



Multi-State Field Demonstrations of Advanced Near Source Ethylene Oxide (EtO) Measurement Techniques in Various Climate Conditions

National Ambient Air Monitoring Conference

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Background

- Ethylene oxide (EtO) continues to be identified as a national cancer contributor and regional cancer risk driver in the 2017-2020 EPA AirToxScreen risk assessments
- EPA finalized new EtO emissions standards for chemical plants (“HON” rule) and commercial sterilizers in 2024
 - For HON Rule, fenceline monitoring will be required after 2 years following time-integrated EPA Method 327 based on EPA Method TO-15A

Development of accurate EtO measurement techniques are needed to inform emissions mitigation efforts and risk assessments



EtO Measurement Challenges

- Recent advancements have been made in EtO measurement technologies that can meet regulatory standards (Performance Specification (PS) 19) for continuous source emissions monitoring
- Near source and ambient EtO monitoring remains a measurement challenge:
 - Need high accuracy, high time resolution, sensitive, selective, and easy implementation

Source Emissions



Measurements in complex sampling conditions

Near Source Monitoring



Rapid measurements for emissions detection and fenceline monitoring

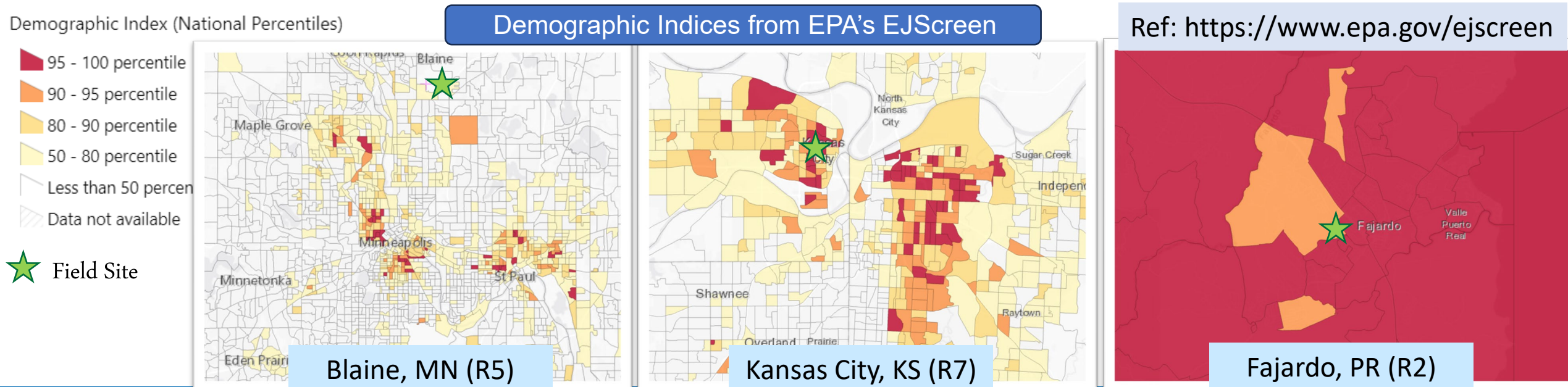
Ambient Monitoring



Trace-level measurements (<10 parts per trillion by volume (pptv))

Regional-ORD Applied Research Effort (ROAR)

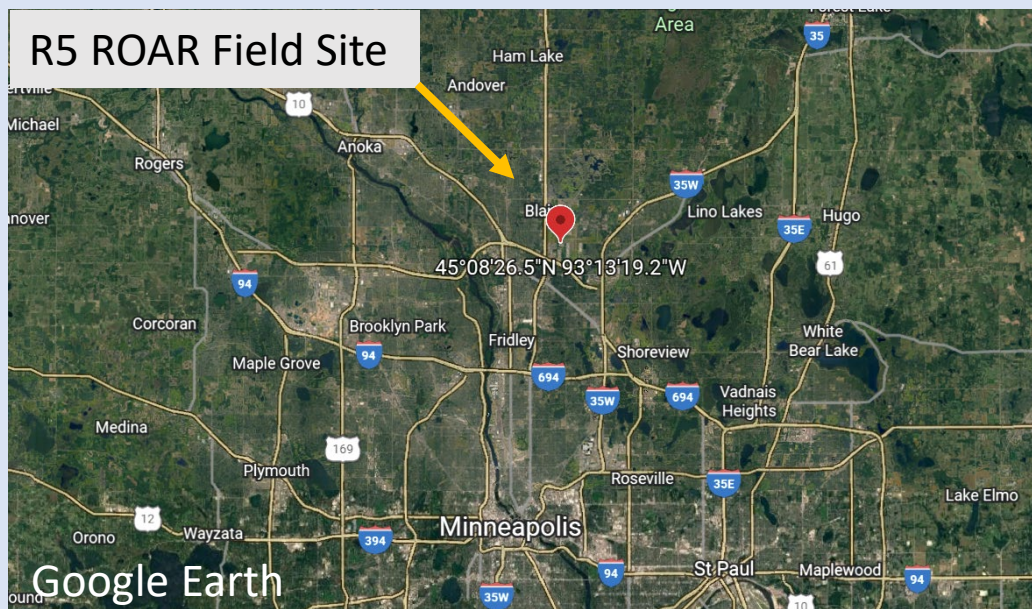
- ROAR project involving EPA ORD, Regions 2, 5, and 7, and state partners
- Project aims to develop and demonstrate novel, cost-effective measurement tools to quantify near source and ambient EtO concentrations in communities
 - Comparison of multiple measurement approaches (online and time-integrated methods) under a range of climate conditions near sources and in urban background
 - Field evaluations conducted near communities with Environmental Justice (EJ) concerns



R5 and R7 ROAR Field Sites

R5 ROAR Field Site

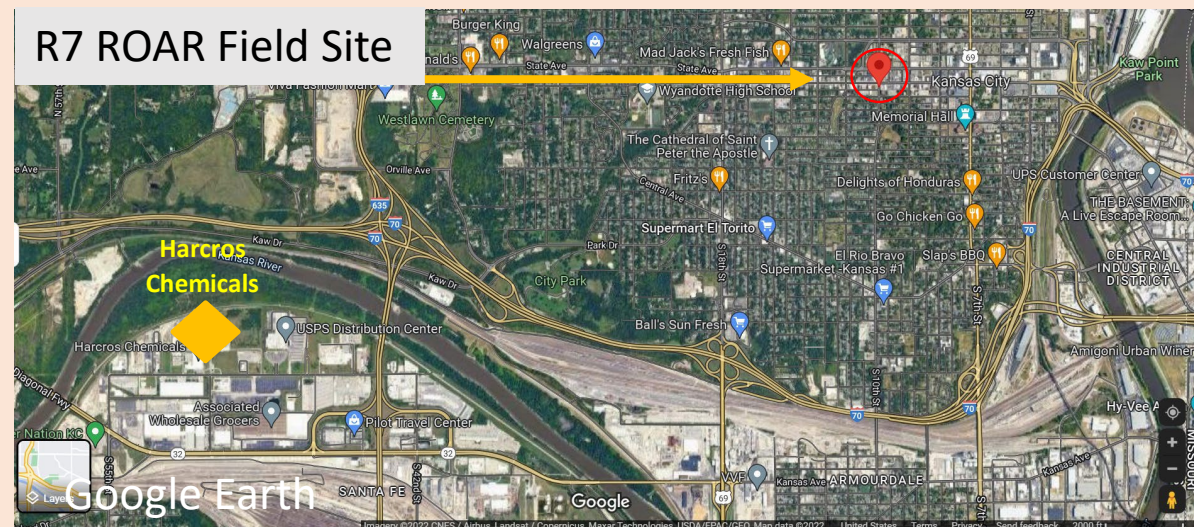
- State air monitoring shelter at Anoka County Airport Air Monitoring Site (Blaine, MN)
- NCORE/PAMS/SLAMS site operated by Minnesota Pollution Control Agency
- Represents cold winter climate conditions and urban regional "background" ambient site



R7 ROAR Field Site

- State air monitoring shelter at JFK Site (Kansas City, KS)
- NCORE/PAMS site operated by Kansas Dept. of Health and Environment
- Approx 3.6 miles downwind of EtO emitting chemical facility representing near source site

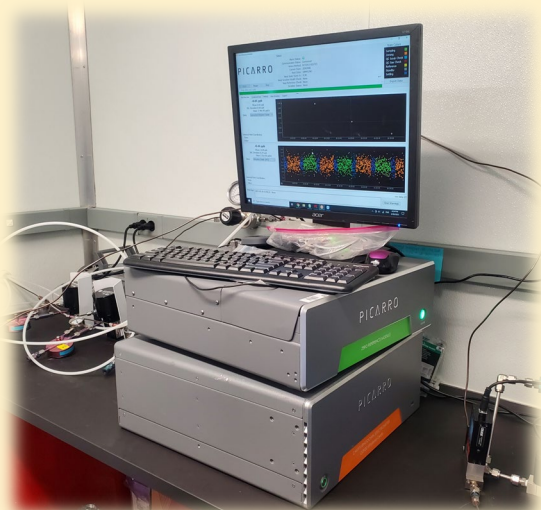
National CORE (NCORE); Photochemical Assessment Monitoring Stations (PAMS); State and Local Air Monitoring Stations (SLAMS)



R5/7 EtO Measurement Approaches

Continuous Approaches

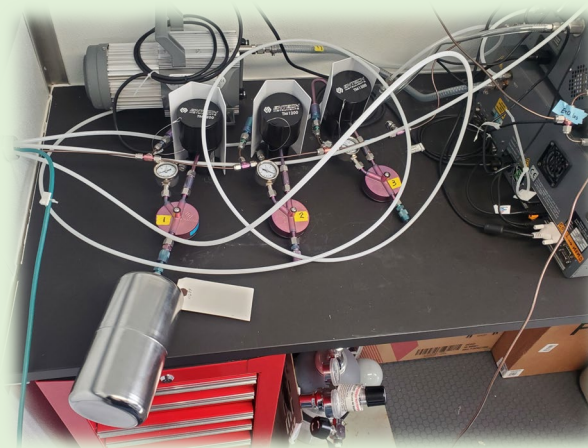
- R5 ROAR: tested AROMA-VOC Analyzer
- Preconcentration-Cavity Ringdown Spectroscopy (CRDS)
- 30 min measurement cycle (5-min sampling)
- MDL ~ 10 pptv



- R7 ROAR: tested Picarro G2920 CRDS with Zero Reference Module
- ~10 min measurement cycle (4-min sampling, 4 min zeroing, 1 min equilibration)
- MDL ~ 0.1 ppbv

Time-Integrated Approaches

- Canister sampling and analysis following EPA Method TO-15A
- MDL ~ 10 pptv
- R5 ROAR: 6 L coated canisters sampled over 22 hr using Entech 1800 Canister Autosampler

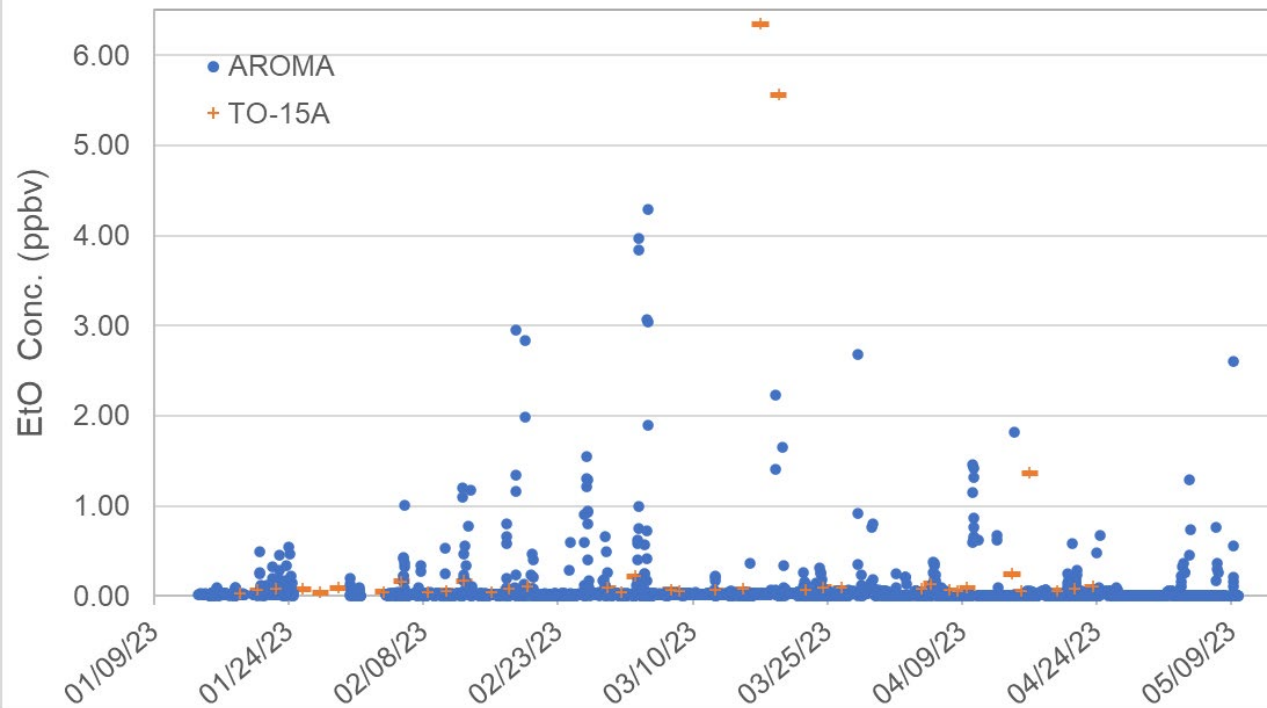


- R7 ROAR: 1.4 L coated canisters sampled over 23 hr using Entech CS1200 Passive Sampler and TM1200 timer

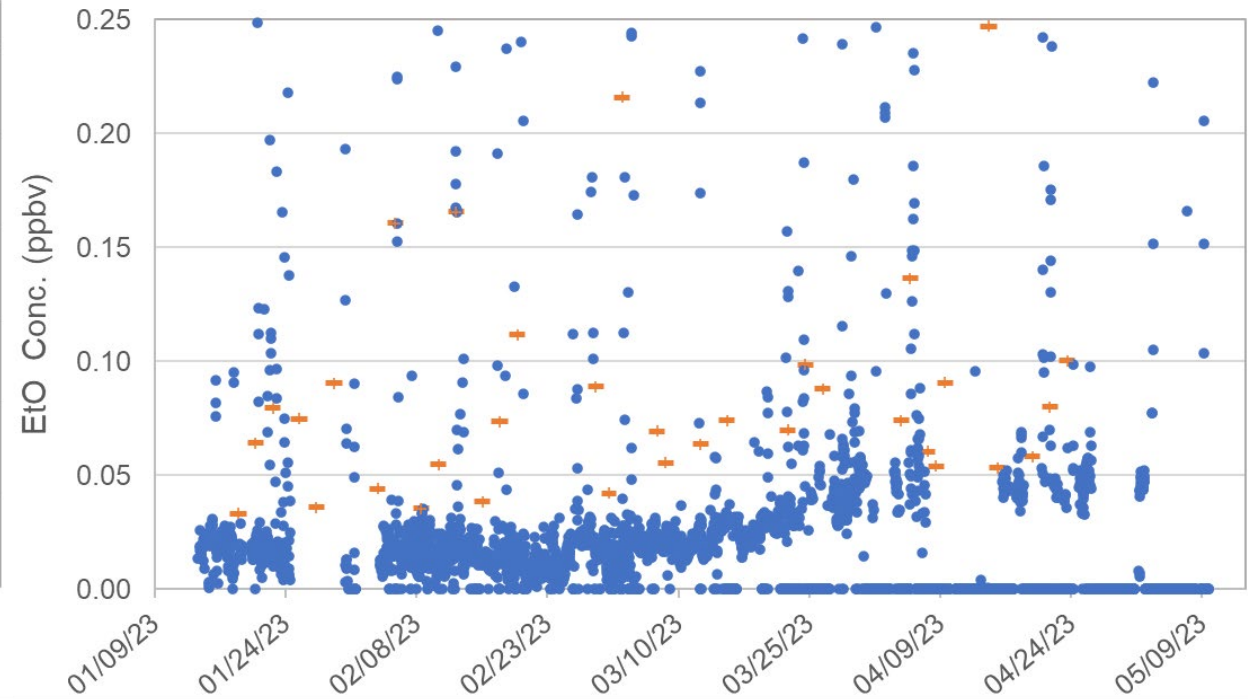
R5 ROAR EtO Measurements

- Short duration elevated EtO values (>1 ppbv) were observed for both AROMA (5 min sampling/30 min measurements) and TO-15A measurements (22 hr. averages)

AROMA & TO-15A Measurements

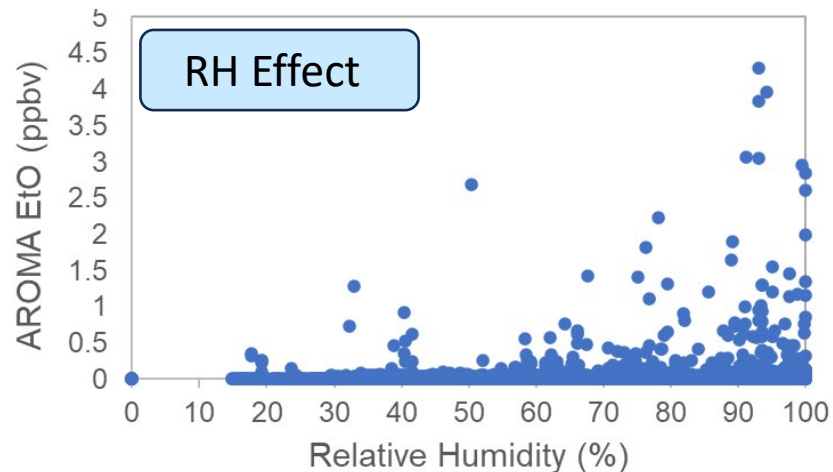
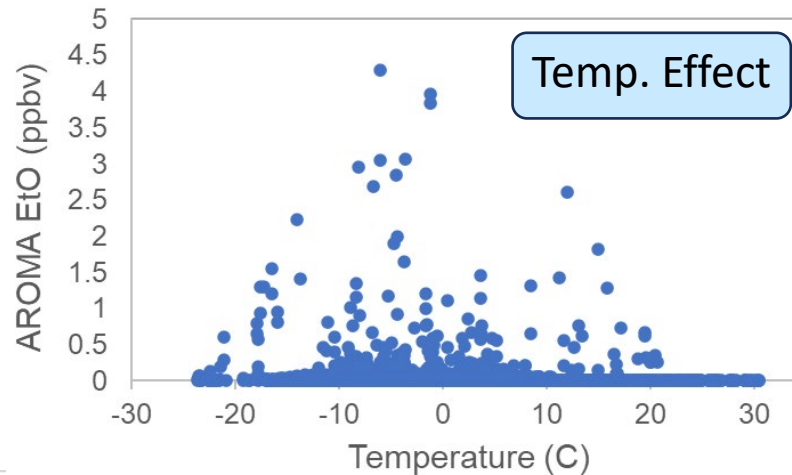
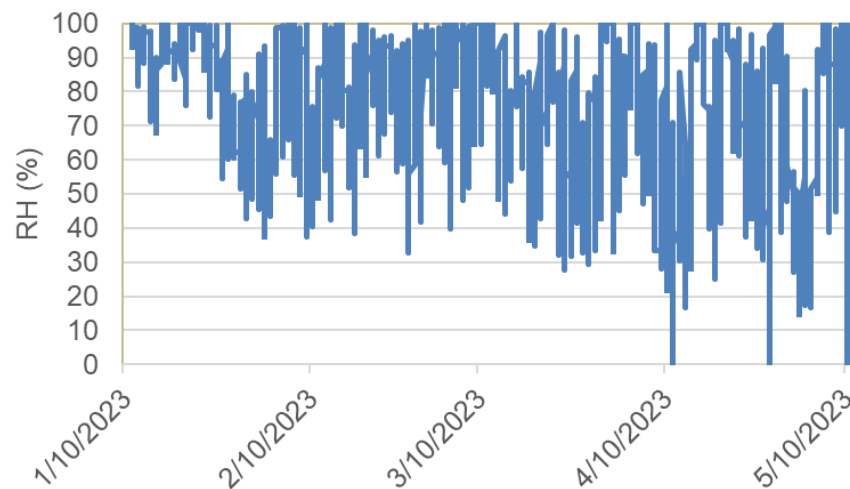
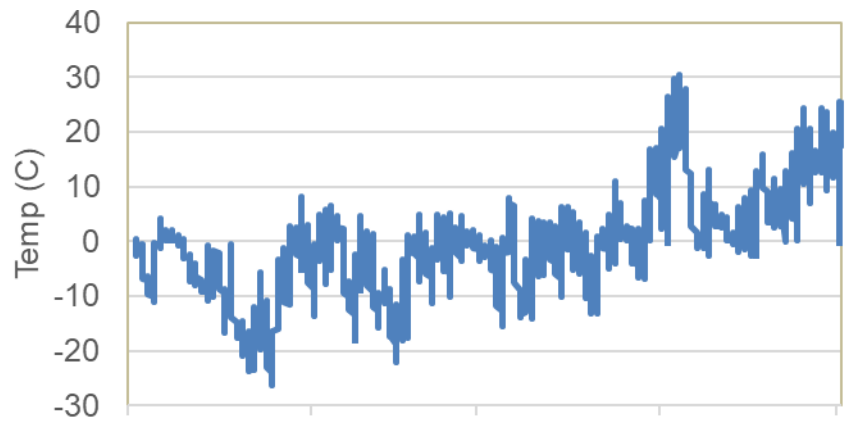


Expanded to EtO < 250 pptv

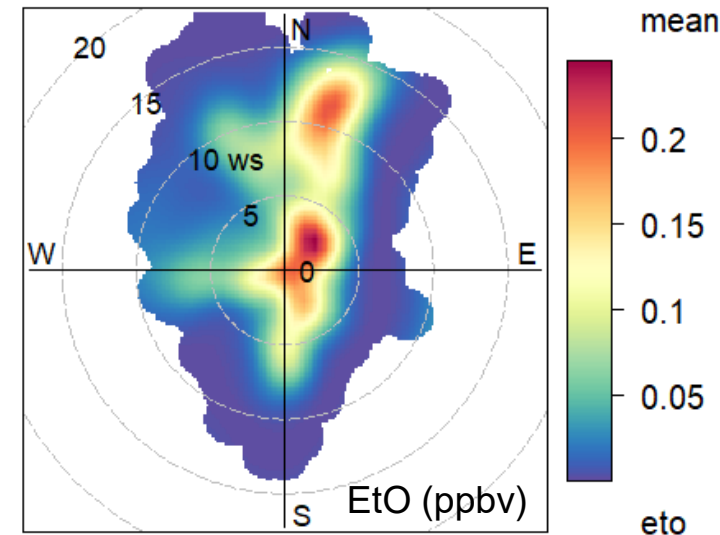
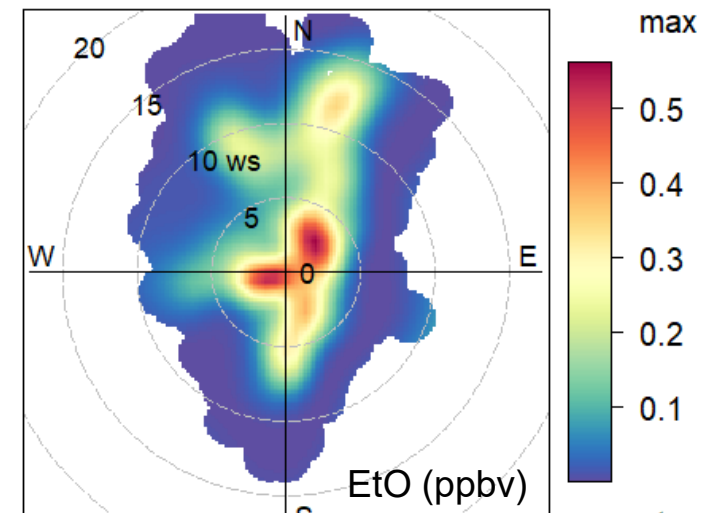


AROMA and Climate Conditions

Temperature and Relative Humidity (RH)

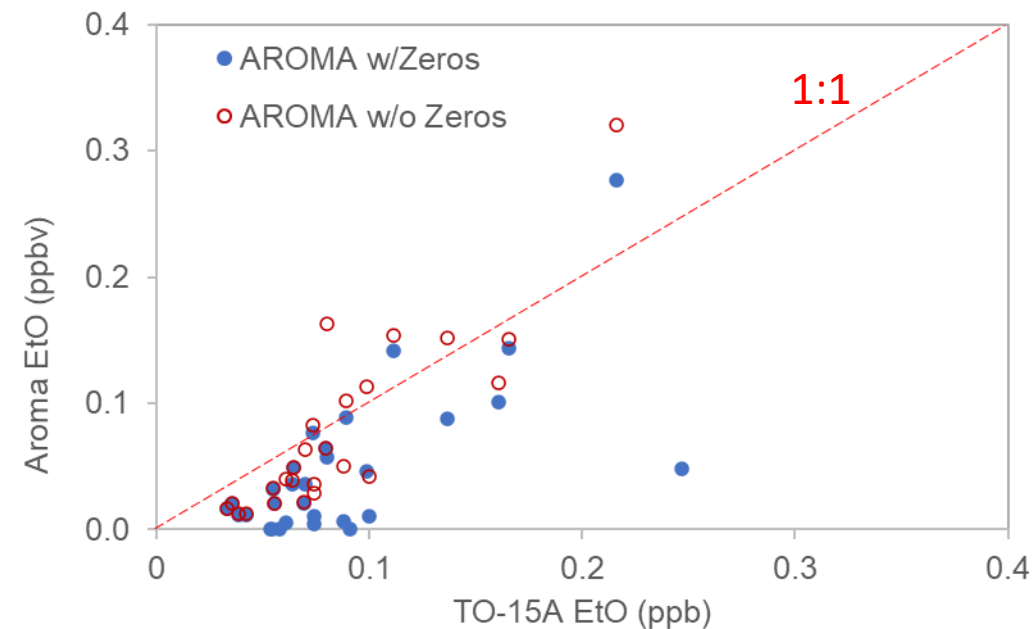
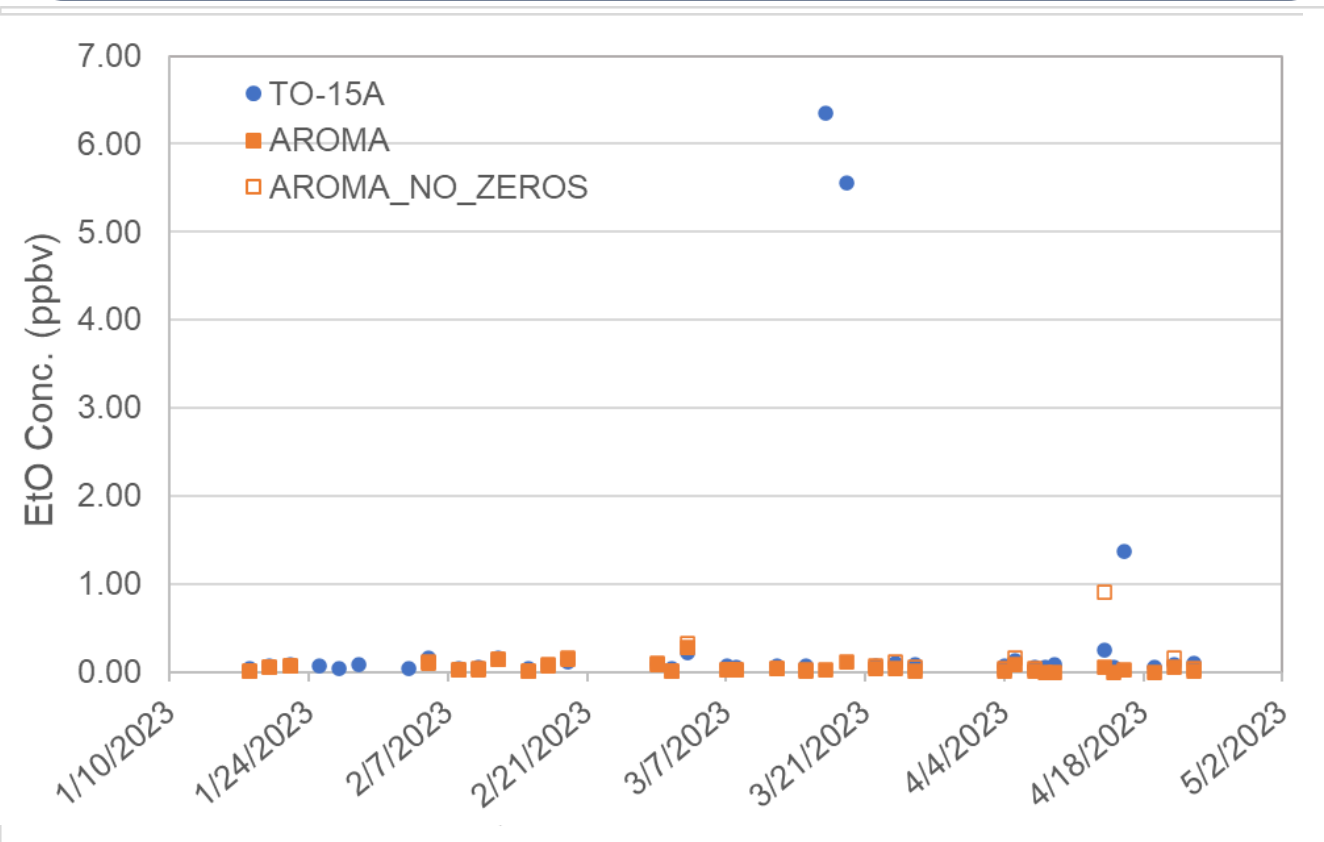


EtO Polar Plots



AROMA and TO-15A Comparison

- AROMA data is time-averaged to match canister sampling times
- A few elevated TO-15A values > 1ppbv skewed the correlations with AROMA values

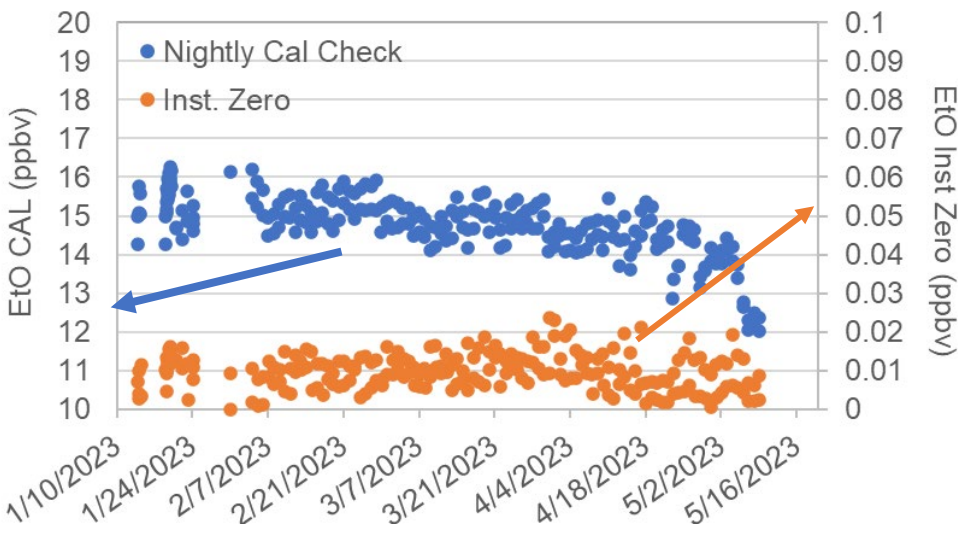


STUDY STATISTICS	AROMA EtO (ppbv) [w/o Zeros]	TO-15A EtO (ppbv) [w/o 3 outliers]
MEAN	0.043 [0.070]	0.49 [0.144]
STD	0.21 [0.26]	1.4 [0.27]
MIN	0 [1.44E-12]	0.033 [0.033]
MAX	4.3 [4.3]	6.8 [1.46]
N	3864 [2396]	49 [46]

R5 ROAR QA/QC

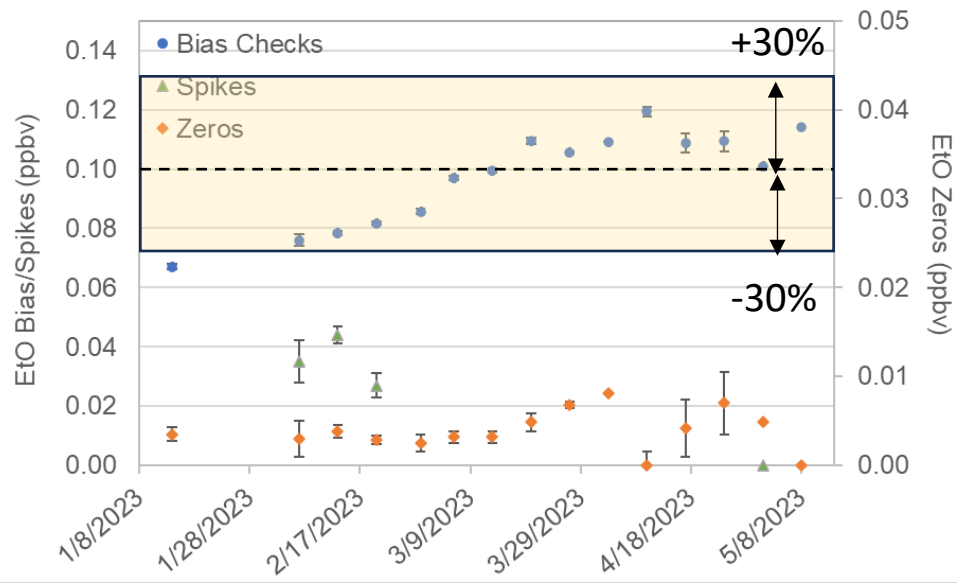
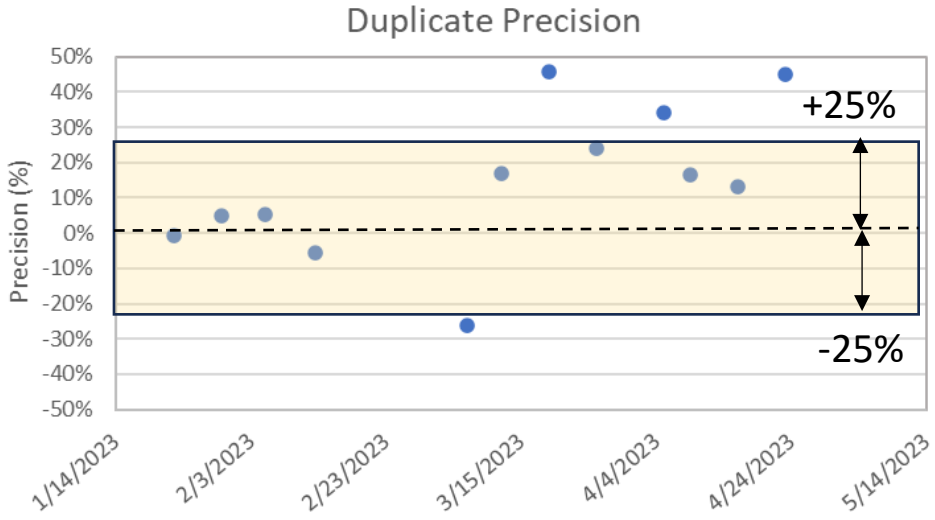
AROMA

TO-15A



Bias check at 10 ppb confirmed calibration bias of the 10 ppb nightly cal. check

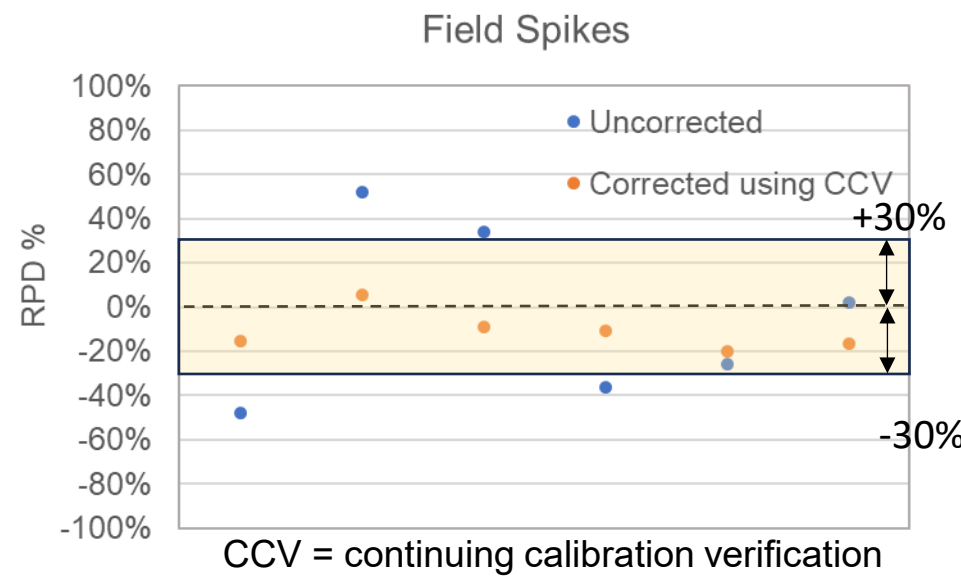
Bias check recoveries increased over time



Field blanks ranged from <MDL to 31 pptv

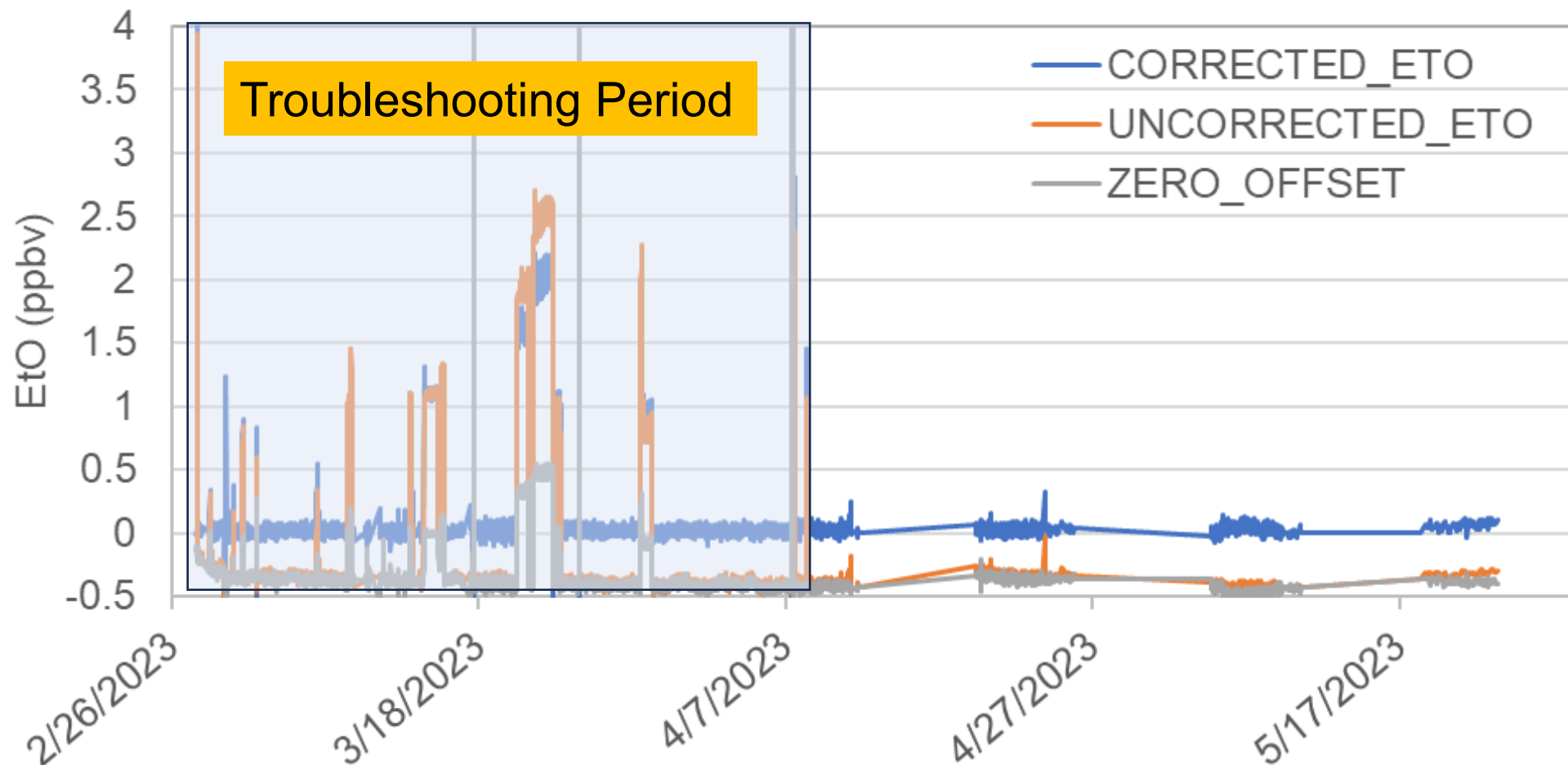
Field spikes were 0.5 to 1 ppbv EtO conc.

Trip blanks leaked and EtO values were up to 13 ppbv; cause is unclear



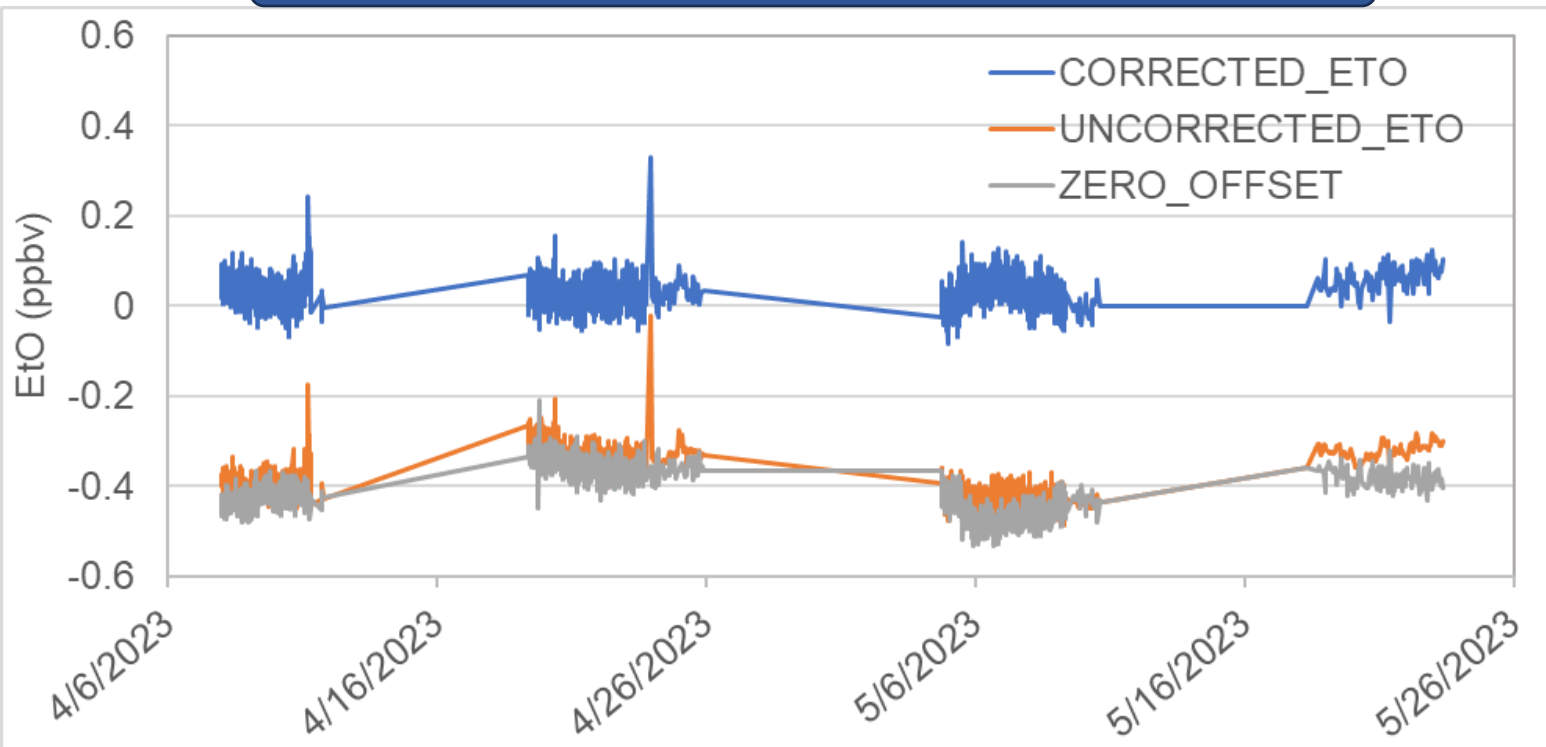
R7 ROAR Results – ZRM+Picarro G2920

- Half of study period was testing system to understand low bias check recoveries; faulty internal ZRM component was repaired in early April



R7 ROAR Results – ZRM+Picarro G2920

ZRM/G2920 Time Series Post-Repair



Summary Statistics

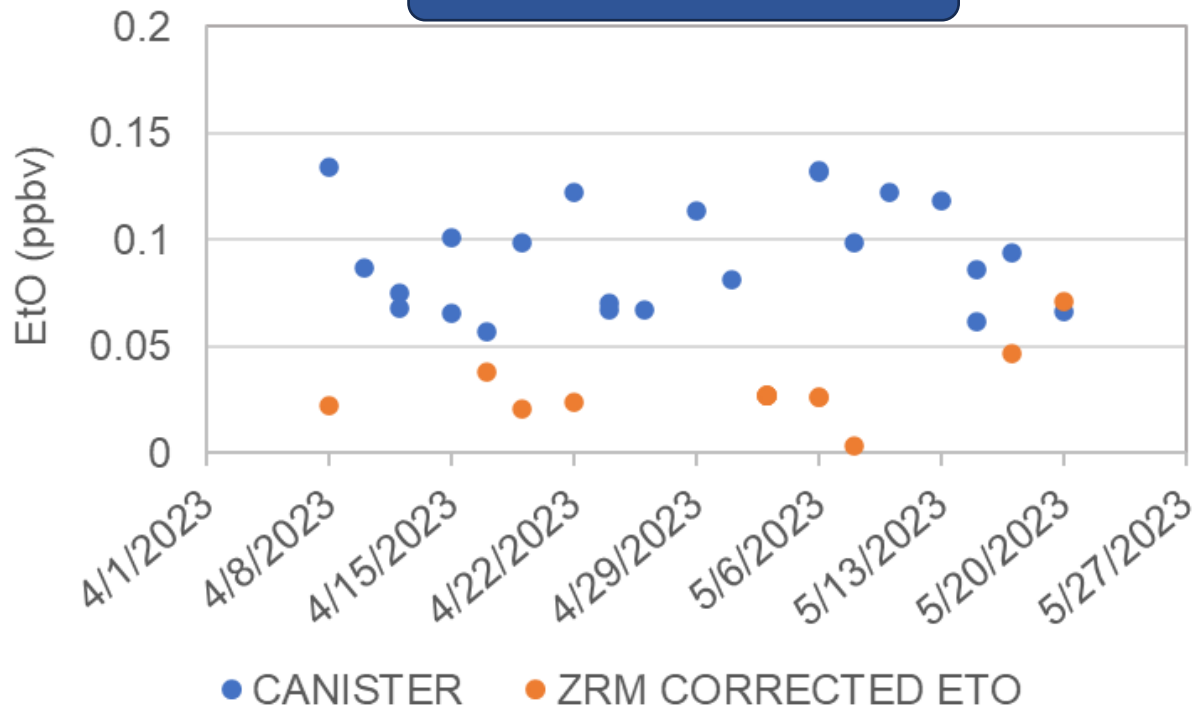
	Uncorrected EtO (ppbv)	Corrected EtO (ppbv)
Mean	-0.377	0.030
Stdev	0.052	0.034
Max	-0.022	0.332
Min	-0.508	-0.084
N	2097	2097

ZRM Method: 4 min. sampling, 4 min. zeroing, 1 min. transition = 10 min per measurement

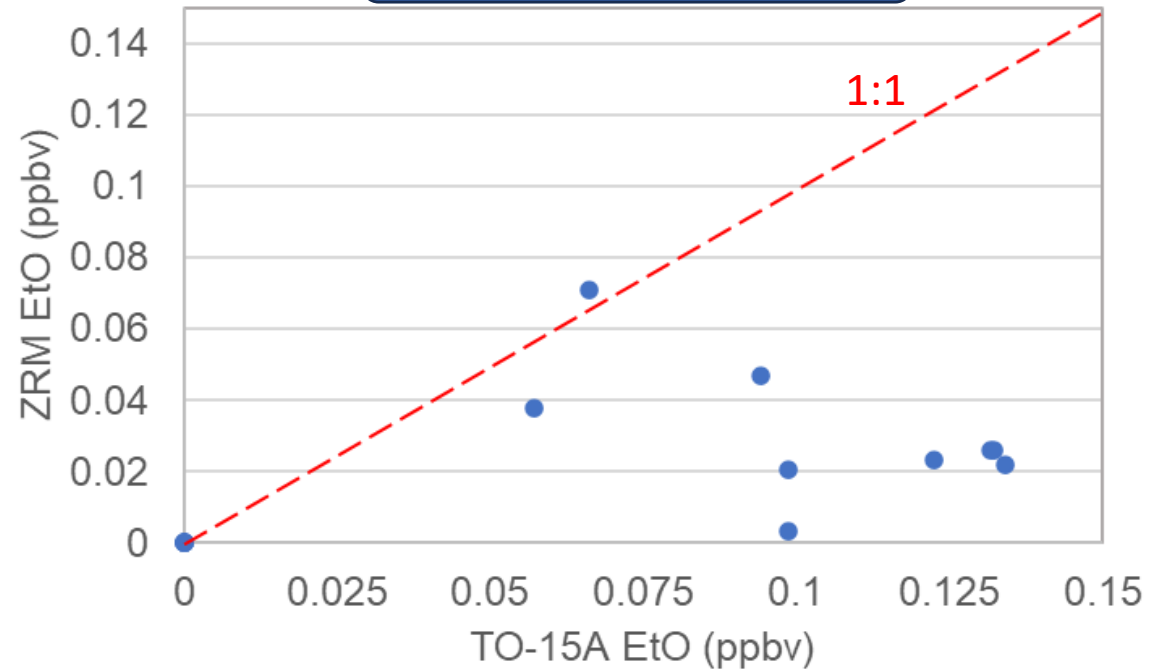
ZRM/G2920 and TO-15A Comparison

- ZRM/G2920 10-min. data were averaged over canister 23-hr. sampling times
- TO-15A EtO values generally higher than ZRM values with weak correlation

Time Series



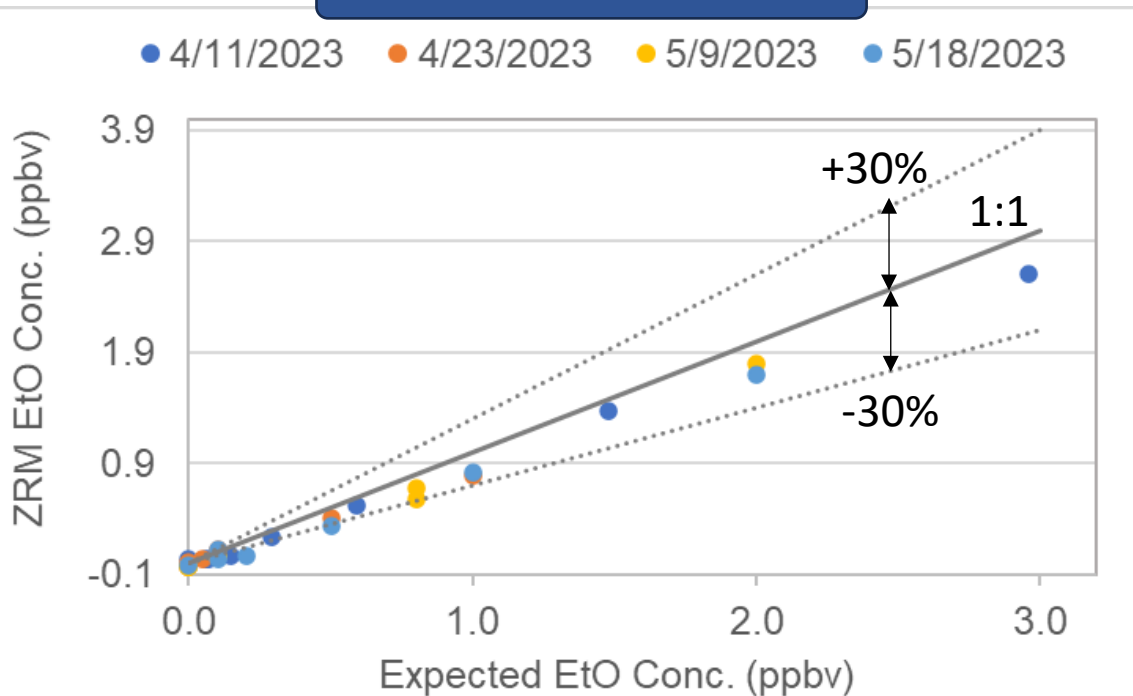
Correlation Plot



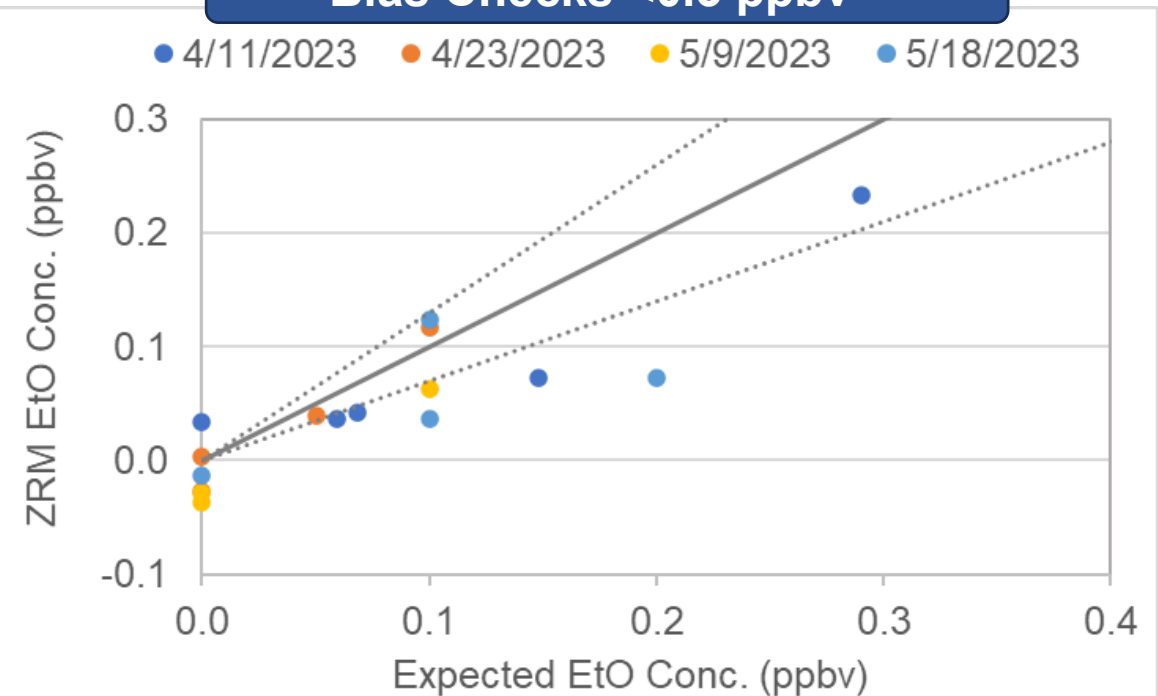
R7 ROAR QC

- Consistent bias check calibration curves during later half of study
- MDL based on zeros/low bias checks ~100 pptv

Bias Checks



Bias Checks <0.3 ppbv



TO-15A QC: Field Spikes = -17 to -42% recovery of 0.5 ppbv;
Field Blanks = <MDL to 0.018 ppbv;
Duplicate Precision = -32 to 43%

R5/R7 Study Challenges

R5 ROAR

- AROMA was approaching required maintenance; analyzer struggled to quantify <50 pptv EtO towards latter half of study (non-detects increased)
- Trip blanks leaked with elevated EtO measured; cold temperature effect?

R7 ROAR

- Faulty ZRM switching valve was introducing EtO scrubbed zero air into sample air
- ZRM software stopped frequently leading to reduced data completeness



R2 EtO Measurement Approaches

EtO Air Monitoring System

- Custom climate-controlled Trailer-based EtO Air Monitoring System (TEAMS)
- Operated Picarro G2920 for EtO measurements
- Meteorological measurements (wind, temp., relative humidity (RH))
- Onboard automated canister sampling based on EtO alarm threshold chosen for this site
- Automated safe power down during power loss and start up



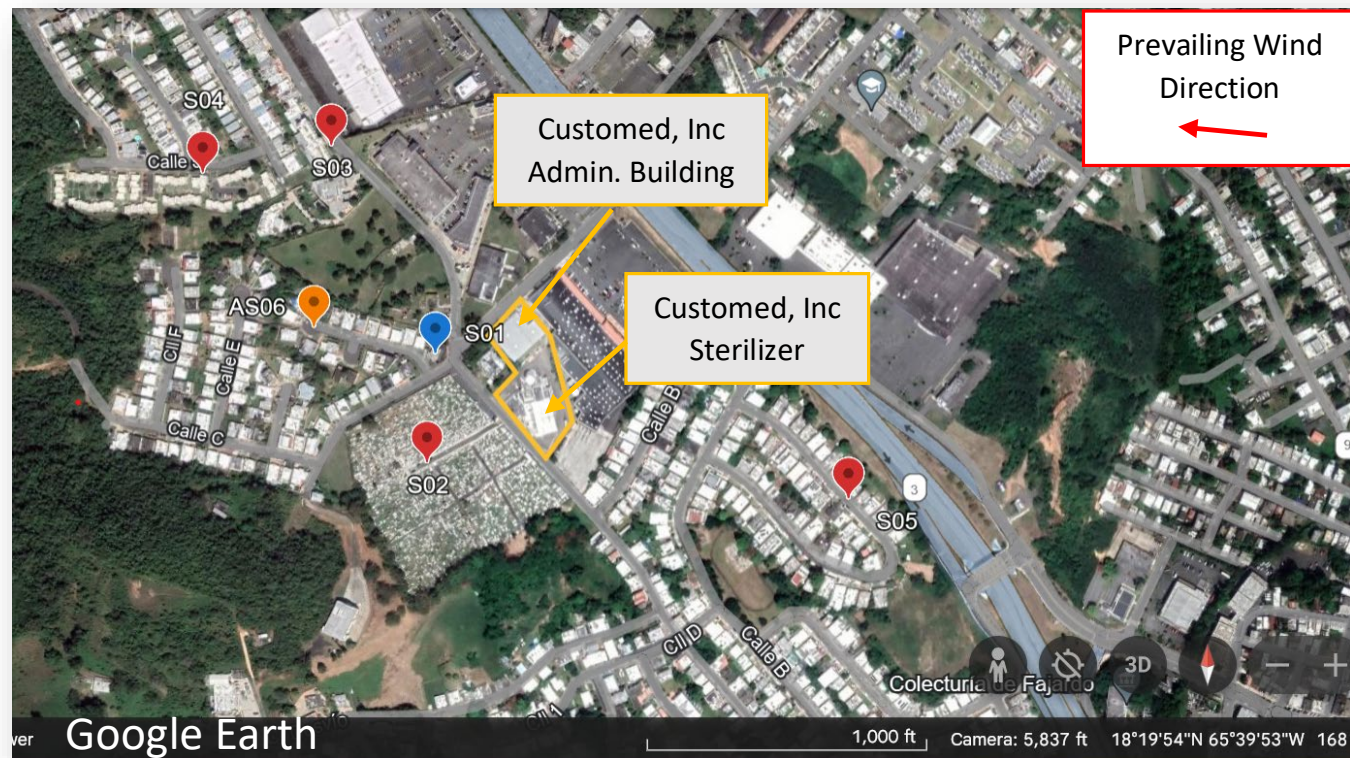
Remotely Operated Canister Sampler (ROCS)

- Solar powered EPA developed sampling technology
- Remote sampling can be initiated by text or by software
- Testing automated triggering through EtO alarm generated by data logging software (*in progress*)



R2 ROAR Field Sites

- Primary site (blue) is at Puerto Rico Aqueduct and Sewer Authority (PRASA) Drinking Water Pump Station across the street and downwind from commercial sterilizer in EJ community
- Additional sites (red) are remotely operated canister samplers (ROCS) installed on utility poles in the community where estimated EtO lifetime excess cancer risk levels were >100 in a million



Deployment is still in progress

<https://www.epa.gov/hazardous-air-pollutants-ethylene-oxide/forms/fajardo-puerto-rico-customed-inc>

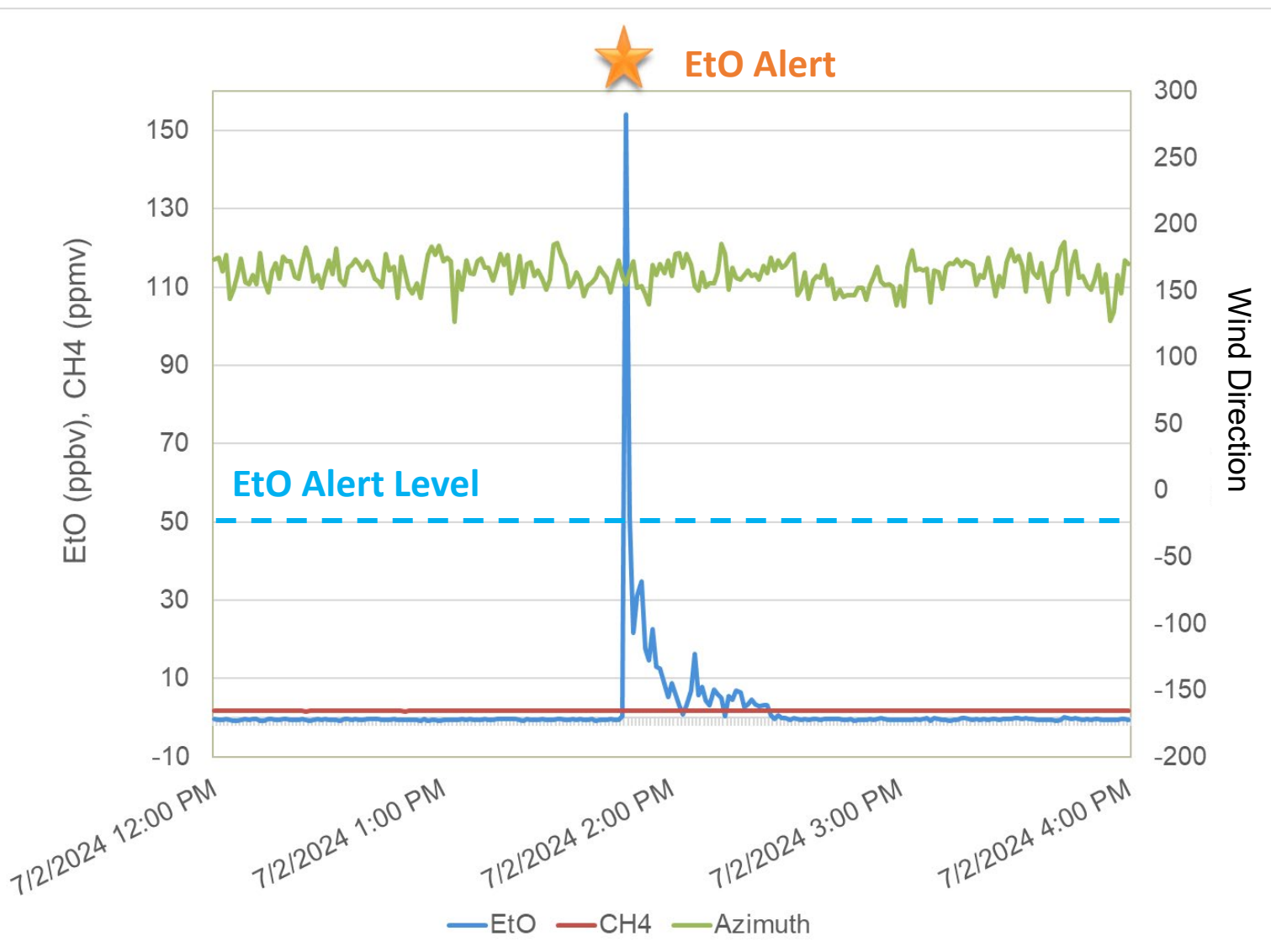
R2 ROAR Status

- Trailer-based EtO Air Monitoring Station (TEAMS) deployed in Fajardo, PR in late May 2024 (w/o trailer)
 - Planned to continue deployment through August 2024
- ROCS units were installed in early August:
 - Triggered by Envidas Ultimate following EtO alerts at specified EtO level
 - ROCS communication by MQTT is being tested in first field evaluation
- Mobile monitoring with Geospatial Measurement of Air Pollution (GMAP) platform was conducted in late May 2024

MQTT = Message Queuing Telemetry Transport



R2 ROAR Example EtO Event



- Short duration (1-2 hr) elevated EtO events during facility operating hours
- EtO alert was triggered during initial spike
- Wind direction was favorable for sampling downwind of facility emissions

Next Steps

- R2 ROAR deployment will be completed at the end of August 2024; this study marks the first field deployment of the TEAMS and ROCS using MQTT automated triggering
- The challenges and lessons learned from the R2/5/7 ROAR field efforts will inform upcoming ORD-Regional field demonstrations to further refine QA/QC
- Planned field efforts will be supported by the Inflation Reduction Act “Fenceline Air Monitoring and Screening Air Monitoring” Provision
- Project team will work towards developing best practices for near source/fenceline EtO air monitoring to inform EPA Regions and state/local/tribal air monitoring agencies

Acknowledgements

Authors:

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Thank You!

Questions?

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