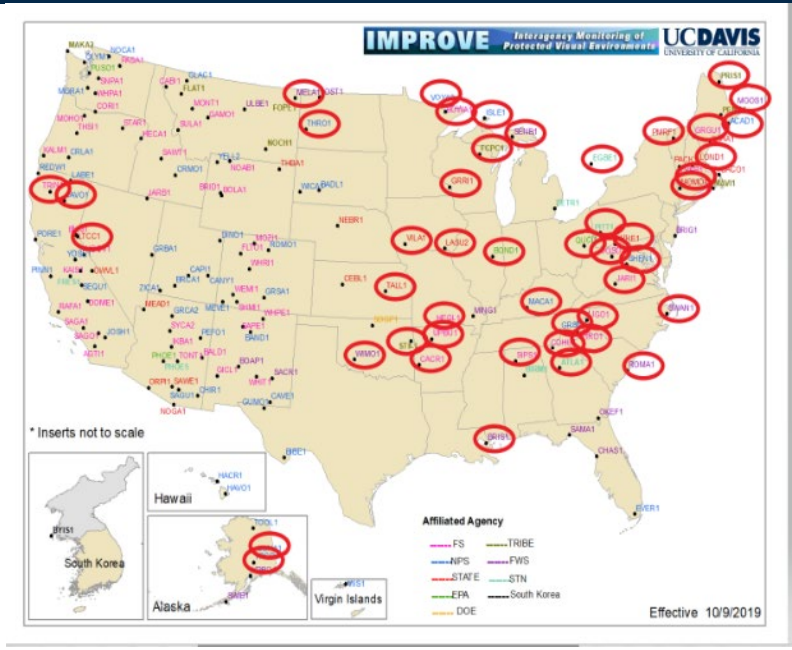
Dual Method Comparison of Chloride Analysis



Percentile	Original Carb/Bicarb (µg/L)	Reanalysis Carb/Bicarb (µg/L)	Reanalysis KOH (µg/L)
25th	29	30	27
50th	41	42	39
75th	65	65	61

IC 2MTS Measurements





Summer-time differences calculated between total sulfur measured by ICP-OES and sulfate measured by IC for 2016 IMPROVE samples.

2MTS detected at sites in 2020 summer IMPROVE samples.

We estimate about 0.020 $\mu g/m^3$ up to 0.10 $\mu g/m^3$ with an average of 0.058 $\mu g/m^3$. There were a few sites that hit as high as 0.40$\mu g/m^3$.

Solutions or Questions

Parameter	Challenge	Response
Chloride Interference	How has this impacted samples previously analyzed?	Evaluating previous chromatography data, reanalysis of archived samples, establish a correction
Solubility	By measuring the total S, sulfate, and organic sulfur in extracted nylon filter samples, we are only addressing the water-soluble components.	Plans are in place to work with Jason and Yuzhi for do some solubility study and validate the freeze-drying approach. We hope to come up with a systematic way to correct for solubility differences between matrices.
Stability	We are not sure how long these OS species are stable on the filter, or in DI water.	We are currently conducting a stability study in DI water and have also partnered with Ann Dillner at UC Davis to evaluate these species on Teflon and Nylon filters.
Quantitation	Need to evaluate the standards using second source standards	Continue to work with researchers to obtain more standards.

Acknowledgements

- Dr. Jason D. Surratt, Ph.D. Professor Dept of Environmental Sciences and Engineering and Department of Chemistry, Gillings School of Public Health, University of North Carolina, Chapel Hill

- Yuzhi Chen, PHD Candidate, Environmental Sciences and Engineering and Department of Chemistry, Gillings School of Public Health, University of North Carolina, Chapel Hill

- Dr. Ann Dillner, Ph.D. Research Engineer, Air Quality Research Center, University of California, Davis

- Dr. Jenny Hand, Ph.D. Senior Research Scientist, Cooperative Institute for Research in the Atmosphere, Colorado State University

- Dr. Keith Levine, Ph.D., Senior Director Analytical Sciences, RTI,
- IC lab team, especially Miranda DeBoskey, Chemist RTI

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