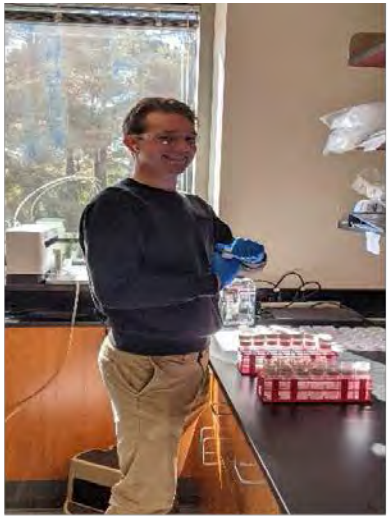
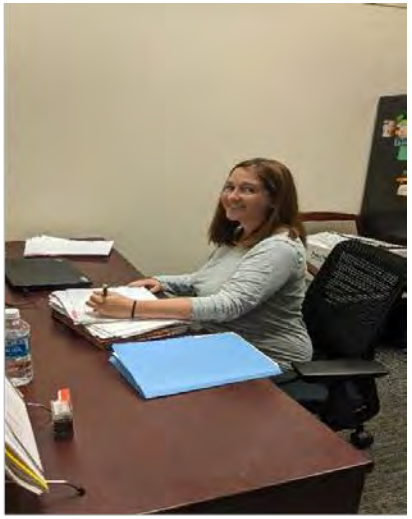
IMPROVE Steering Committee Meeting

Plymouth New Hampshire, November 2022

Tracy Dombek, Ions Report

RTI International



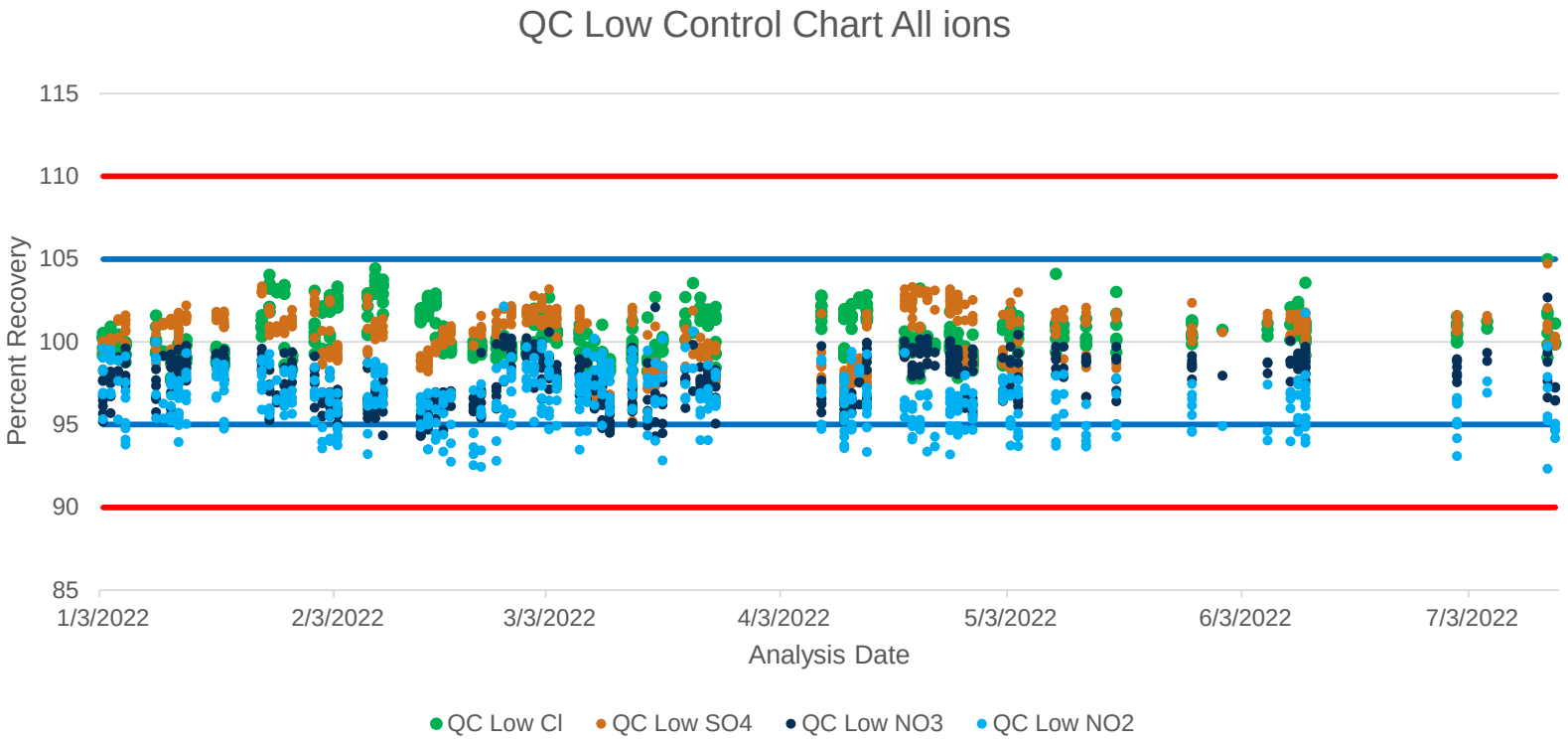


Minimum Detection Limits & Process

- 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.

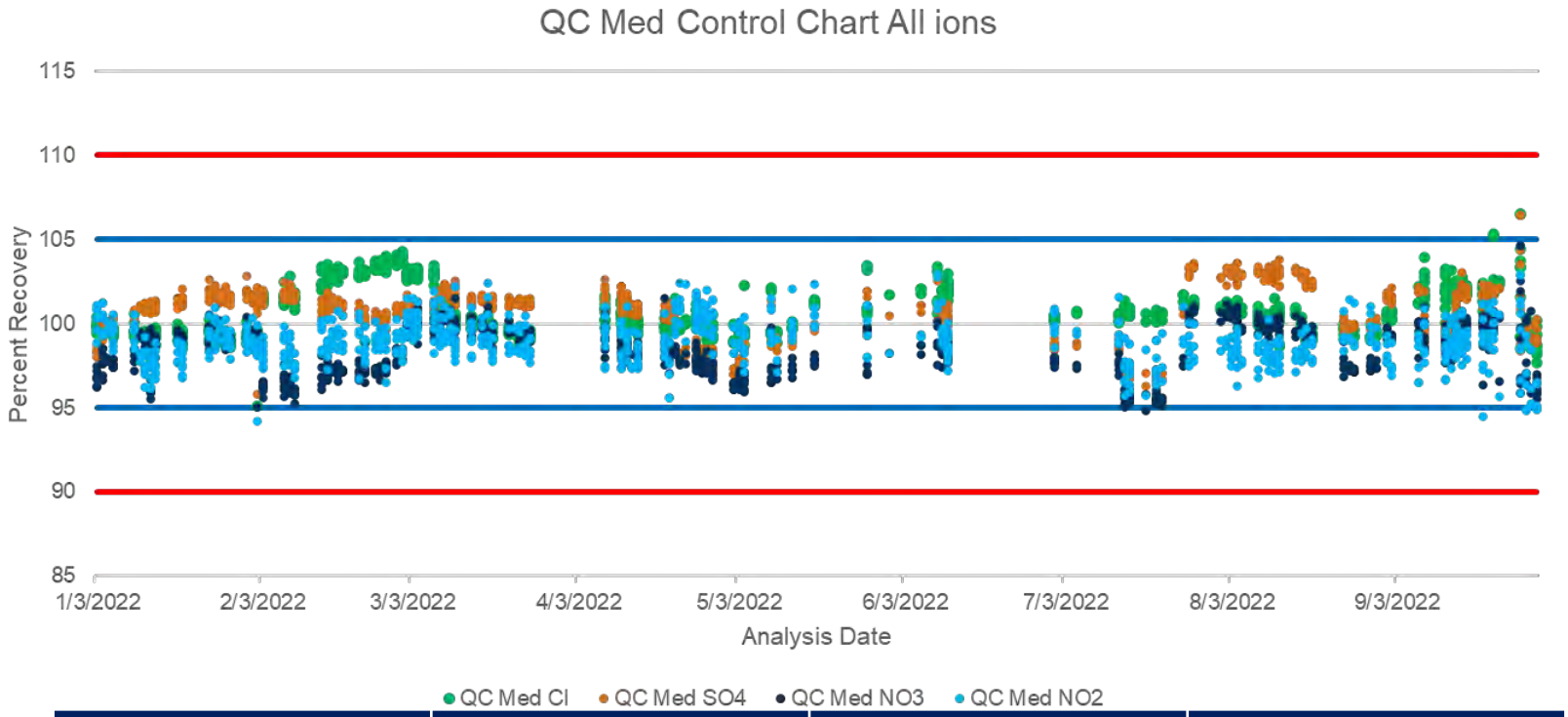
	Chloride	Nitrite	Nitrate	Sulfate
2022	0.005 ppm	0.010 ppm	0.008 ppm	0.011 ppm

Instrument Control Charts



Ion	Median Percent Recovery	Average Percent Recovery	Count
Chloride	101%	101%	882
Sulfate	101%	101%	882
Nitrate	98.7%	98.5%	882
Nitrite	99.0%	98.9%	882

Instrument Control Charts



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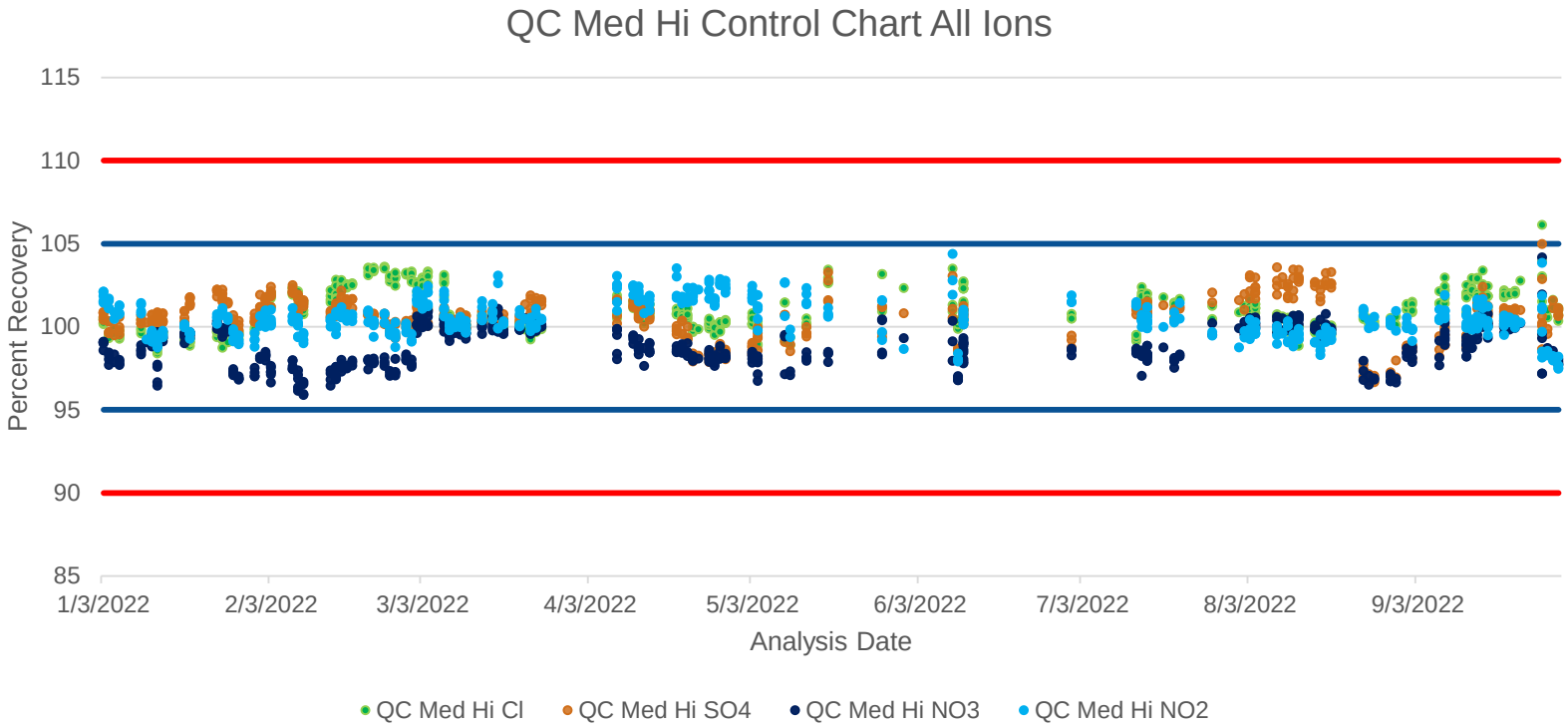
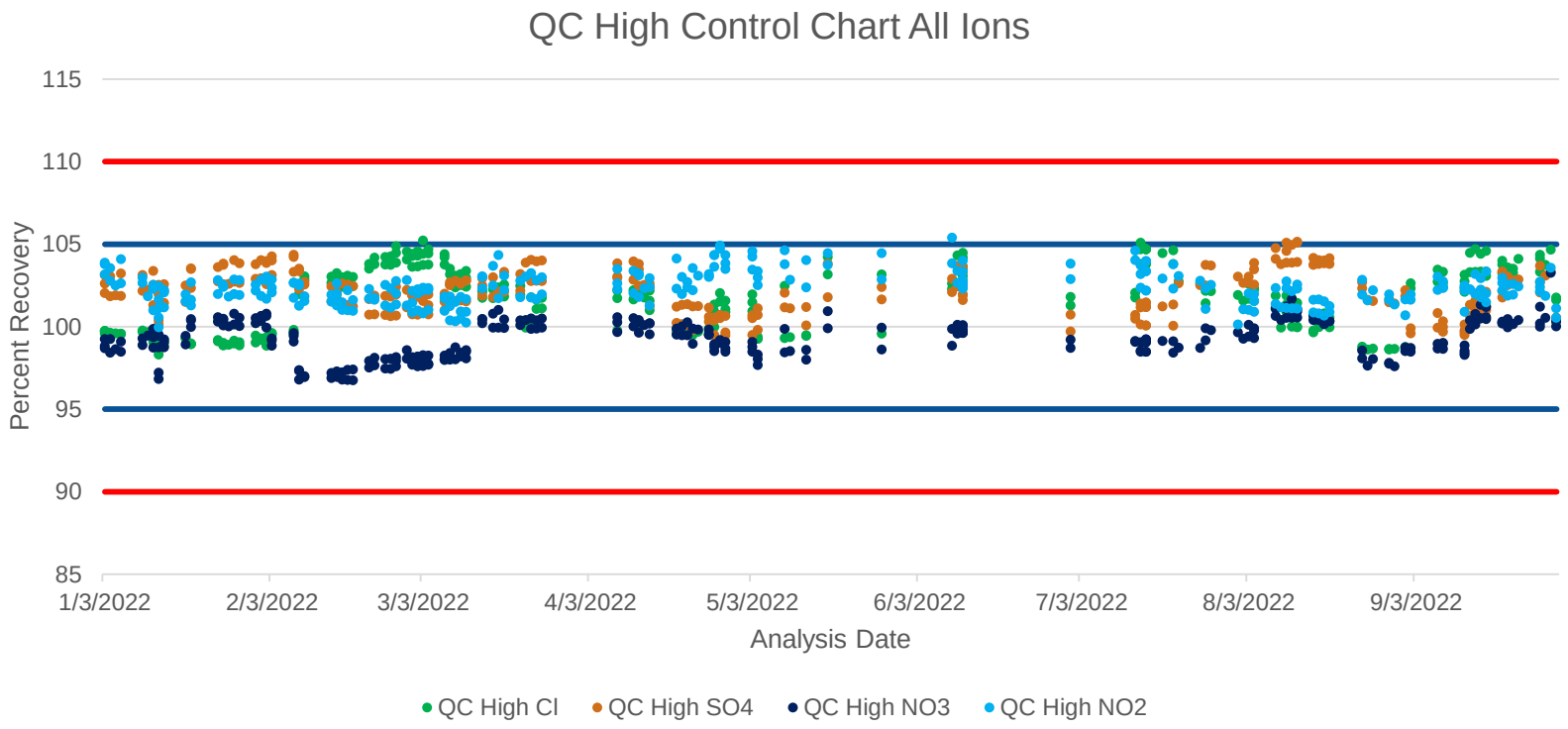
Instrument Control Charts



Ion	Median Percent Recovery	Average Percent Recovery	Count
Chloride	101%	101%	520
Sulfate	101%	101%	520
Nitrate	98.8%	99.1%	520
Nitrite	100%	101%	520

Instrument Control Charts



Ion	Median Percent Recovery	Average Percent Recovery	Count
Chloride	102%	102%	274
Sulfate	102%	102%	274
Nitrate	99.3%	99.2%	274
Nitrite	102%	102%	274

25th Percentile All Ions

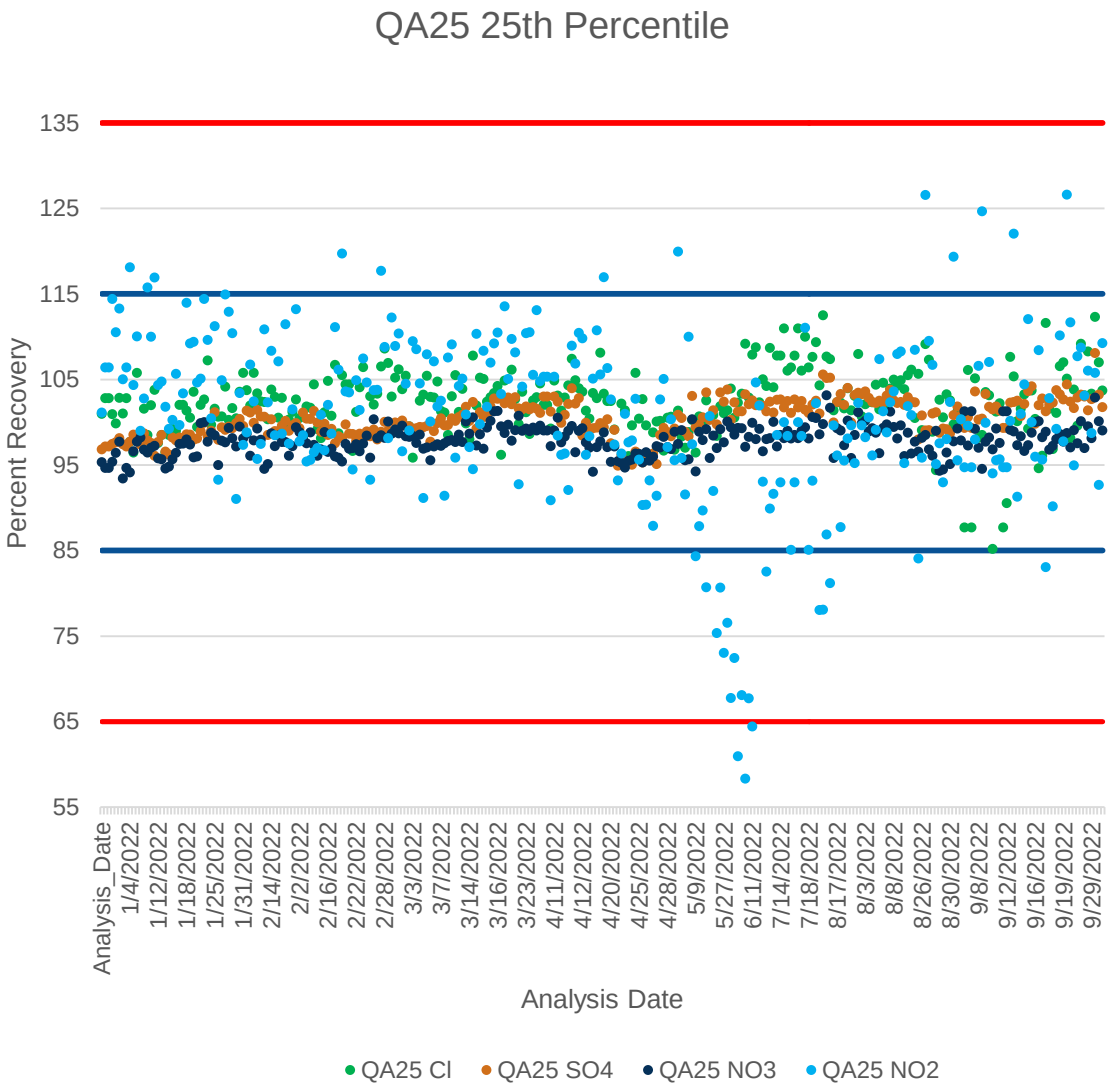
Approximate Air Concentration

Chloride - 0.016 µg/m^3

Sulfate - 0.300 µg/m^3

Nitrate - 0.092 µg/m^3

Nitrite - 0.007 µg/m^3



50th Percentile All Ions

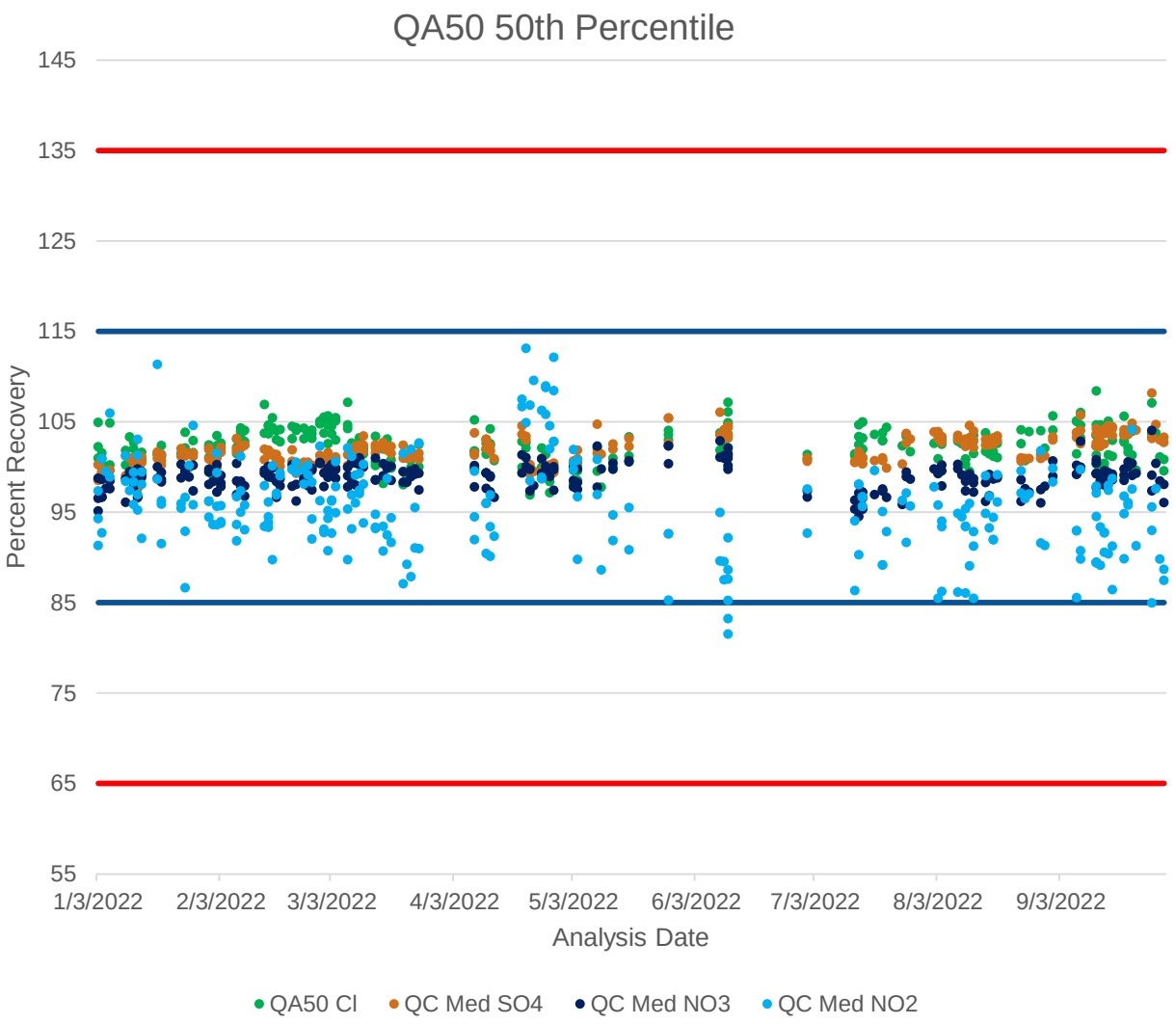
Approximate Air Concentration

Chloride - 0.031 µg/m^3

Sulfate - 0.60 µg/m^3

Nitrate - 0.180 µg/m^3

Nitrite - 0.013 µg/m^3



75th Percentile All Ions

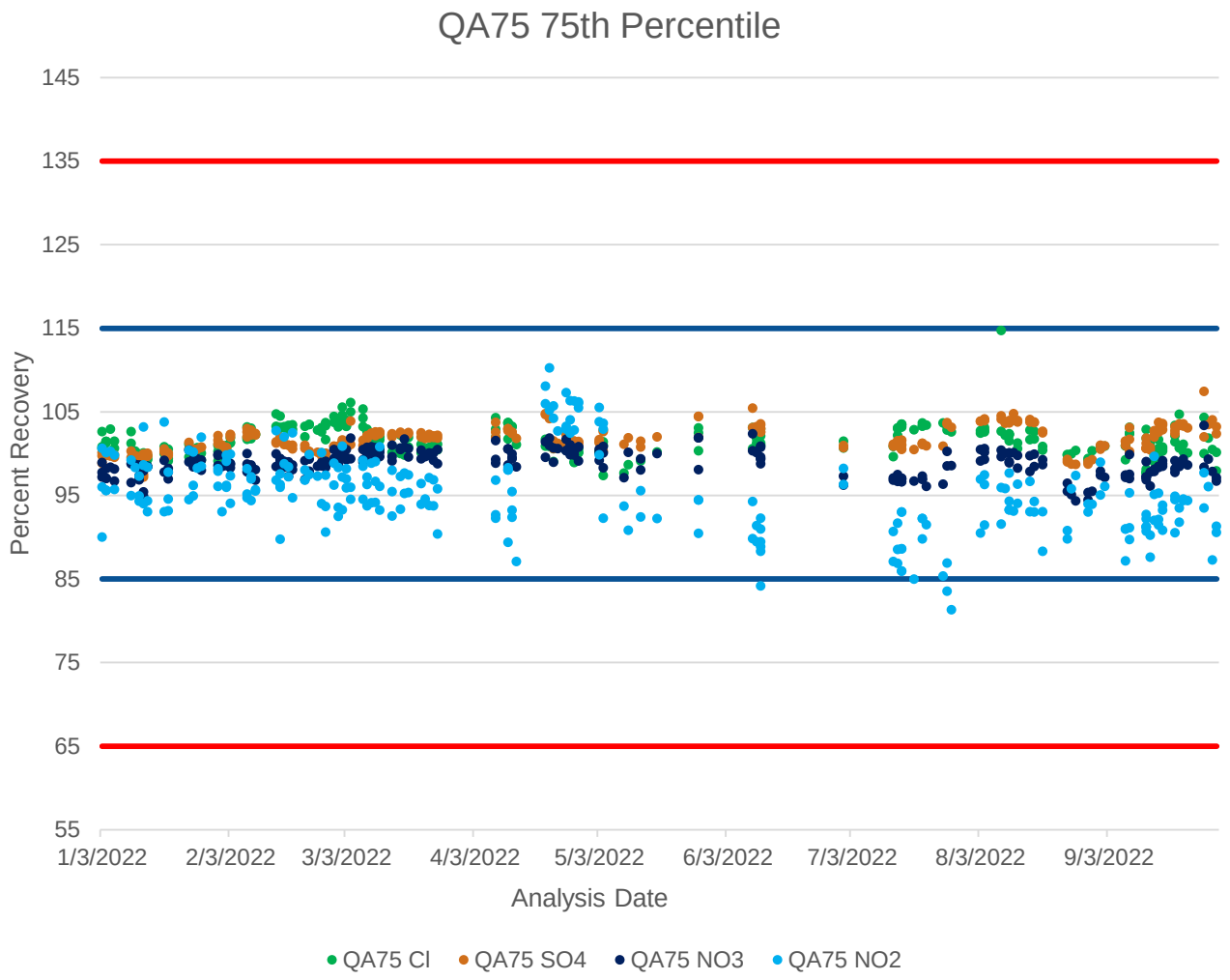
Approximate Air Concentration

Chloride - 0.061 µg/m^3

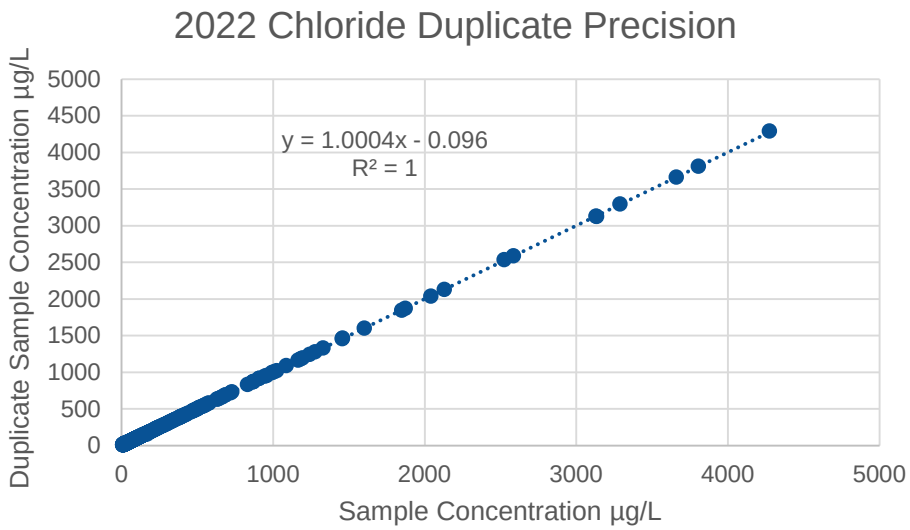
Sulfate - 1.2 µg/m^3

Nitrate - 0.36 µg/m^3

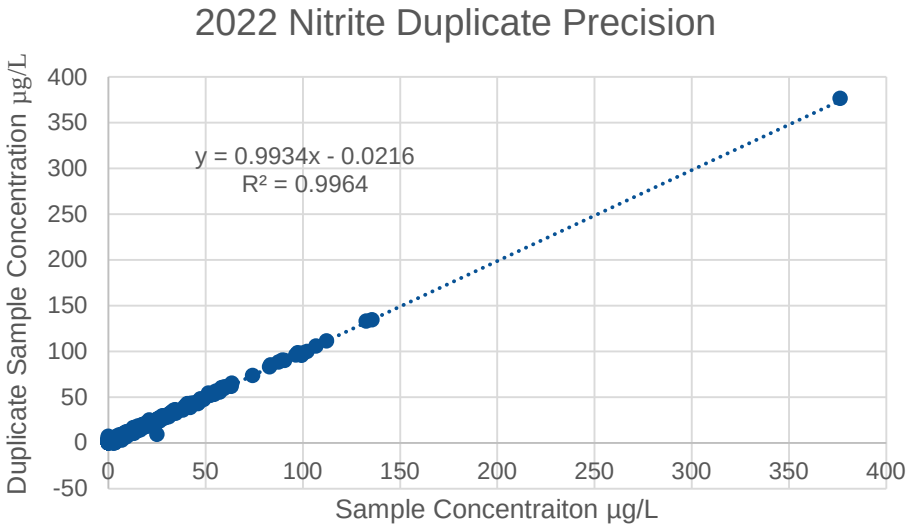
Nitrite - 0.026 µg/m^3



Duplicate Precision

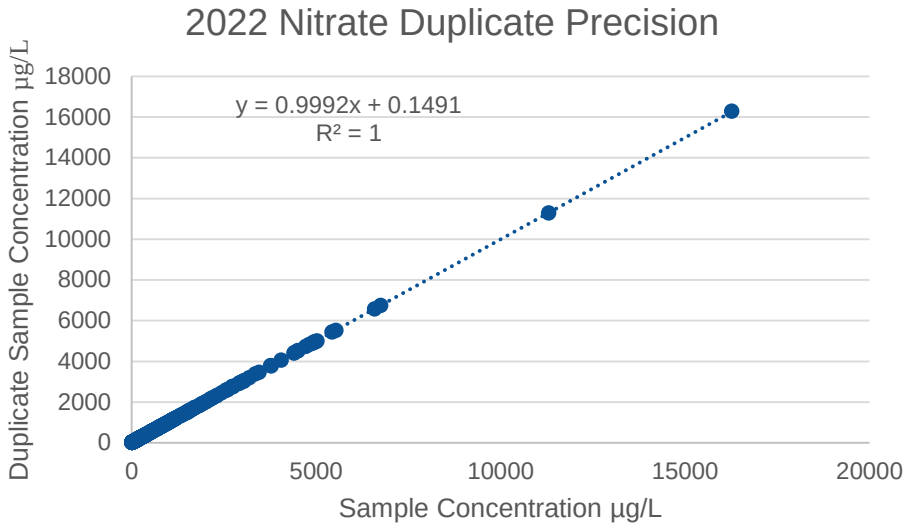


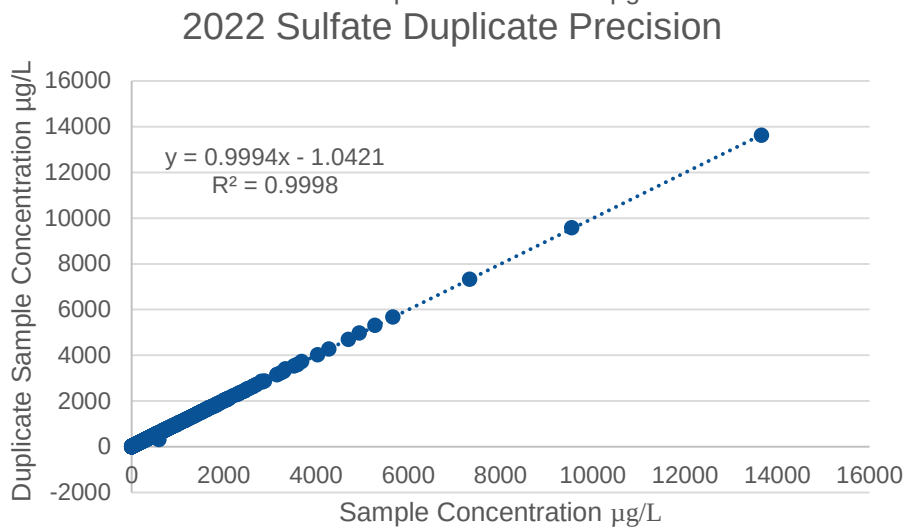
Chloride Percent Differences
Average = 0.03%
Median = 0.04%
Maximum = 28.0%
Minimum = -29.3%
Count = 843
Failures 0%



Nitrite Percent Differences
Average = 0%
Median = 0%
Maximum = 200%
Minimum = -200 %
Count = 843
Failures 0%

Duplicate Precision





Nitrate Percent Differences
Average = 0%
Median = -0.05%
Maximum = 49.8%
Minimum = -200 %
Count = 843
Failures 0.23%

Sulfate Percent Differences
Average = 0%
Median = 1.9%
Maximum = 200%
Minimum = -49.1%
Count = 843
Failures 0.23%

Reanalysis

	Chloride	Nitrite	Nitrate	Sulfate
2022 median Percent Difference	0.16%	1.4%	-0.10%	-0.08%
2022 Average Percent Difference	-0.36%	2.3%	-2.0%	-0.64%

- Roughly 5% of each batch of 400 NPS samples are reanalyzed after the original analysis.
- The percent differences are calculated (difference/average) and verified against the DQO requirements.
- Any samples failing to meet DQO's are reanalyzed a third time to check.

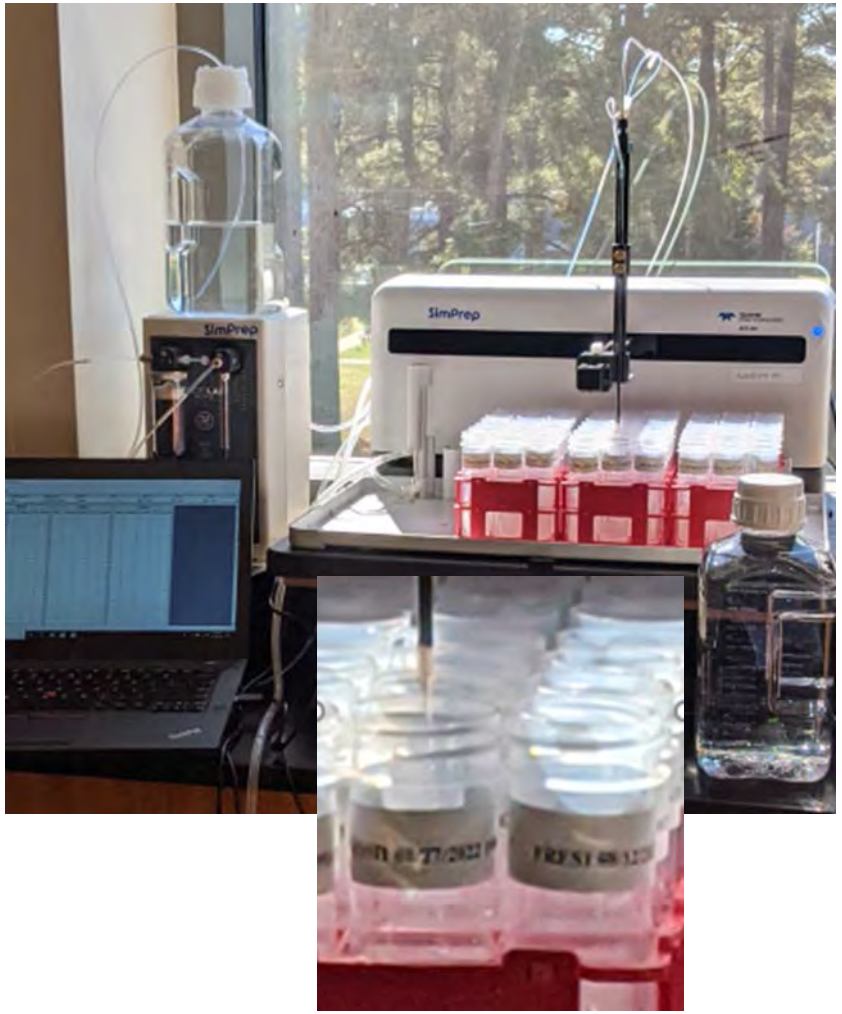
Routine Filter Re-Extraction

- Extraction efficiencies were evaluated on nearly 120 samples.
- Efficiency is determined by dividing the result measured on the re-extracted filter by the sum of the original and re-extracted results when the measured value on the re-extracted filter contains a result greater than the MDL.

Chloride	Nitrite	Nitrate	Sulfate
100%	96.6%	99.7%	100%

Documentation of New Instruments

- Two new systems for automated extractions of samples were purchased
- Validated mass measurements
- Contamination tests
- Placed into service June 2022



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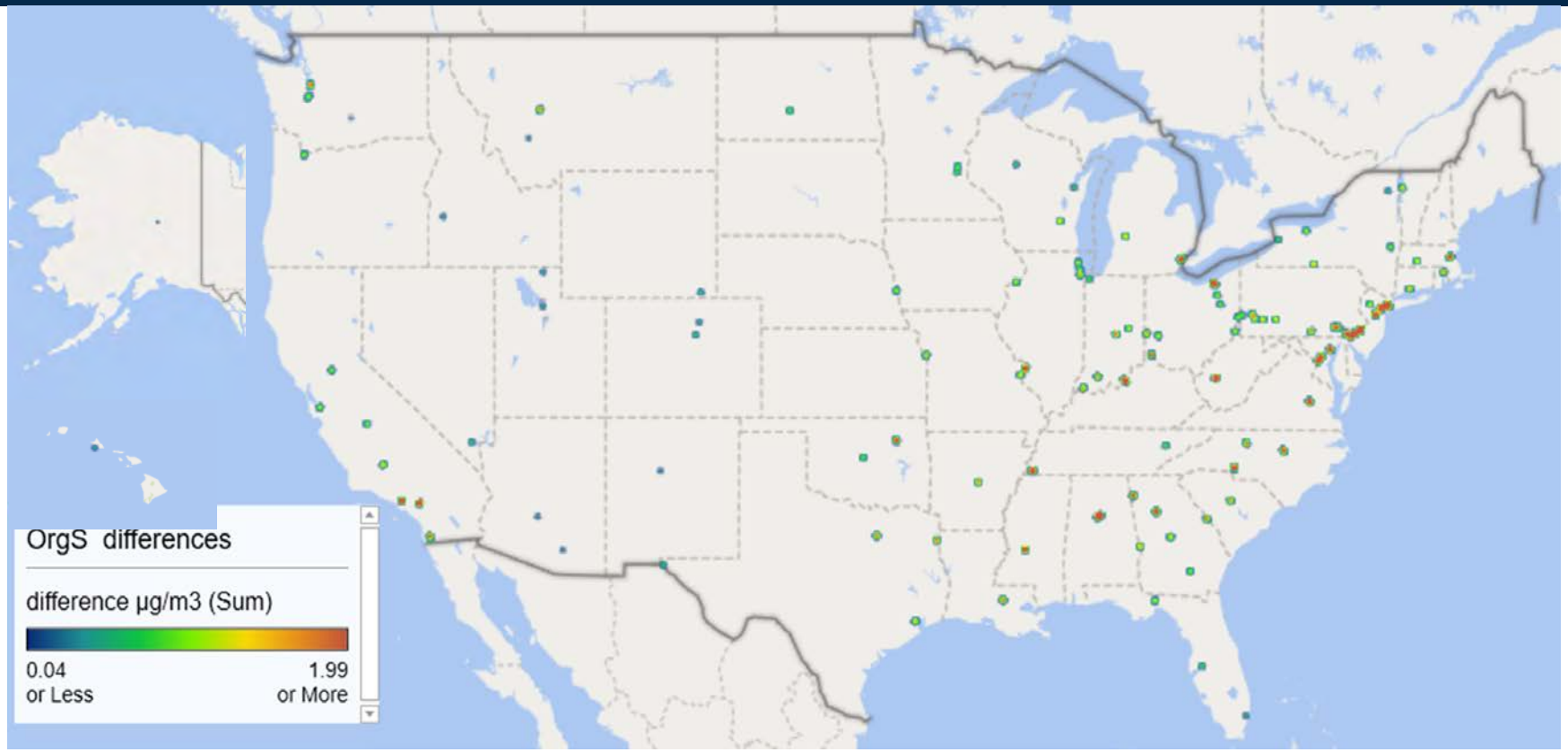
Method Development and Research

Last year, RTI contributed to our research efforts by providing $70K to support research and method development

RTI International

Total sulfur measurements by ICP-OES indicative of organic S (OrgS) in CSN samples collected during August 2019



- The differences between TPS (ICP-OES) and IC correlate well for all sites.
- Inferred differences of OrgS range from 0.04 up to 2.0 µg/m^3 across the network.
- Geographically, the patterns are similar to those observed for IMPROVE samples collected during the summer with some of the highest differences occurring in the Southeastern sites.

Evidence of Organic Sulfur in $PM_{2.5}$ throughout the United States
Tracy Dombek[1]; Eric Poitras[1]; Yuzhi Chen[2]; Jenny Hand[3]; Miranda De Boskey[1] ; Katarina Lindskog[1]; Phillip Berger[1]; Bret A. Schichtel[4]; Jason Surratt[5]; Keith E. Levine[1]

Research Efforts to Support OrgS analysis

- Solution stability, we have evaluated OrgS that have been identified as the most abundant in PM samples for solution stability.
- Currently evaluating the stability of OrgS loaded onto filters with Ann Dillner and Marife Anunciado at UC Davis
- Have established IC methods for quantitation.
- Beginning work to validate methods using UPLC/MS to perform Non targeted and targeted analysis to measure OrgS, OrgN, carboxylic acids and sugars in PM samples.

Non-Targeted Analysis

Non-Targeted Analysis is an approach to characterize thousands of unknown chemicals that have not been previously measured.

Typically, this involves a high-resolution mass spectrometer coupled to either gas or liquid chromatography.

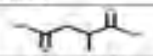
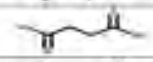
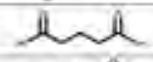
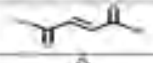
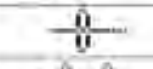
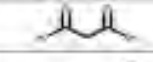
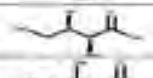
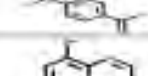
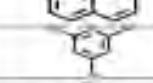
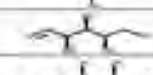
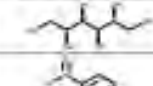
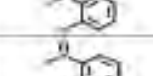
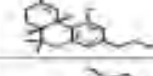
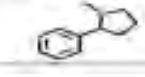
The approached is qualitative rather than quantitative.

Sample Prep:

- $PM_{2.5}$ nylon filters were collected during the 2020 calendar year for the IMPROVE network
- Filters were extracted in deionized water
- Multiple (4-7) time points were composited, dried, and concentrated by site

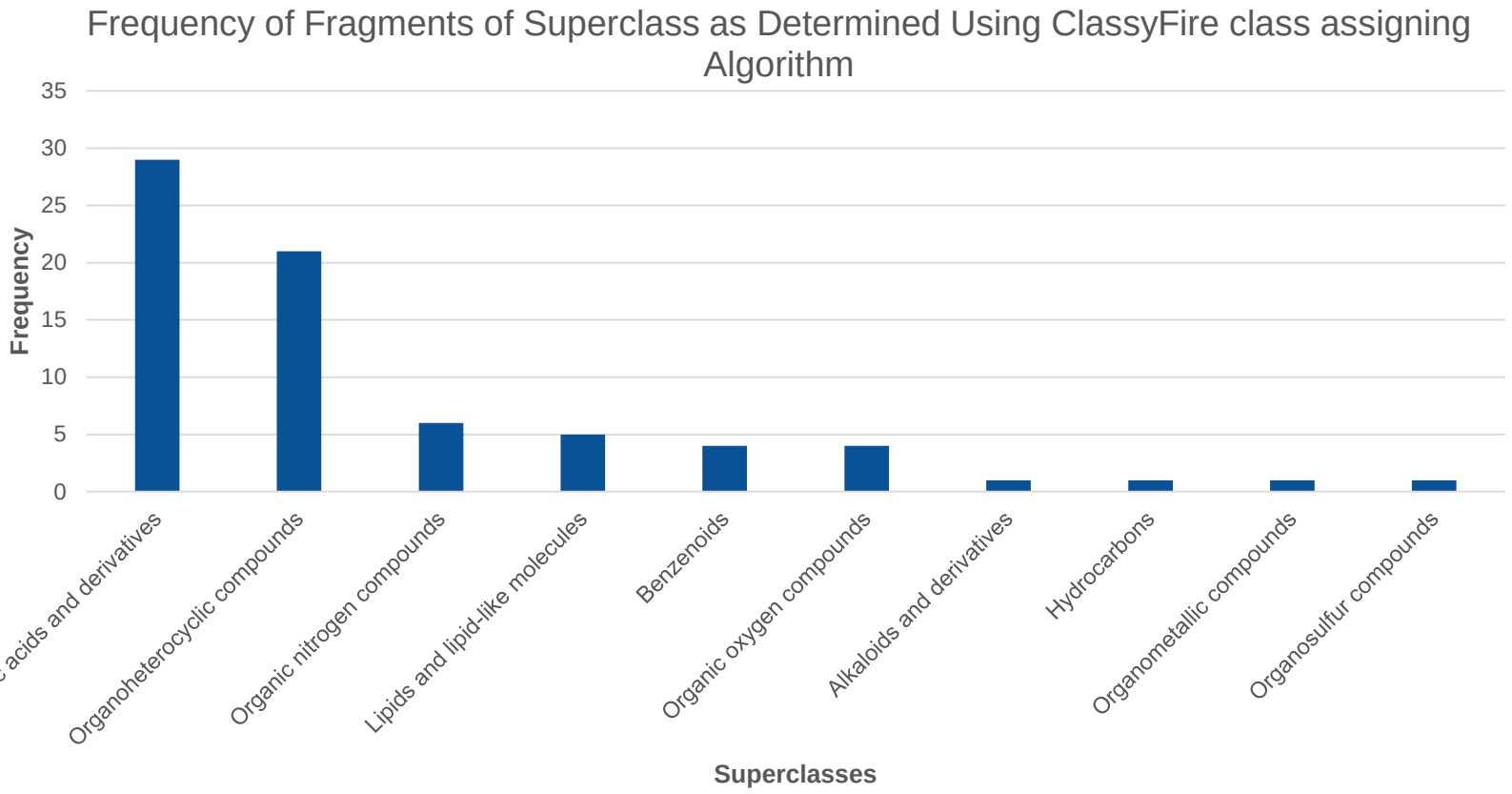
Separation and Detection

- UPLC – HRMS/MS

Name	CAS #	LOC	Polarity	Structure	Source
Methyl Succinic Acid	498-21-5	1	-		SOA', wildfires
Succinic Acid	110-15-6	1	-		SOA', wildfires
Glutaric Acid	110-94-1	1	-		SOA', wildfires
Fumaric Acid	110-17-8	1	-		SOA', wildfires
Methane Sulfonic Acid	75-75-2	2	-		SOA', wildfires
Malonic Acid	141-82-2	2	-		SOA', wildfires
Indole-3-acetic Acid	87-51-4	2	-		Plant Hormone and Metabolite
Cyanuric Acid	108-80-5	2	-		Industrial
L-Threonic Acid	7306-96-9	2	-		Plant Metabolite
2,3-Dihydroxybenzoic Acid	303-38-8	2	-		Plant Metabolite
Terephthalic Acid	100-21-0	2	-		Industrial
3-Hydroxyquinoline	148-24-3	2	+		Industrial
Melamine	108-78-1	2	+		Industrial
Xylose	58-86-6	2	-		Plant Sugar
Mannitol	69-65-8	2	-		Plant Sugar
Nitrophenol	100-02-7	2	-		Industrial
Nitrocatechol	3316-09-4	2	-		By-product of Nitrophenol
Delta-9 THC	56354-06-4	4	+		Plant
Nicotine	54-11-5	2	+		Plant

The Occurrence of Water Soluble Organic Pollutants in $PM_{2.5}$ Collected During Wildfire Events in the Western United States
Phillip Berger[1], Nicole Manalis[1], Sophie Brenner[1], Tracy Dombek[1], Imari Walker[1]

Results



A subset of the 386 compounds underwent further analysis to determine their potential chemical ontology via an algorithm called ClassyFire.

73 compounds were assigned ClassyFire chemical ontologies for analysis. The figure represent the frequency of a specific superclass or class assignment to these compounds. This gives us identifications with a confidence level 3 (uses in silico fragmentation modeling).

Thank you

Acknowledgments

RTI Team: Sophie Brenner, Miranda De Boskey, Katarina Lindskog, Nicole Manalis, Laurie Stella, Laura Haines, MaCade Hunter, Imari Walker, Phillip Berger and Keith Levine

UC Davis Team: Ann Dillner & Marife Anunciado, Indu Thekkemeppilly Sivakumar, Nicky Smith, Alex Murrain, Anthony Kawamoto, Gabriela A Rico Monrroy, Tasha Coleman, and Sarahi Lynneth Vargas Garcia

delivering **the promise of science**
for global good

RTI INTERNATIONAL

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