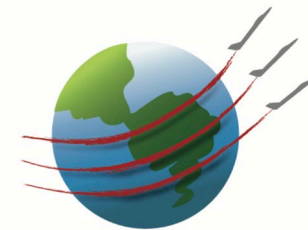


Ethylene Oxide Monitor with Ultra-Low Limit of Detection



AERODYNE RESEARCH, Inc.

Tara Yacovitch, Conner Daube, Christoph Dyroff,
J. Rob Roscioli, J. Barry McManus, Scott C. Herndon
NAAMC 2022

Acknowledgements:

Small Business Innovative Research



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Angela Haar, South Coast Air Quality Management District
Elisabeth Galarneau, Environment Canada

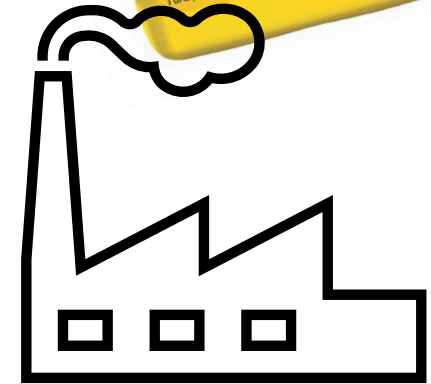
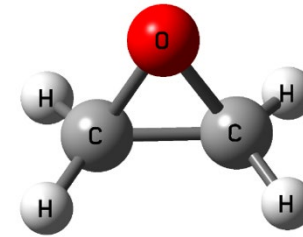
EPA Ethylene Oxide SBIR program

Contract Number: 68HERC21C0047

This work has not been reviewed by US EPA. The views and conclusions expressed are strictly based on the evaluation of Aerodyne's scientist only. US EPA funded this instrument development, but no formal review of these results has been conducted

Ethylene Oxide Background

- Toxic
 - Even at part-per-trillion levels
 - 10 ppt = one grain of sand out of 25 pickup truck beds
- Very reactive
 - Penetrates lungs, becomes free-radical = carcinogen
 - Useful for sterilization
 - Medical equipment (especially plastics)
 - Large-scale sterilization companies
 - Hospital sterilizers
 - Grains/powders (agriculture)
 - Used to make other chemicals
 - Ethylene glycol (antifreeze)



Pacemaker

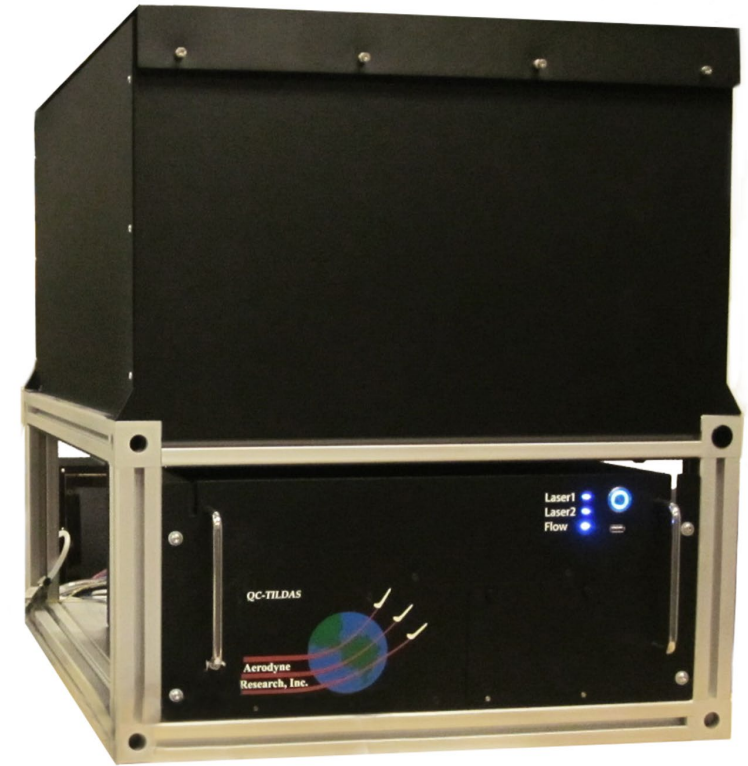


3M ethylene oxide sterilizer and cartridges

Aerodyne TILDAS for EtO detection

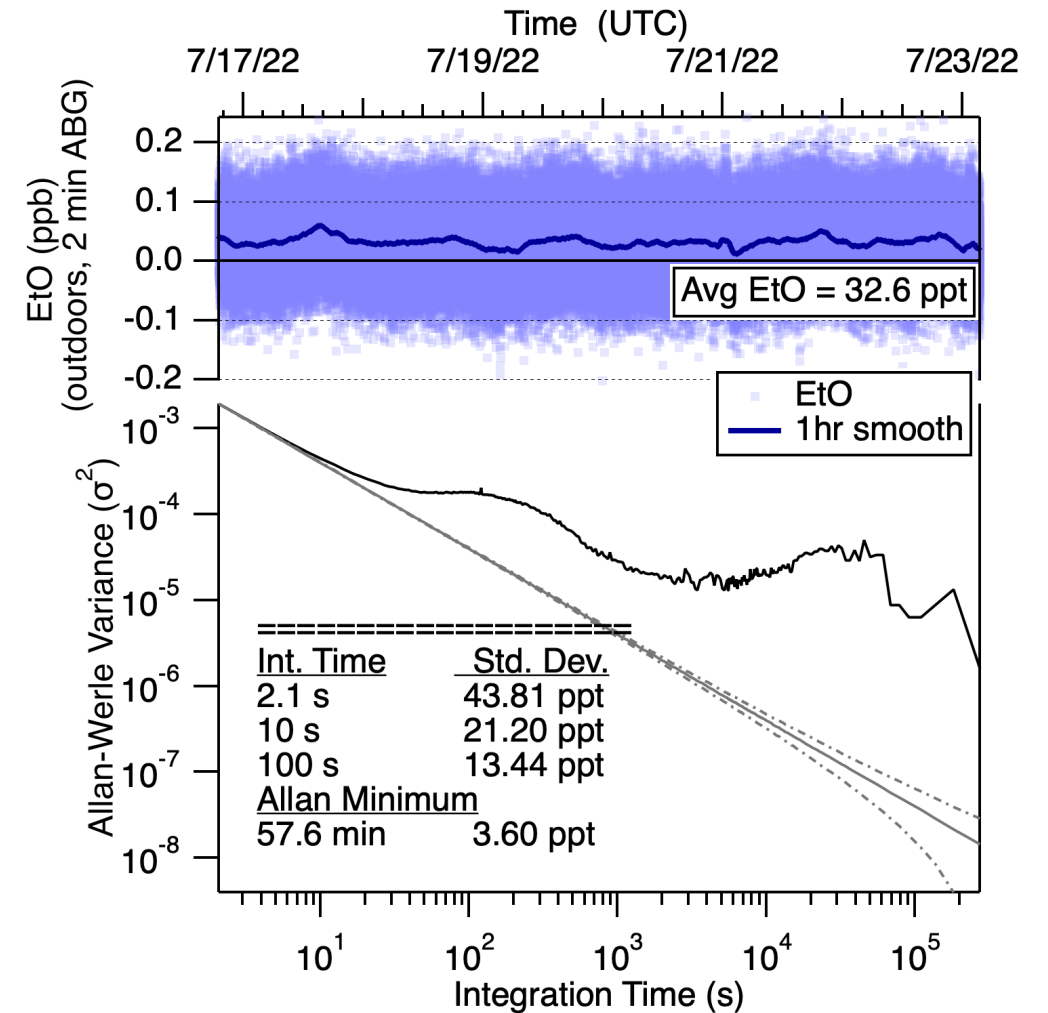
Tunable Infrared Laser Direct Absorption Spectrometer

- No pre-treatment or pre-concentration
- In-situ measurements
 - No storage concerns
- Selective and sensitive
 - <50 ppt (1s 1sigma);
 - Average down to << 10 ppt with aggressive backgrounding
- Mobile, rapid 1Hz measurements possible
 - Point source detection

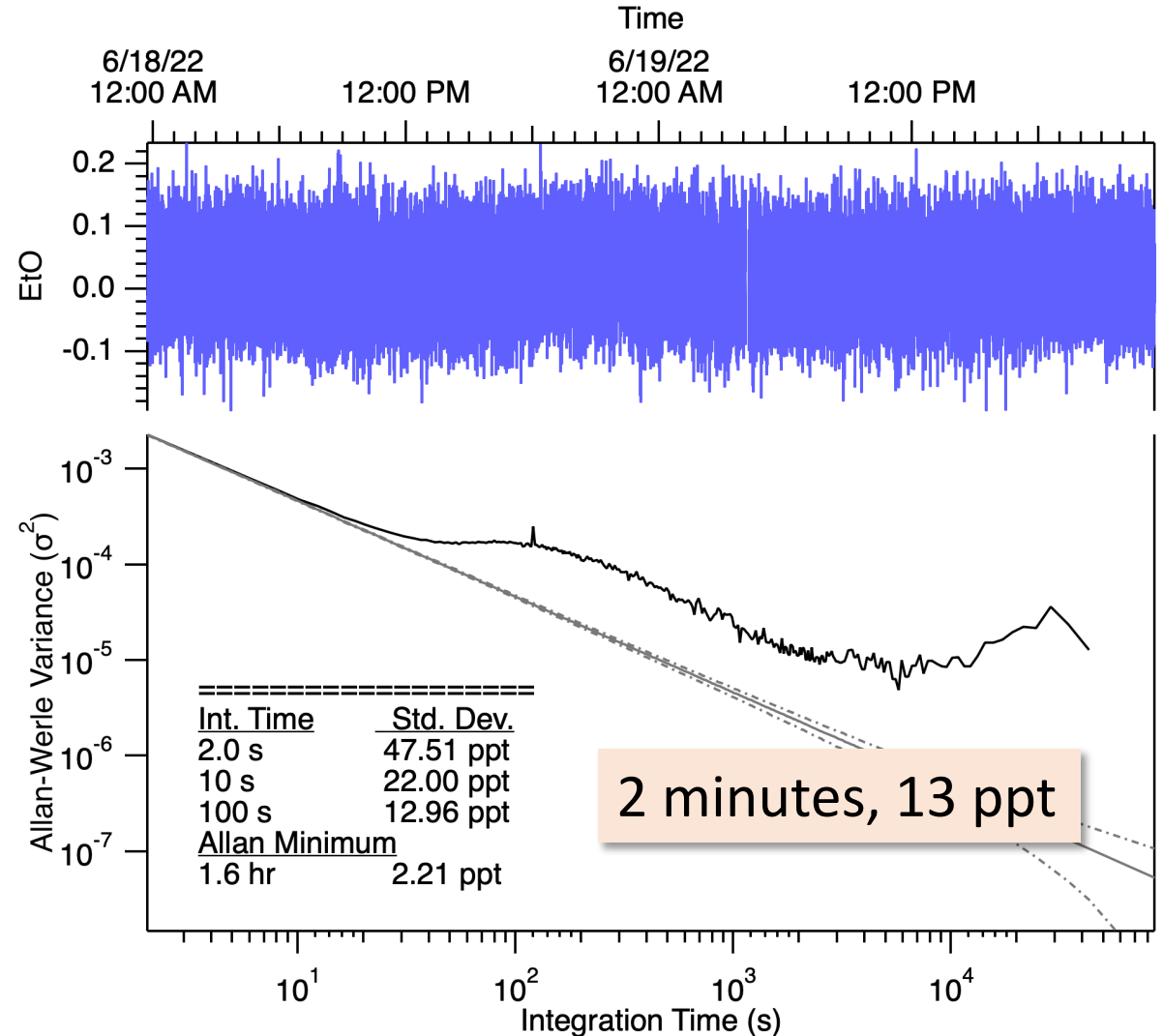
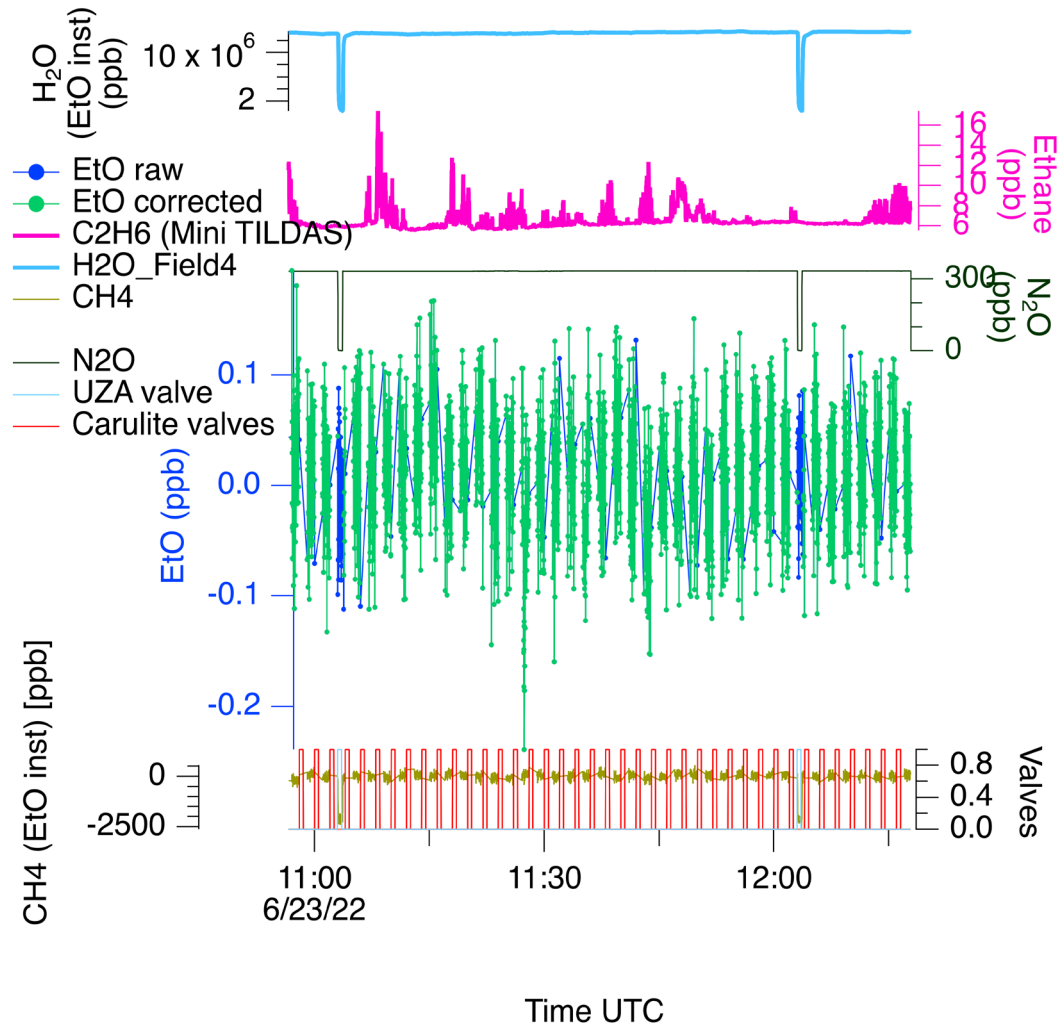


TILDAS-FD-EtO with 413 m Cell

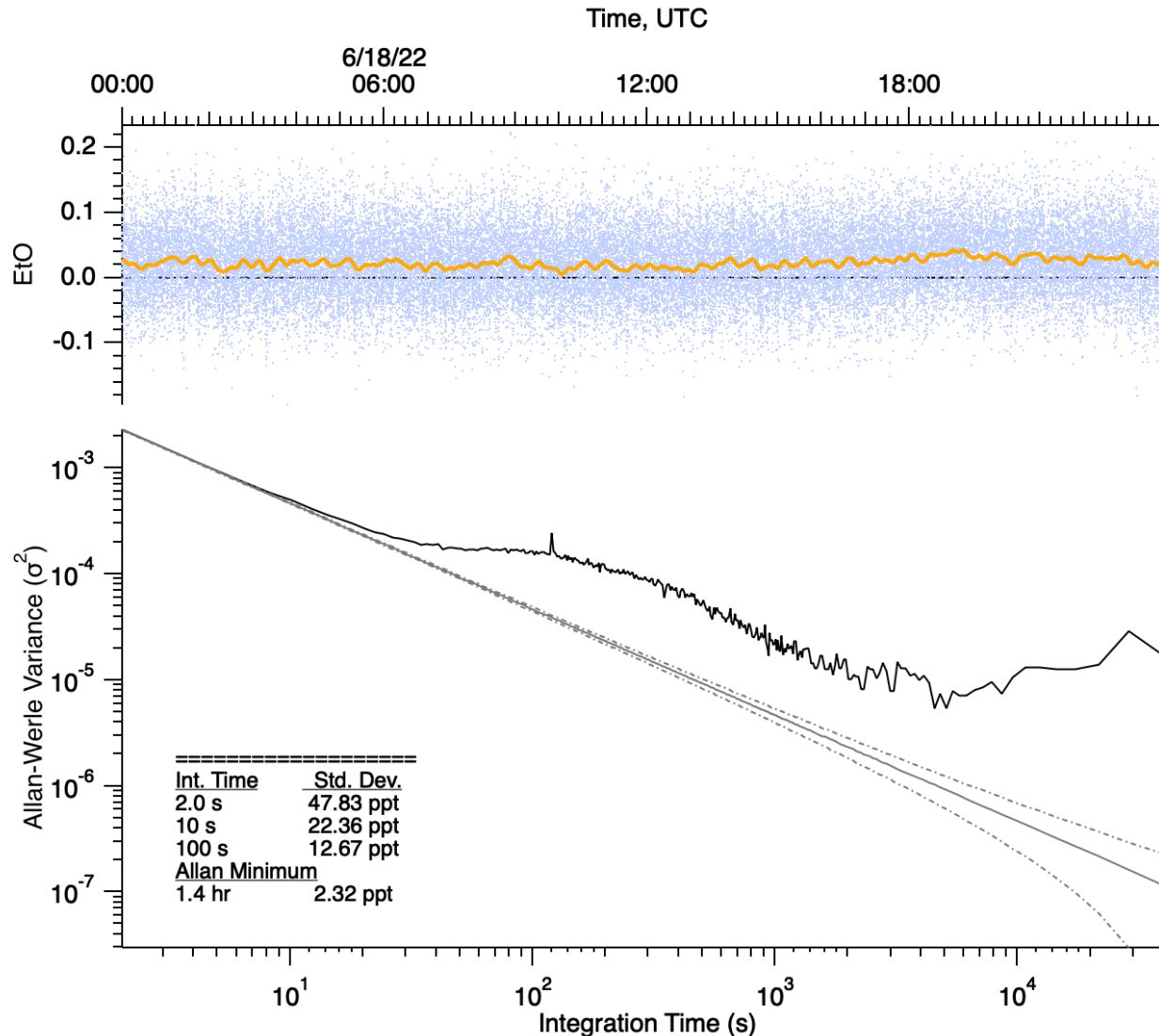
Instrument Performance



Aggressive ABG cycle = best averaging



24 hour Allan-Werle variance



Is this "real" EtO above background ?

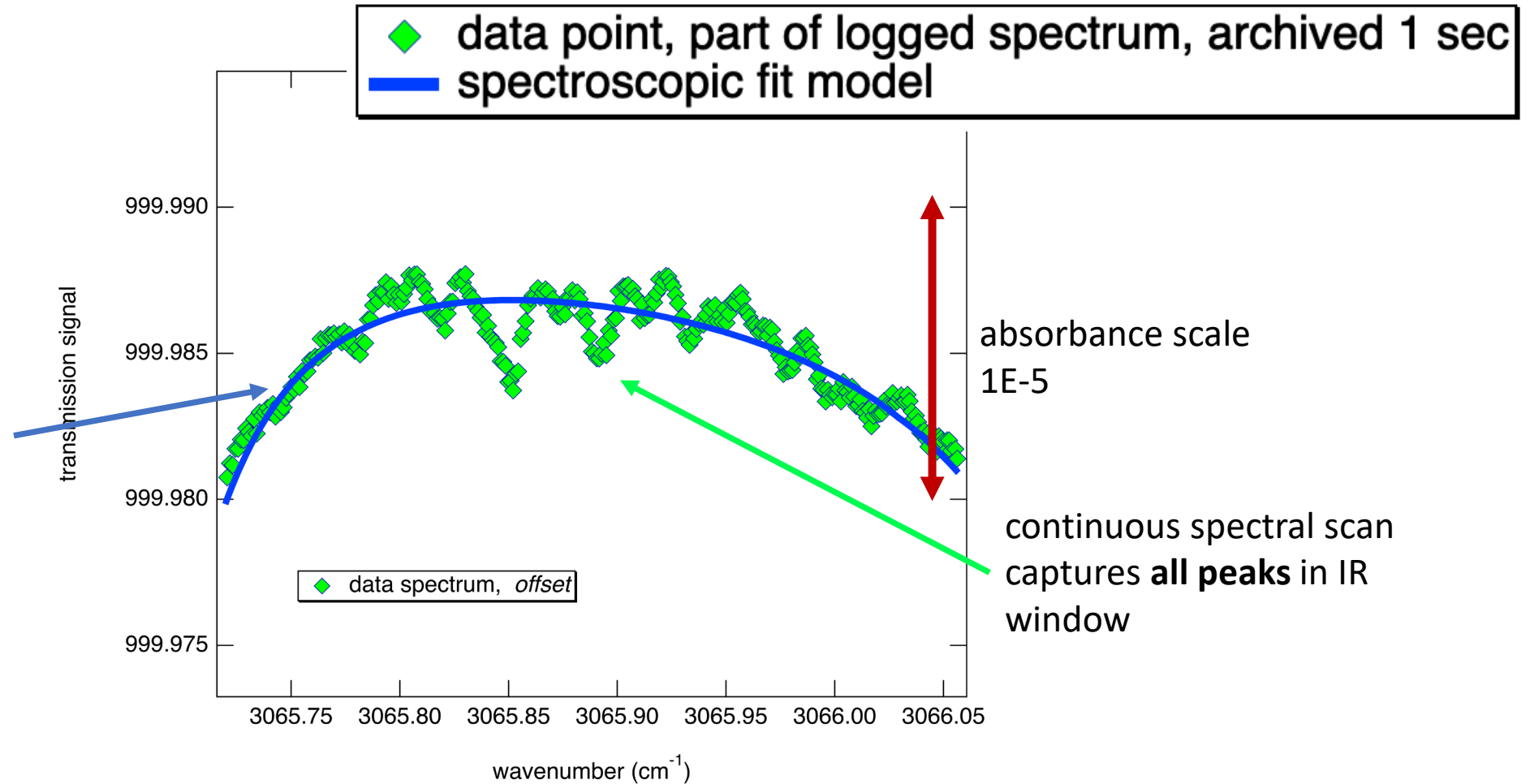
24 hr average
6/18/2022 (UTC)

wavestats root:EtO
V_npts= 42477;
V_avg= 0.0229492;
V_sdev= 0.050536;
V_sem= 0.000245202;
V_rms= 0.0555022;
V_adev= 0.0402072;
V_skew= 0.0117858;
V_kurt= 0.0560467;

Spectroscopic Analysis Model

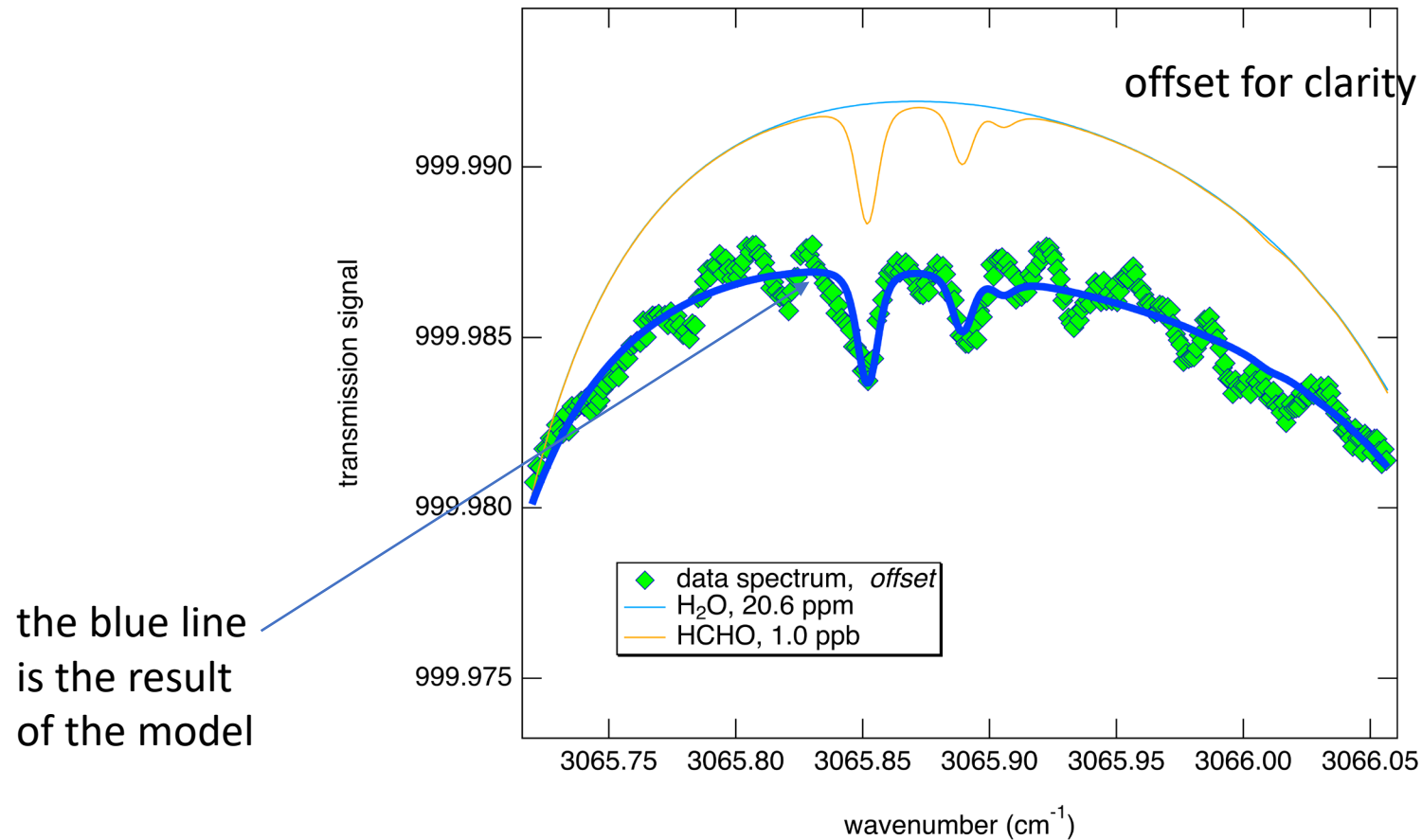
Water lines (left and right)
of this IR window form
upside down 'U'

water, in the fit model
alone does not describe
these peaks $\sim 3e-6$



Spectroscopic Analysis Model

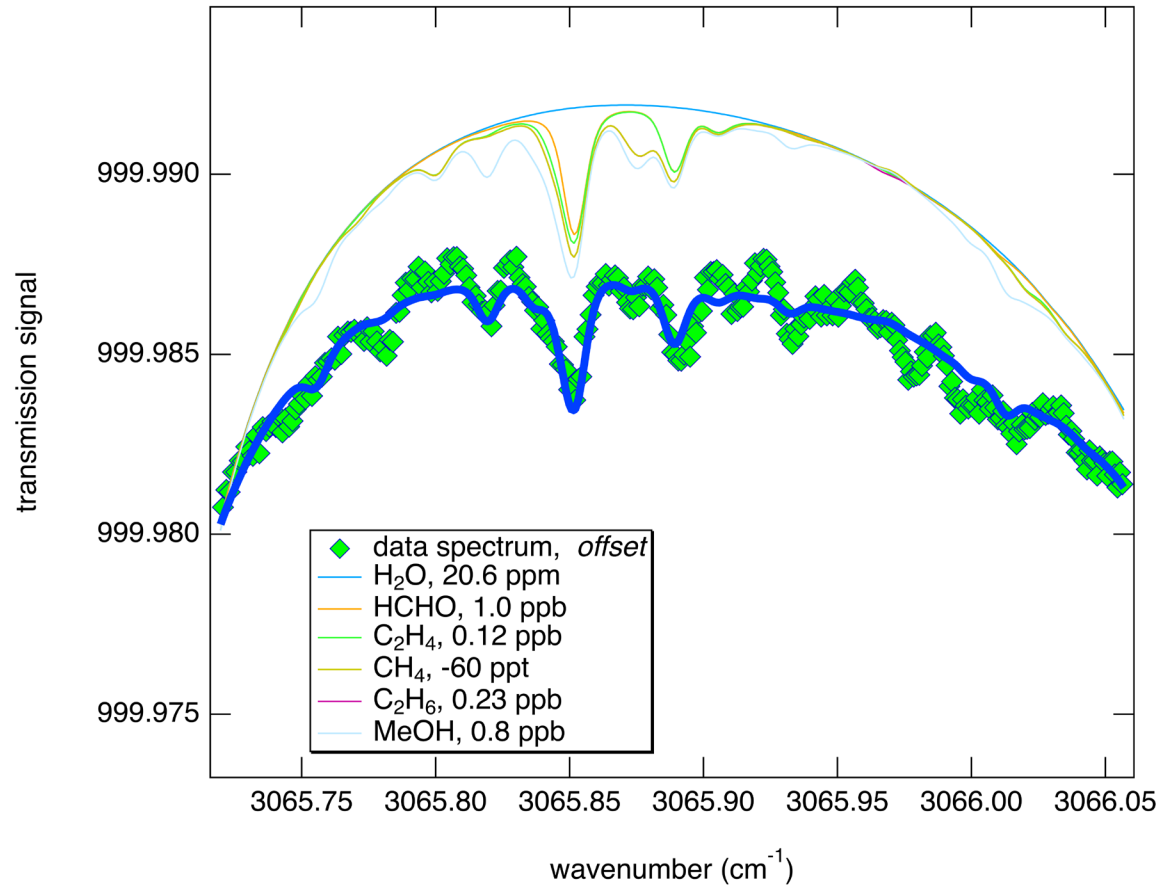
formaldehyde, in the fit model describes a few these peaks



complete wavelength resolved spectrum

Spectroscopic Analysis Model

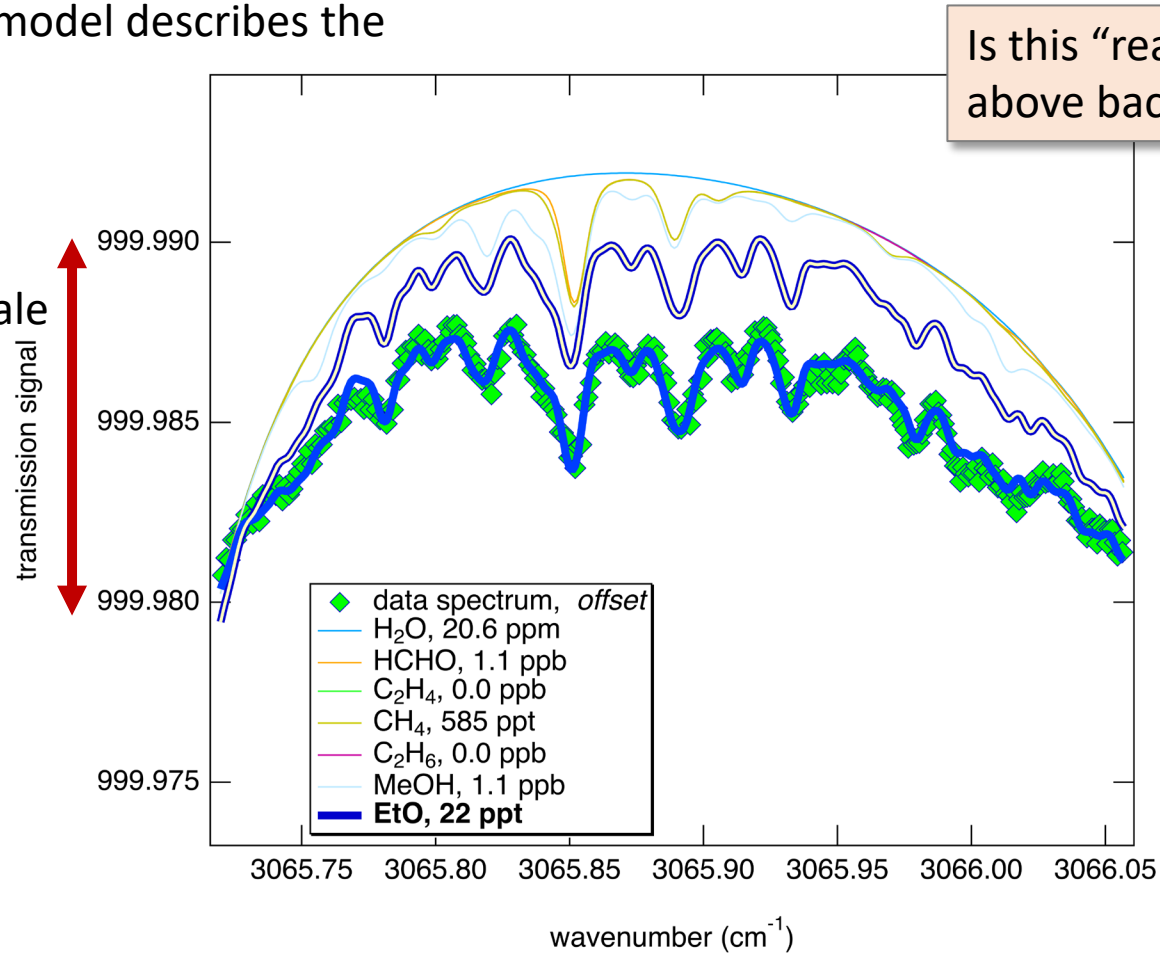
adding ethane, ethylene,
methane and methanol helps



Spectroscopic Analysis Model

the addition of EtO to the fit model describes the *distinct fingerprint* structure in this window

absorbance scale
 $1E-5$

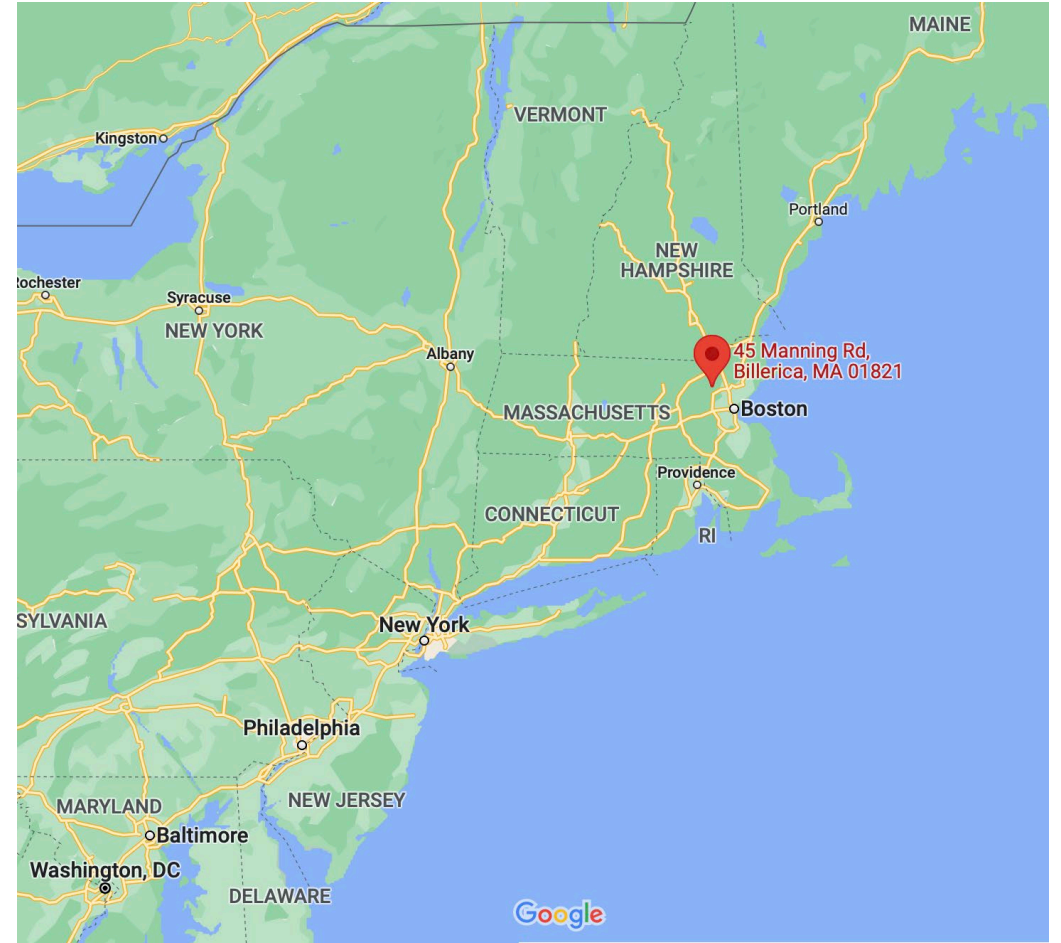


Is this “real” EtO
above background ?

Yes!, **22 ppt** spectral
match is excellent
and apparent

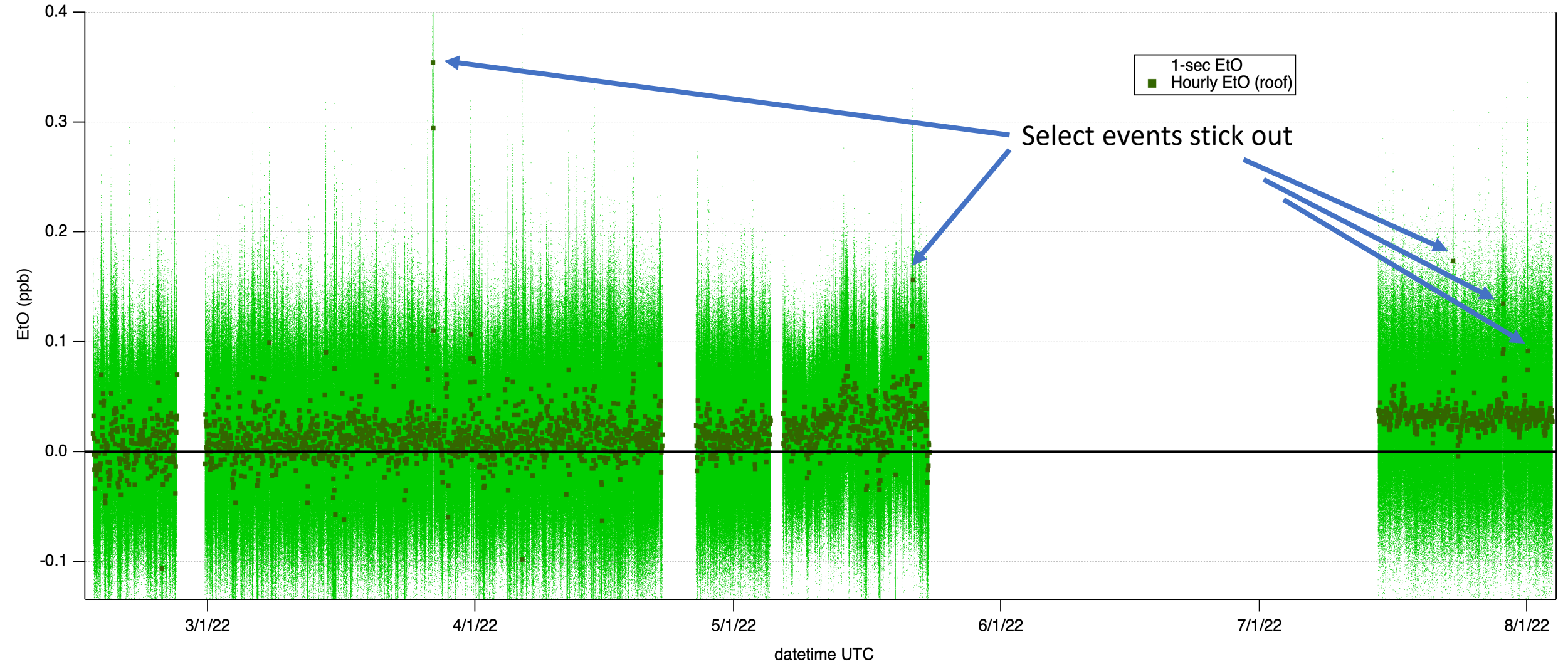
detectivity $7e-11 \text{ cm}^{-1}$

Ambient Measurements

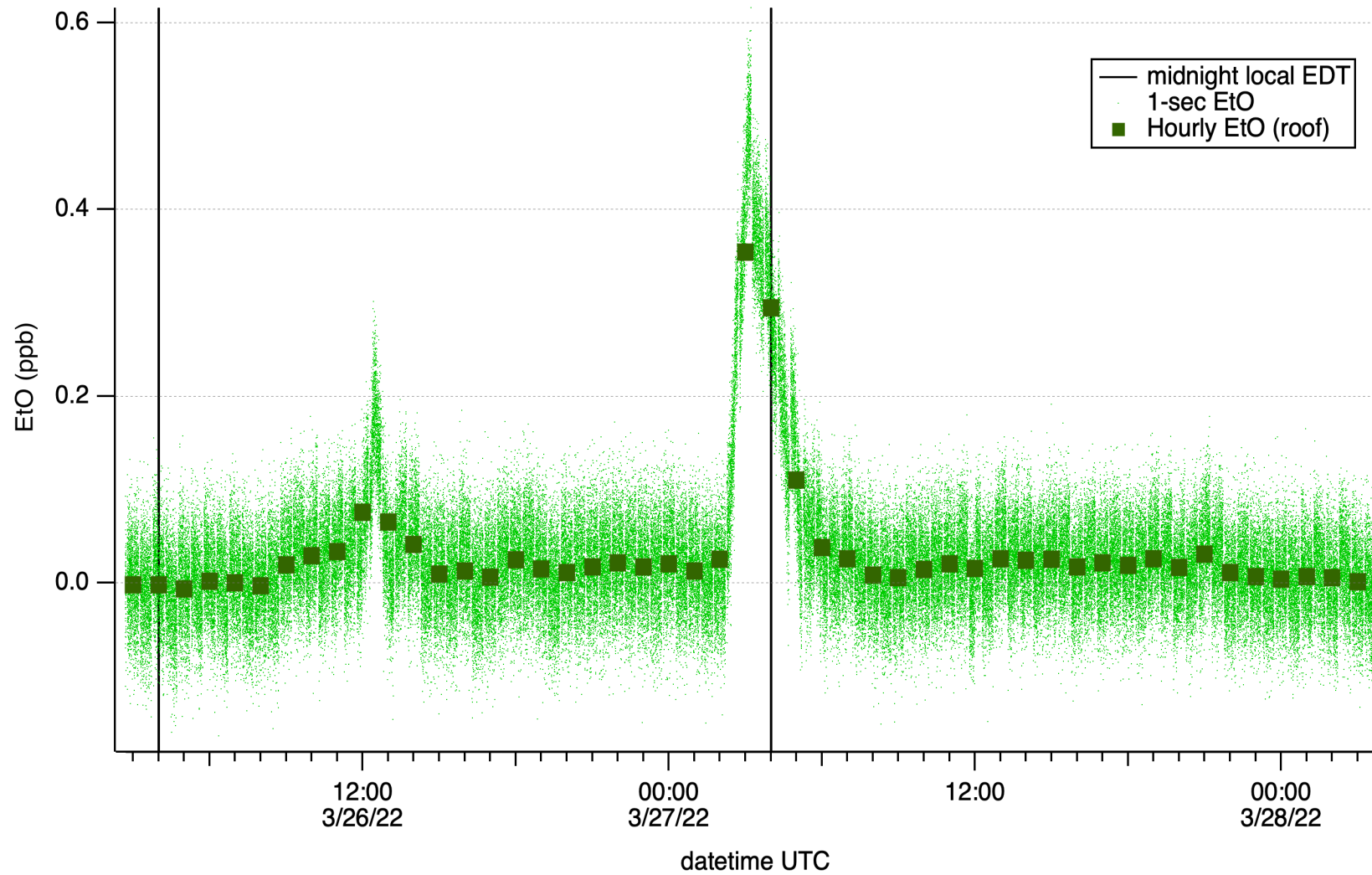


Clear Enhancement Events

Are these due to a point source with the rooftop footprint?

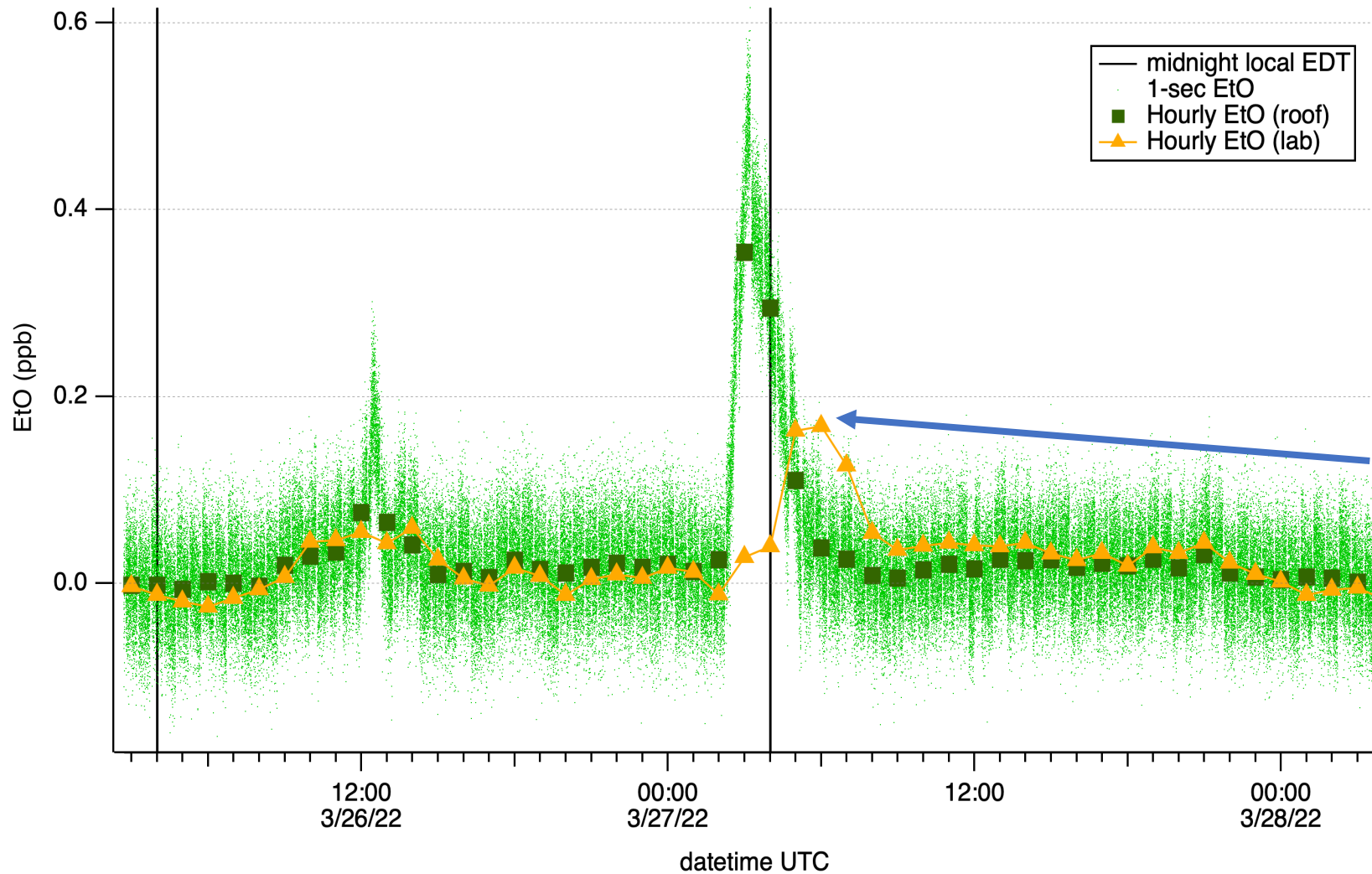


Plumes lasting several hours



Would be washed out in a 24hr canister

Plumes lasting several hours

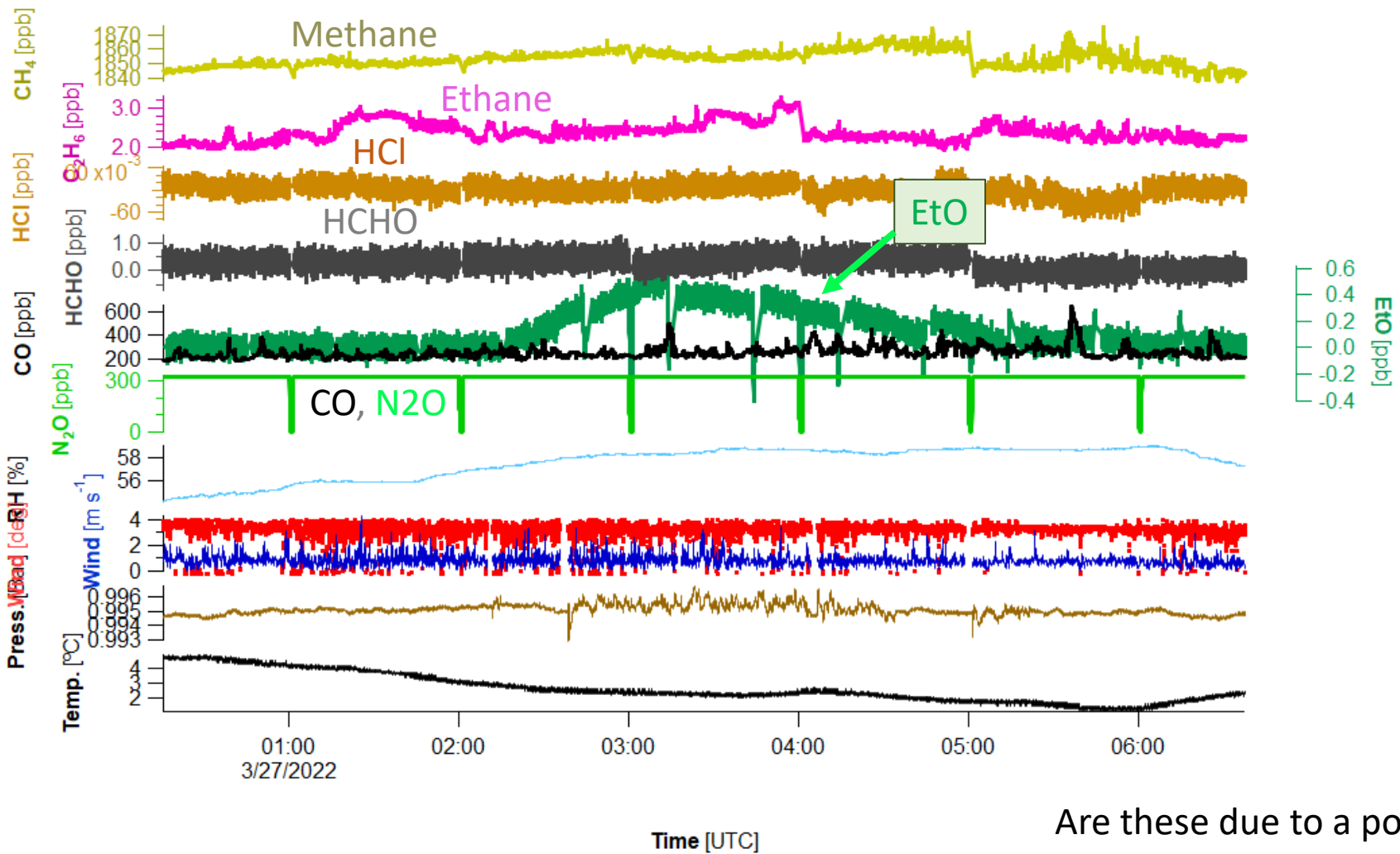


Lab air shows EtO echo as ventilation system mixes in outdoor air

A side-effect of the zeroing scheme: instrument briefly switches to lab air then switches to scrubber.

being inside does not provide protection

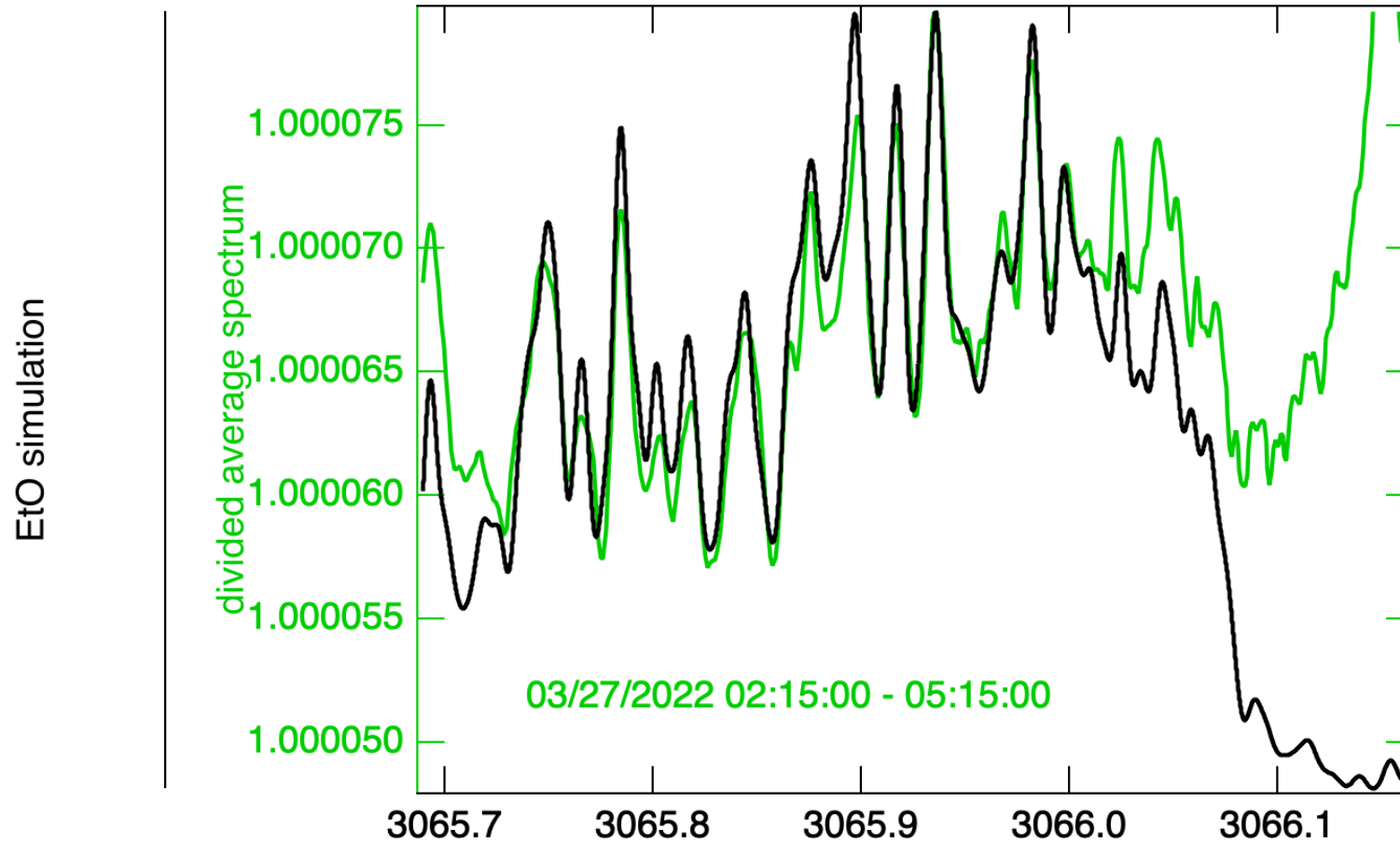
EtO plume is not correlated to other tracers



The 3/27 event lasted approximately 3 hours. This extended duration plume also mixed into lab air after a few hours, as can be seen by the brief lab air samples every 30 minutes.

Are these due to a point source with the rooftop footprint?

Spectral Signature of EtO is Clear



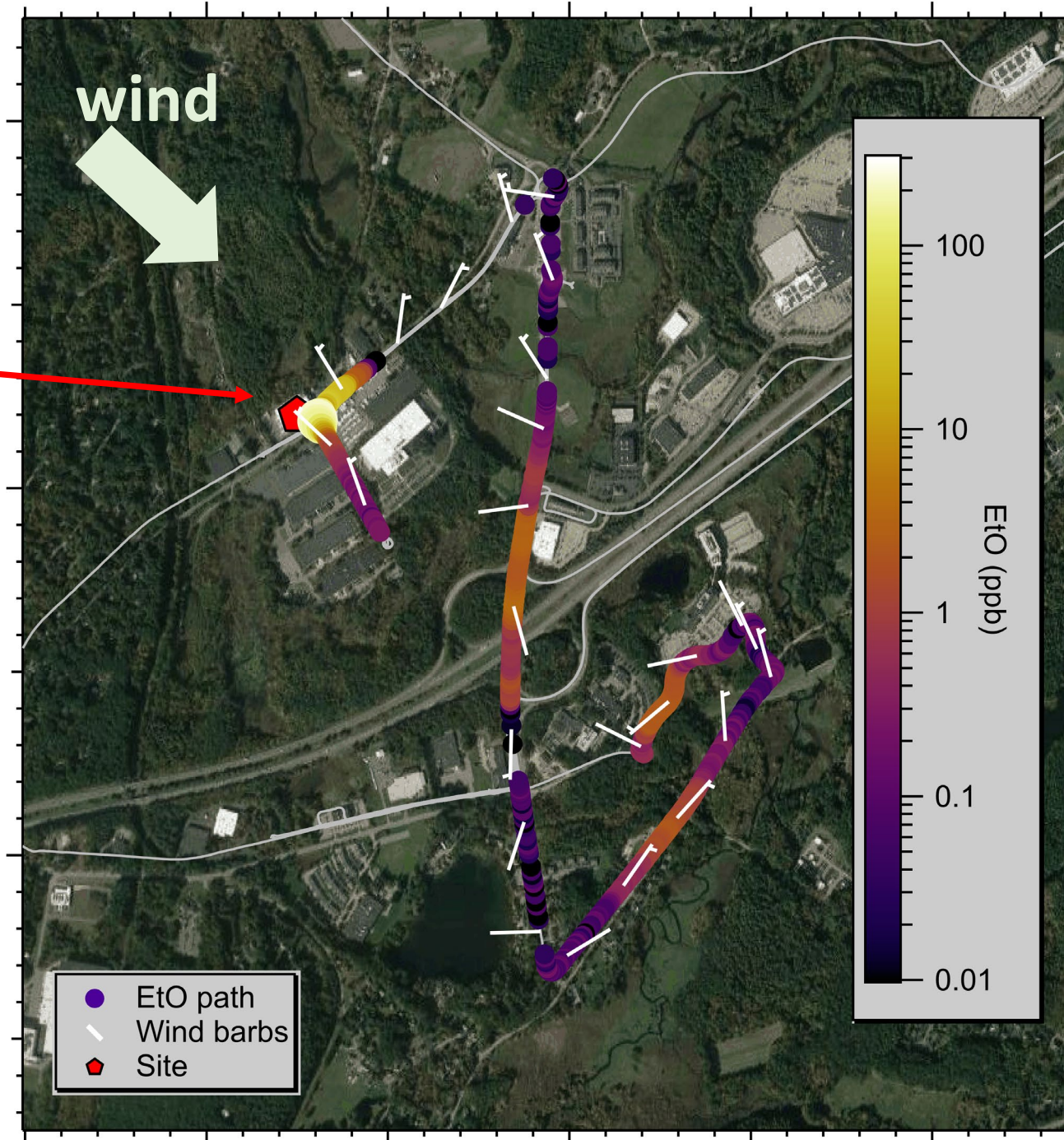
There are two potential sources in Massachusetts, notably a nearby sterilizer equipment manufacturer, and a sterilization company that accepts EtO deliveries, further away.



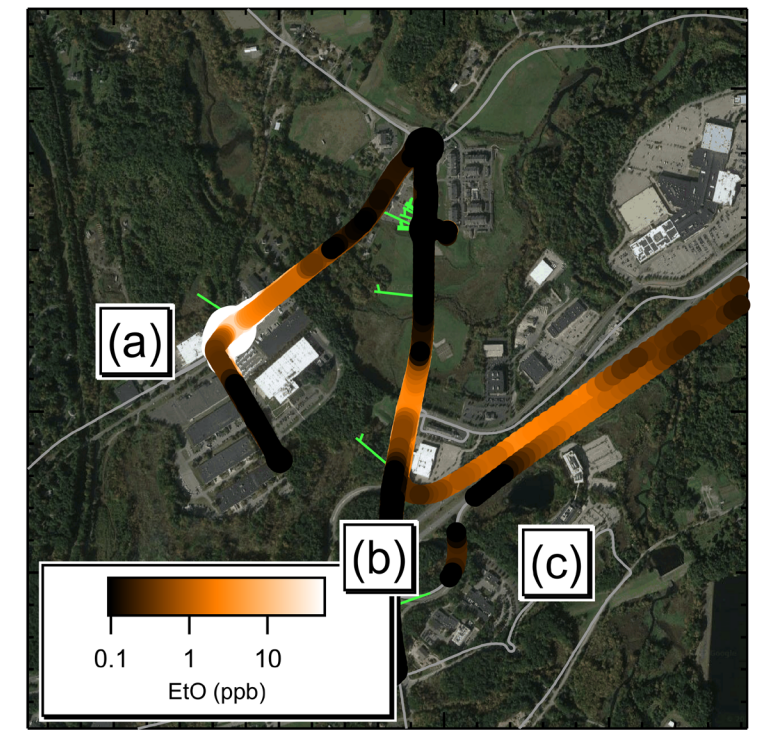
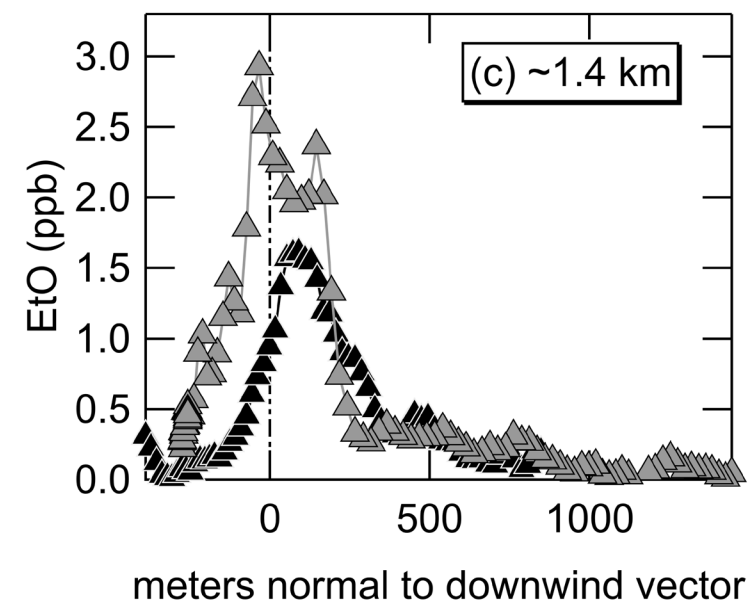
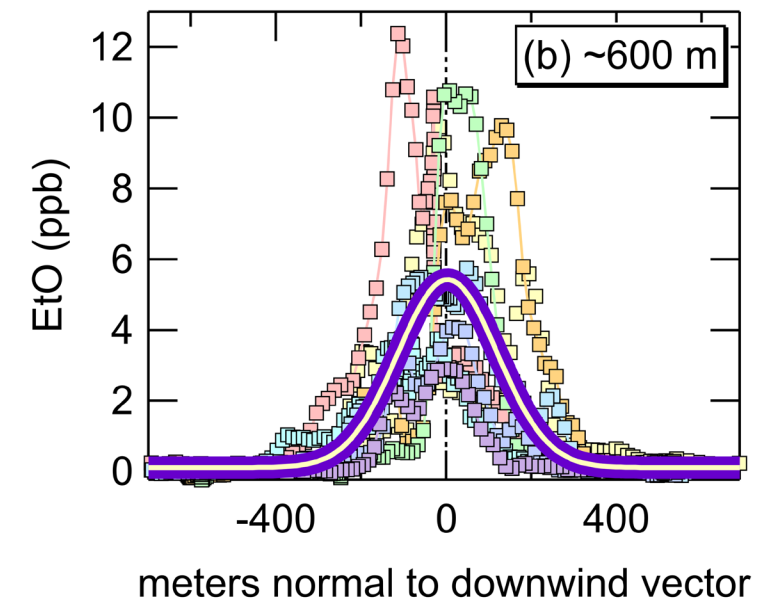
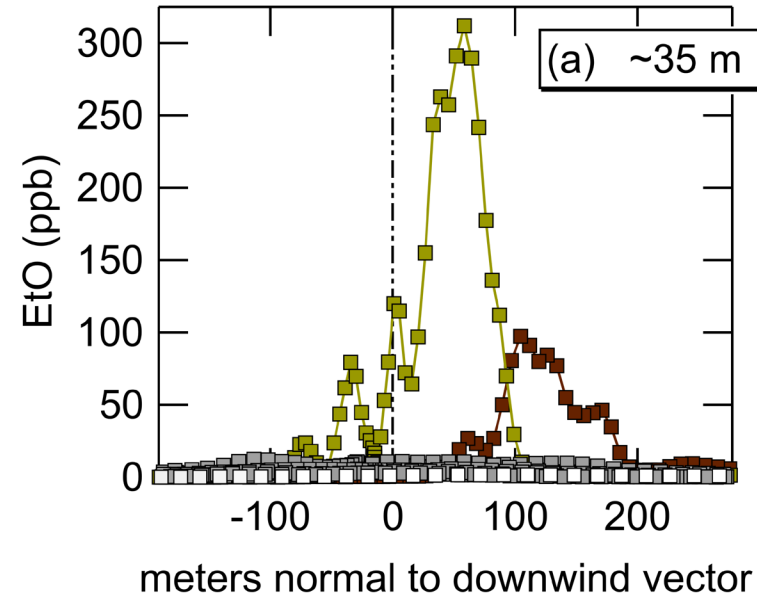
Potential Source
22 miles away

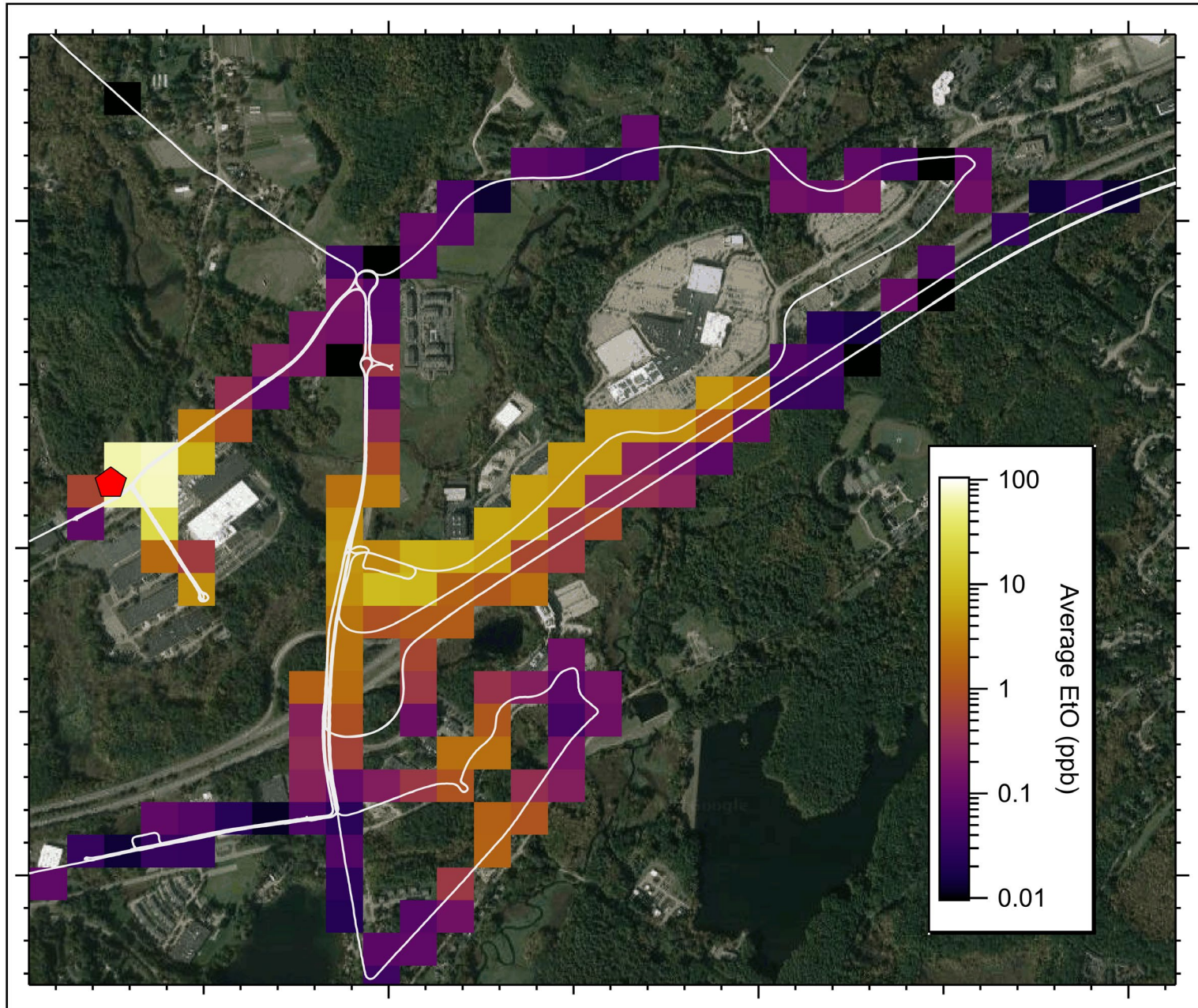
EtO Mobile Measurements at Predicted Location

EtO point emission source diluting downwind



EtO Mobile data downwind





EtO Mobile Measurements at Predicted Site

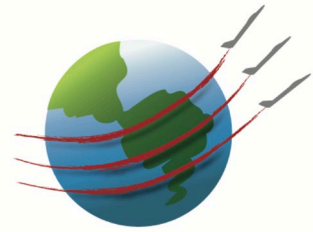
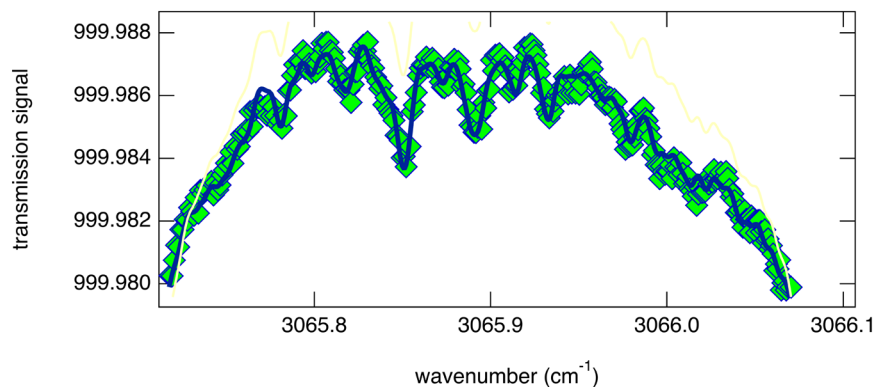
0900-1100

1300-1500

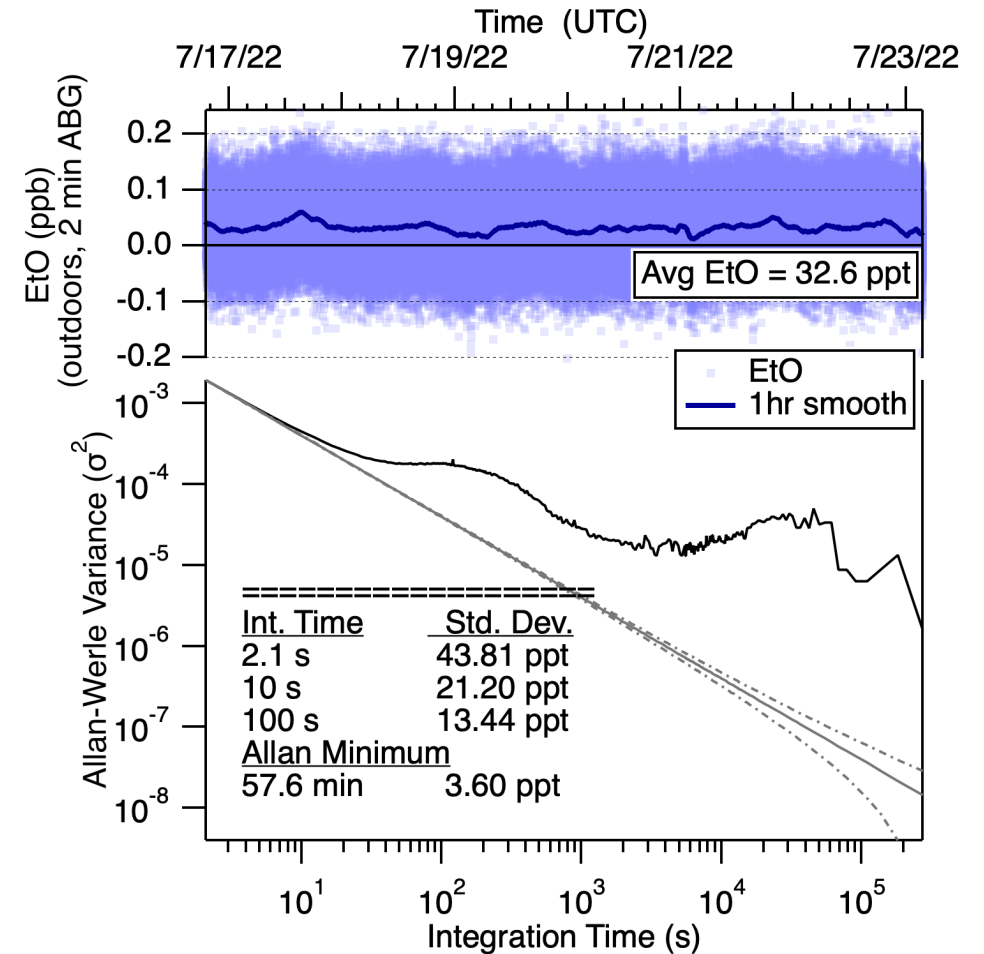
gridded average,
~ 4hr in two
times of day

Conclusions

- ❖ Aerodyne TILDAS-FD with 400 m cell < 50 ppt 1Hz (1σ)
- ❖ averages to $\ll 10$ ppt (1σ)
- ❖ Ambient Monitoring and/or Mobile point source measurements demonstrated
- ❖ Spectra provide backup and **accountability**, critical for regulatory applications.

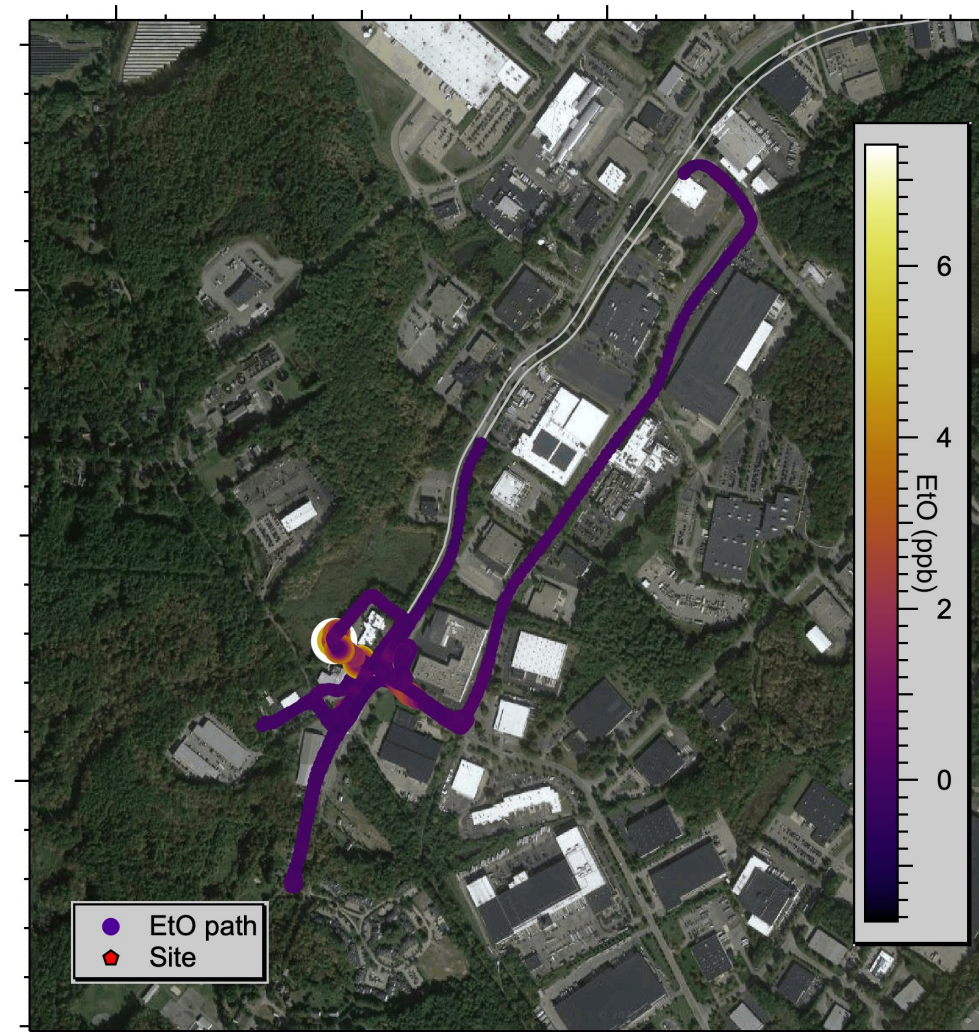
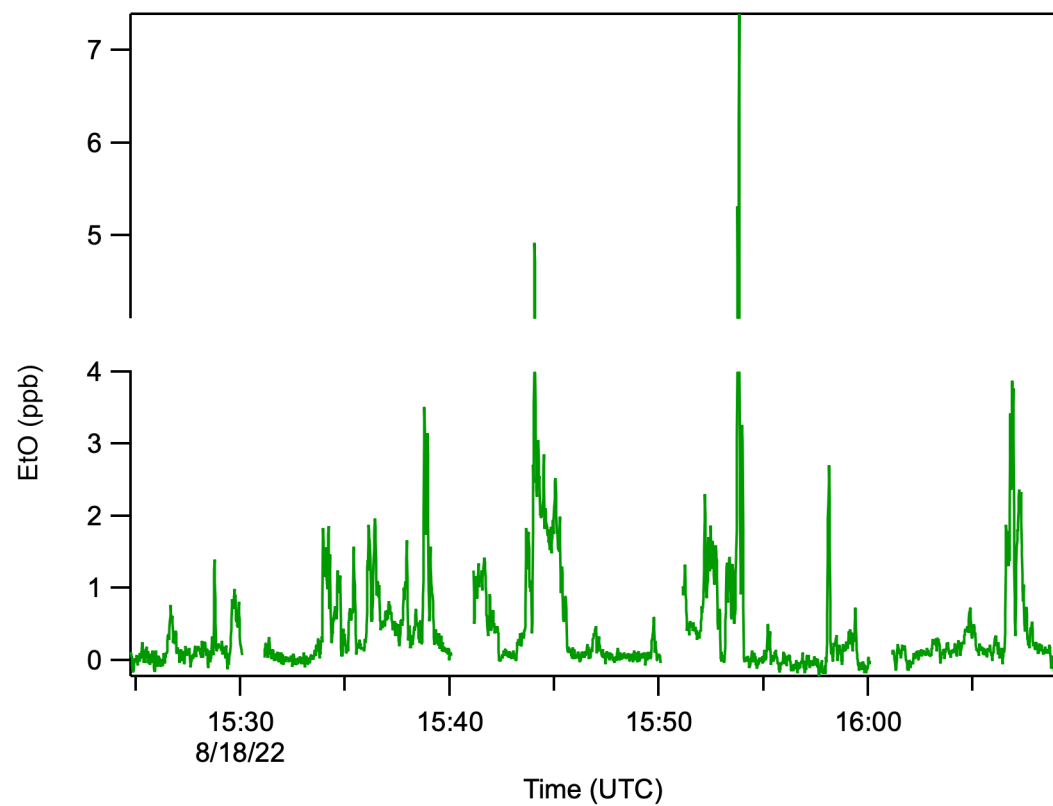


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Supplemental Slides

Bonus Site

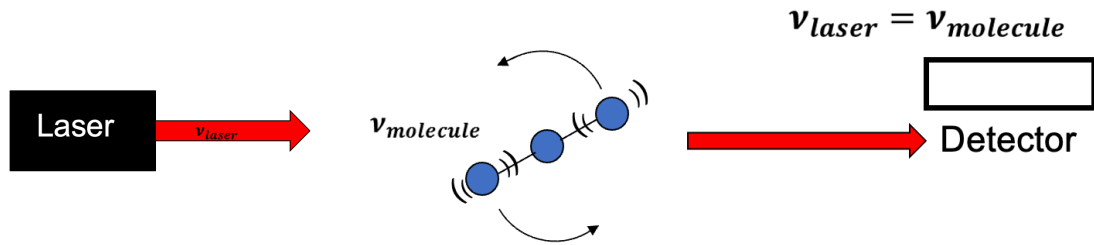


EtO components are ubiquitous

Ordering Information

	Product	Catalog No.	Description	Packaging	Shipping
	3M™ Steri-Vac™ Sterilizer/ Aerator GS Series	GS5-1D, GS5-2D	4.8 cubic foot chamber EO sterilizer	1/unit	1 unit/carton
		GS8-1D, GS8-2D	7.9 cubic foot chamber EO sterilizer	1/unit	1 unit/carton
	3M™ Ethylene Oxide (EO) Abator	50	Converts EO exhaust into CO ₂ and water vapor	1/unit	1 unit/carton
	3M™ Steri-Gas™ EO Gas Cartridges	4-100	100 gram (3.5 oz.) Cartridge for Models GS5-1D, GS5-2D, 5XL	12 each/box	8 boxes/case
		8-170	170 gram (6 oz.) Cartridge for Models GS8-1D, GS8-2D, 8XL	12 each/box	8 boxes/case

Principle of Operation – Absorption Spectroscopy



Tunable Infrared Laser Direct Absorption Spectroscopy

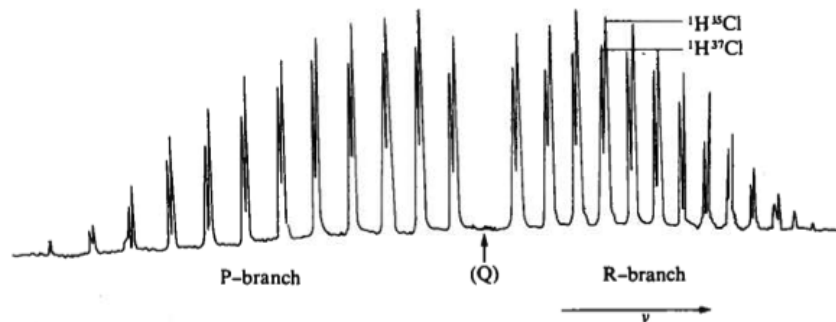
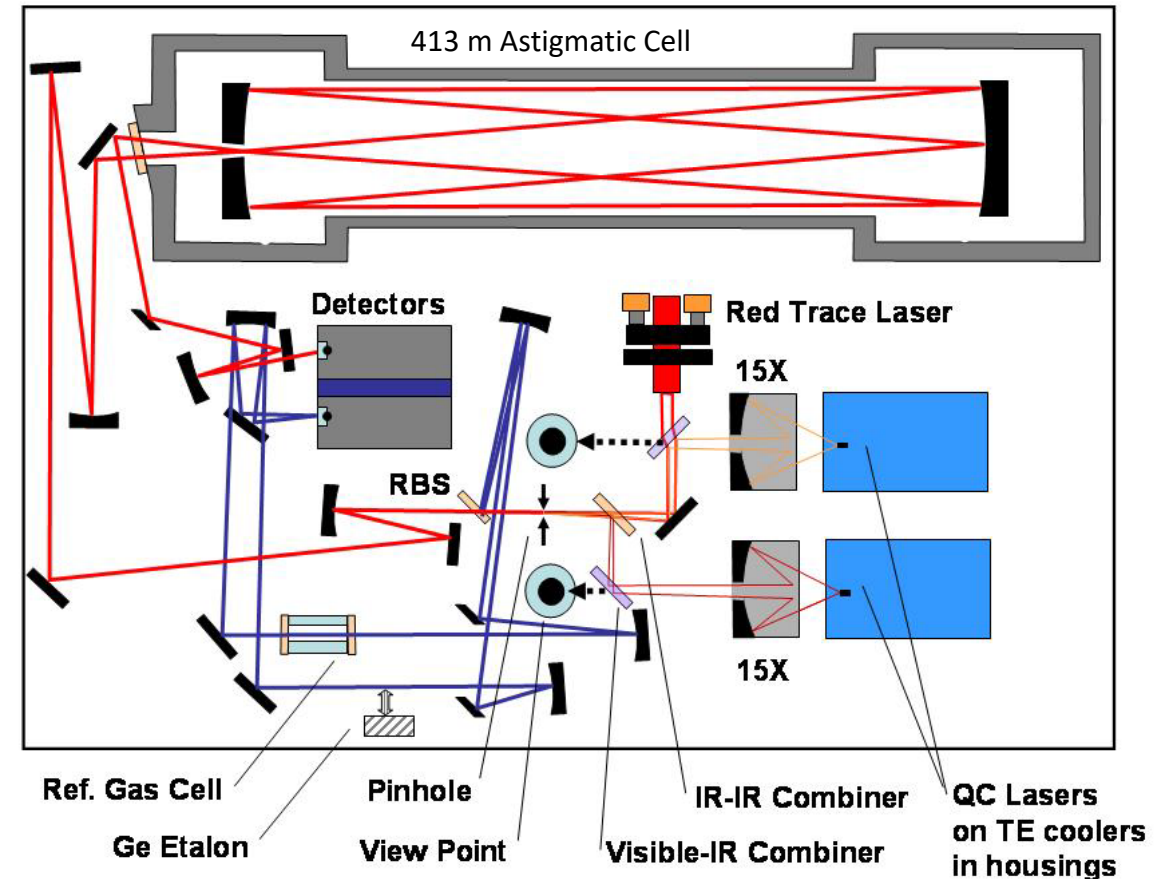
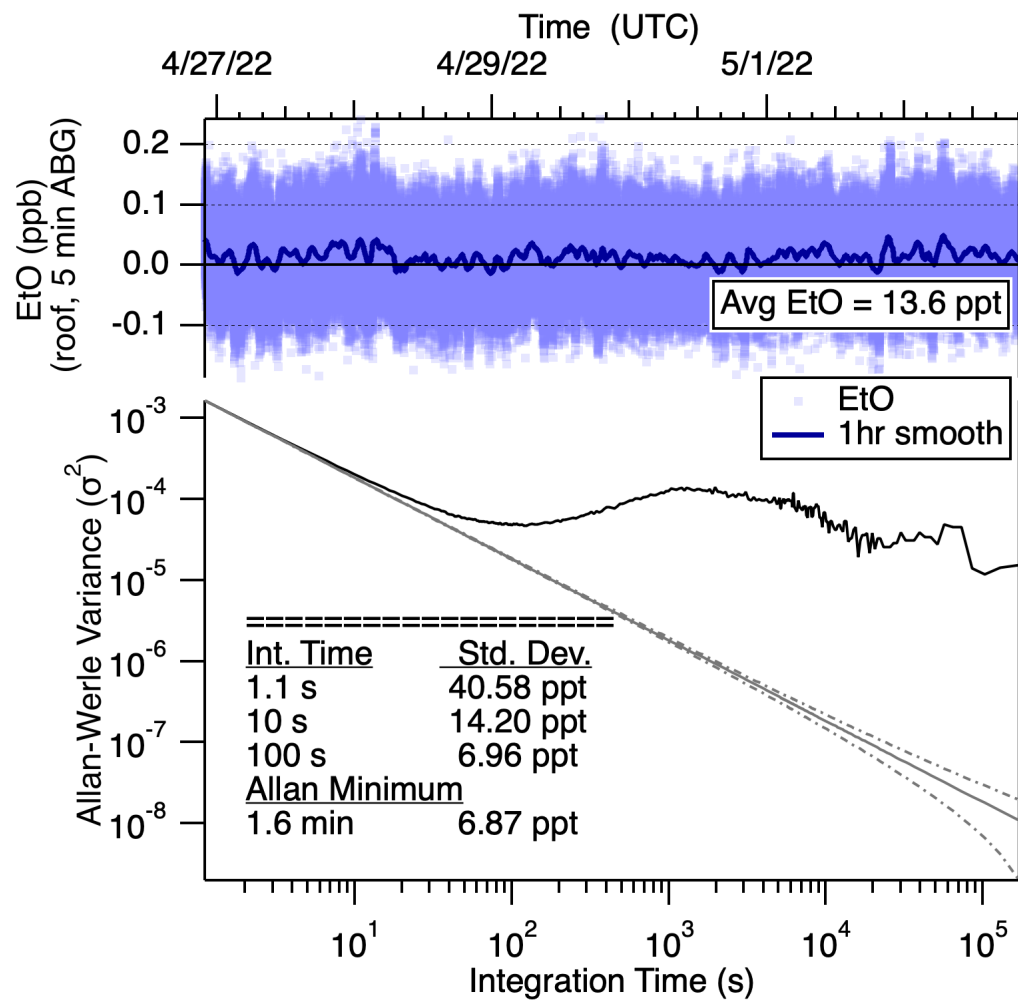


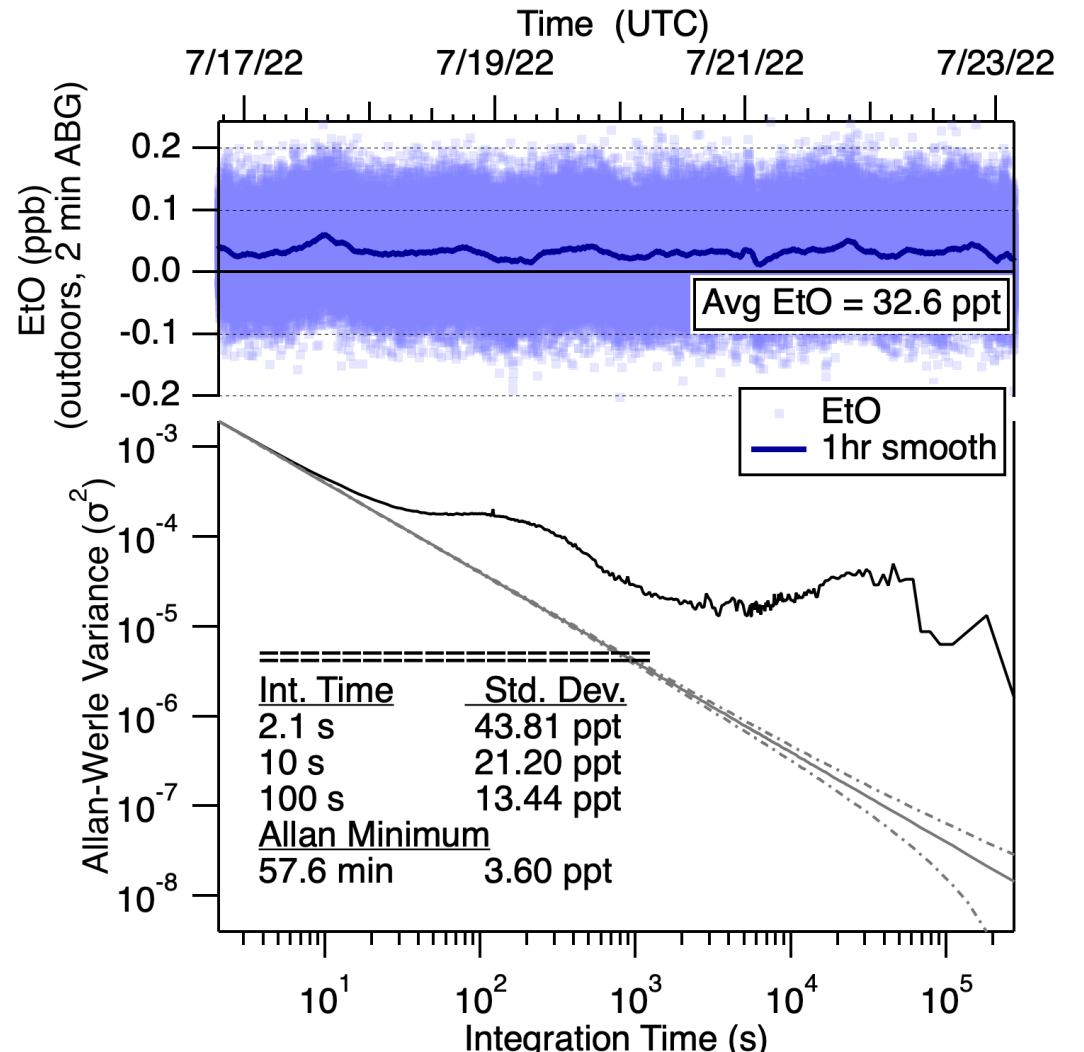
Fig. 17.14. A high-resolution vibration-rotation spectrum of HCl.



2-story Inlet 5-min ABG

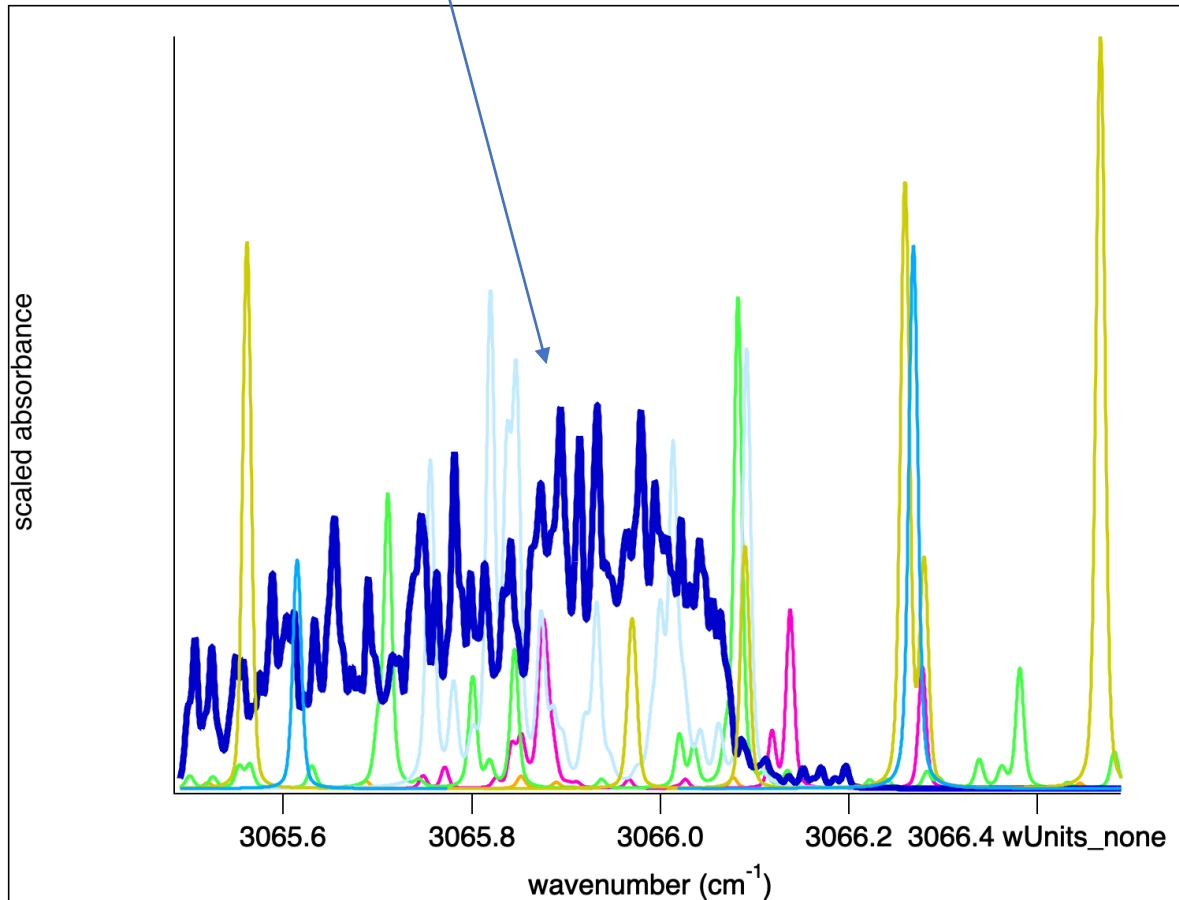


3m Inlet 2-min ABG



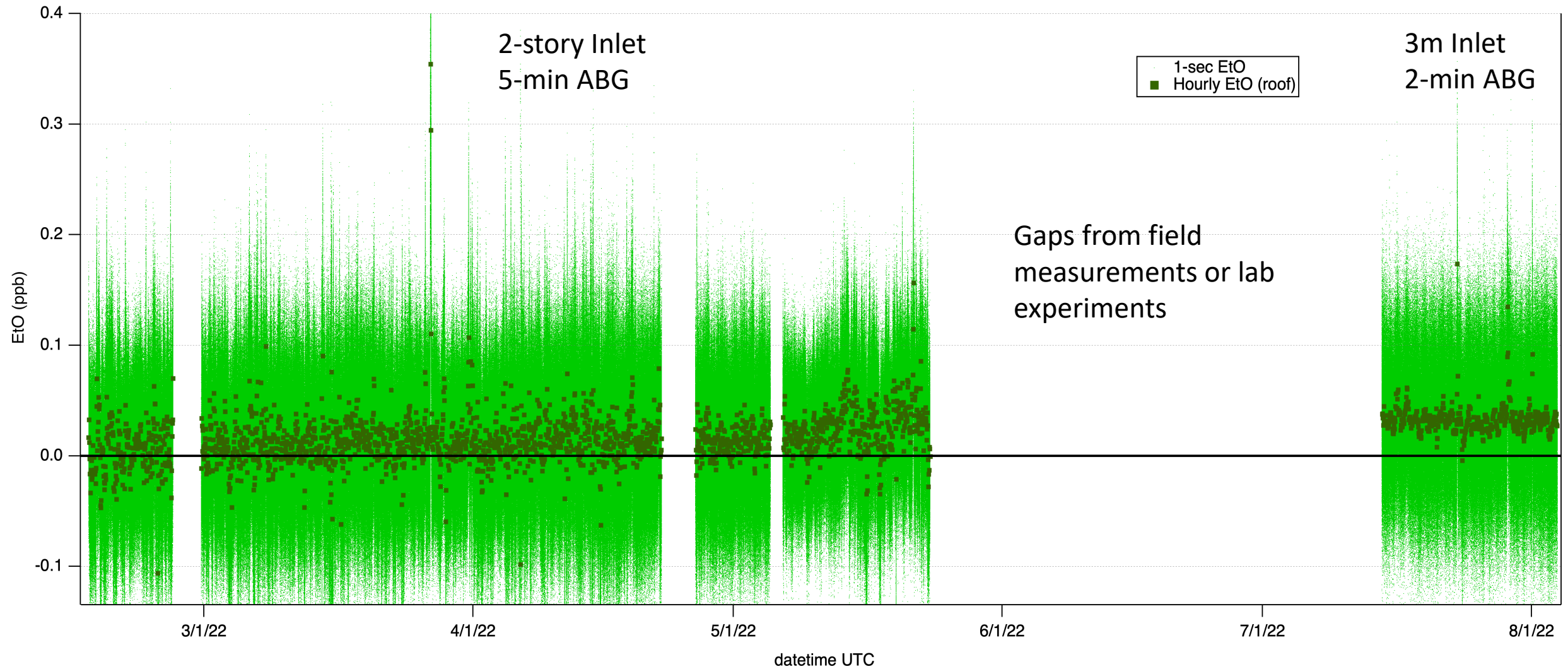
Spectroscopic Accountability

these ridges are the
fingerprint for **unambiguous**
EtO quantification

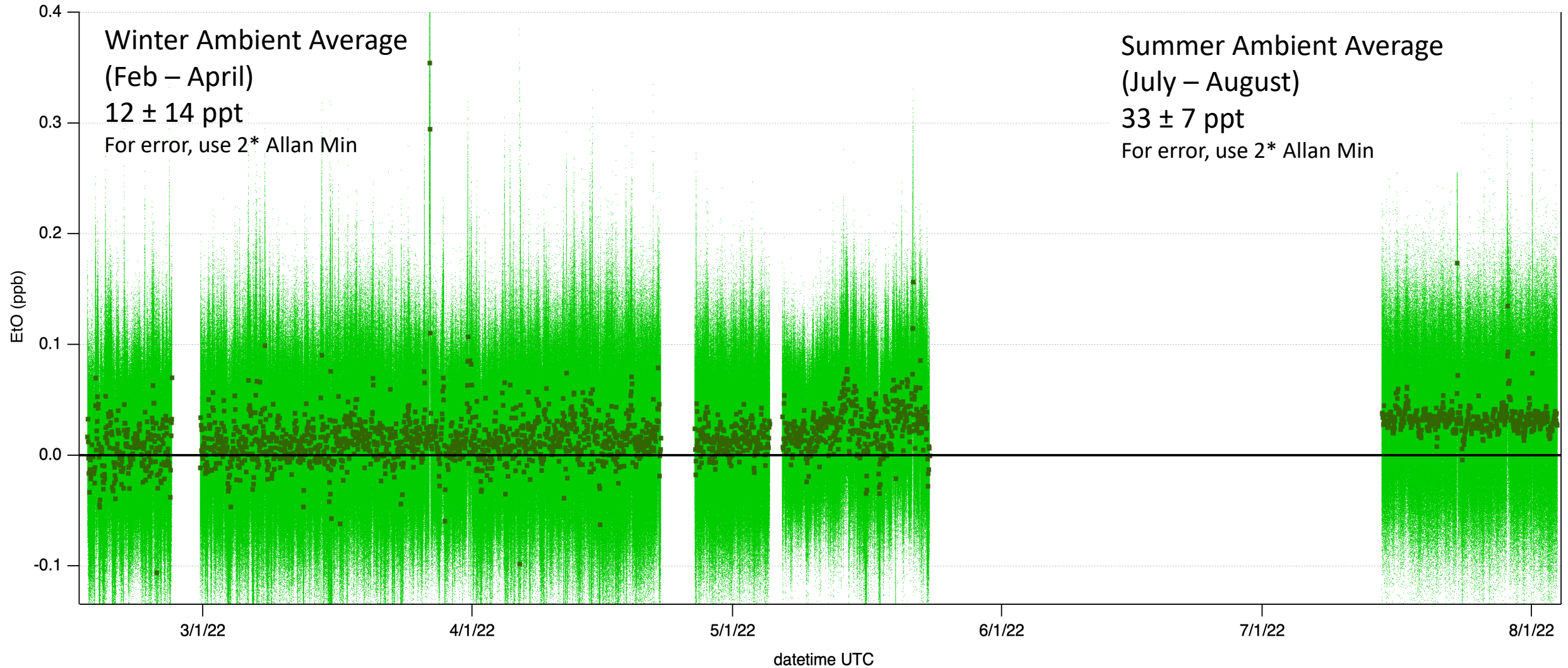


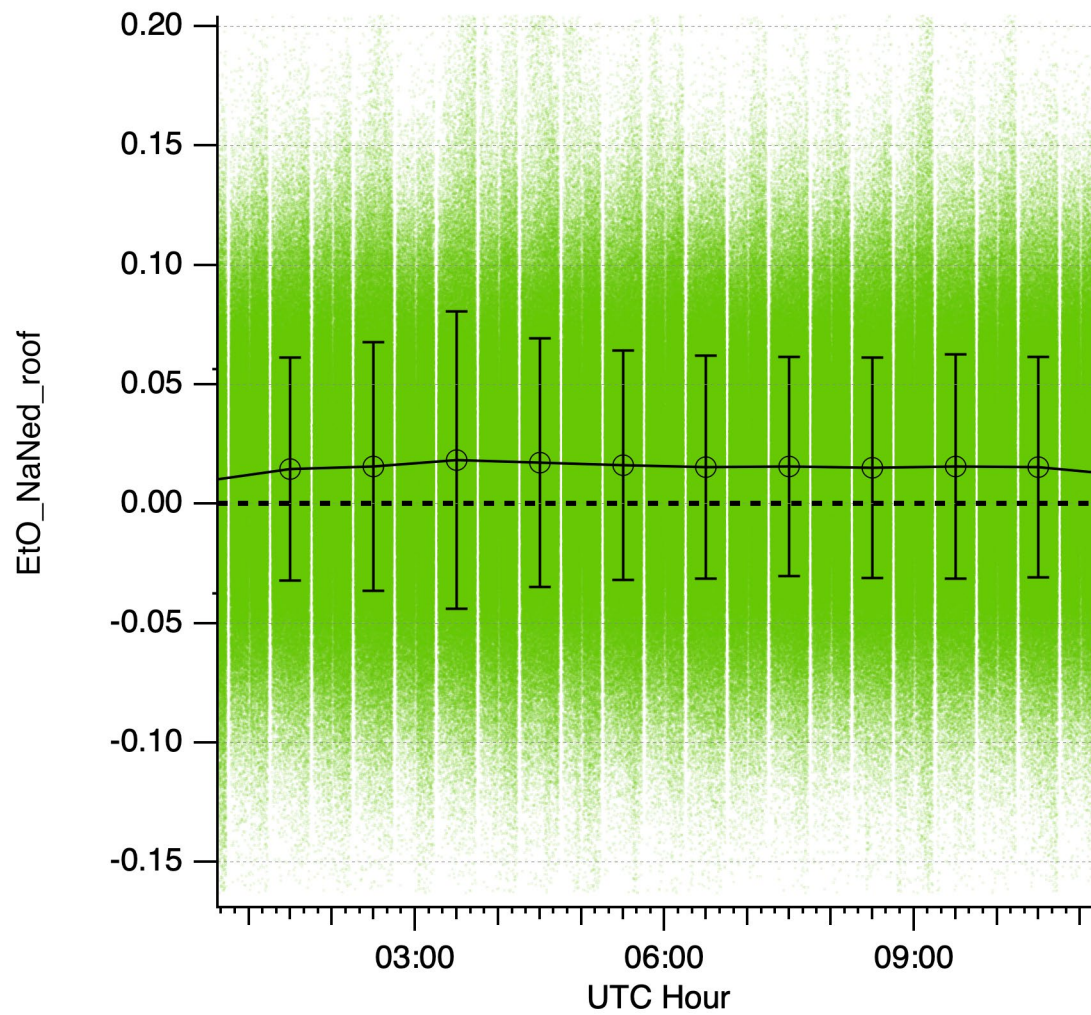
In the Aerodyne TILDAS,
all spectra are saved and user accessible
to back-up the normal automatic
reported retrieval (mixing ratio)

Months-long ambient monitoring record



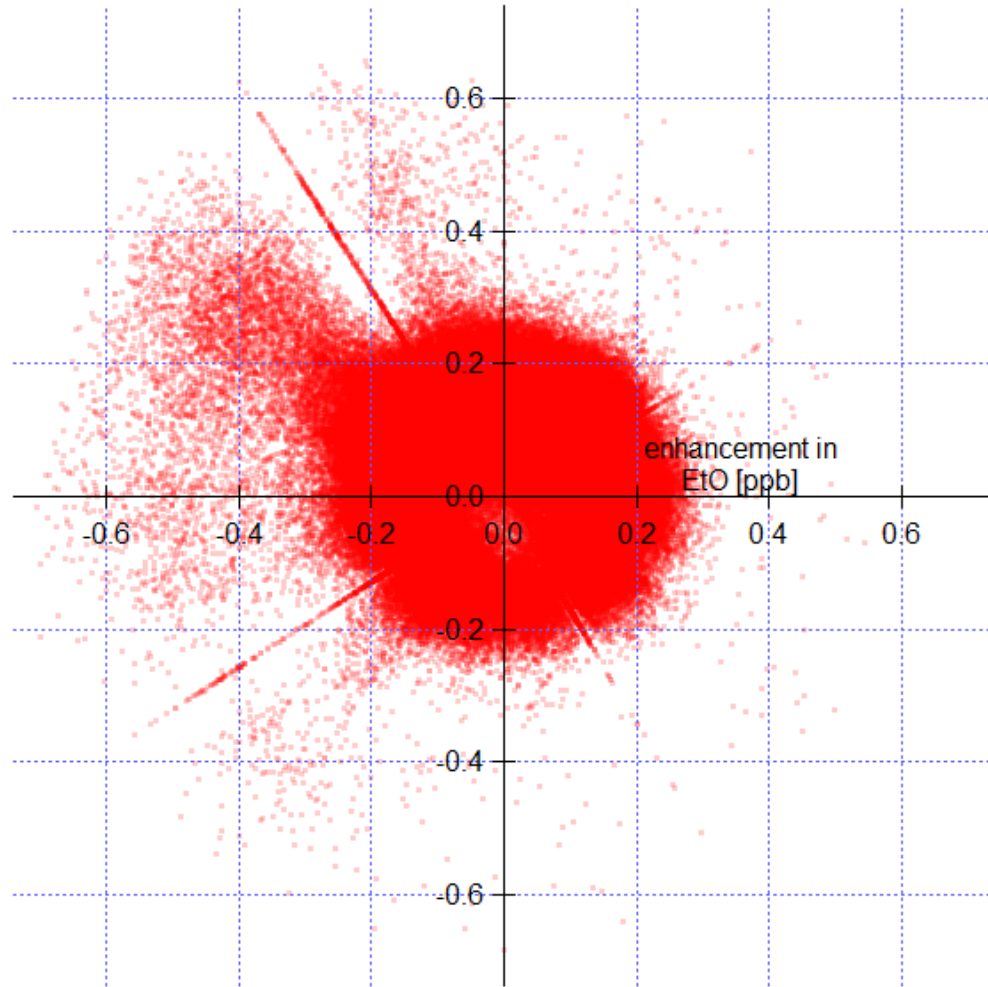
Months-long ambient monitoring record



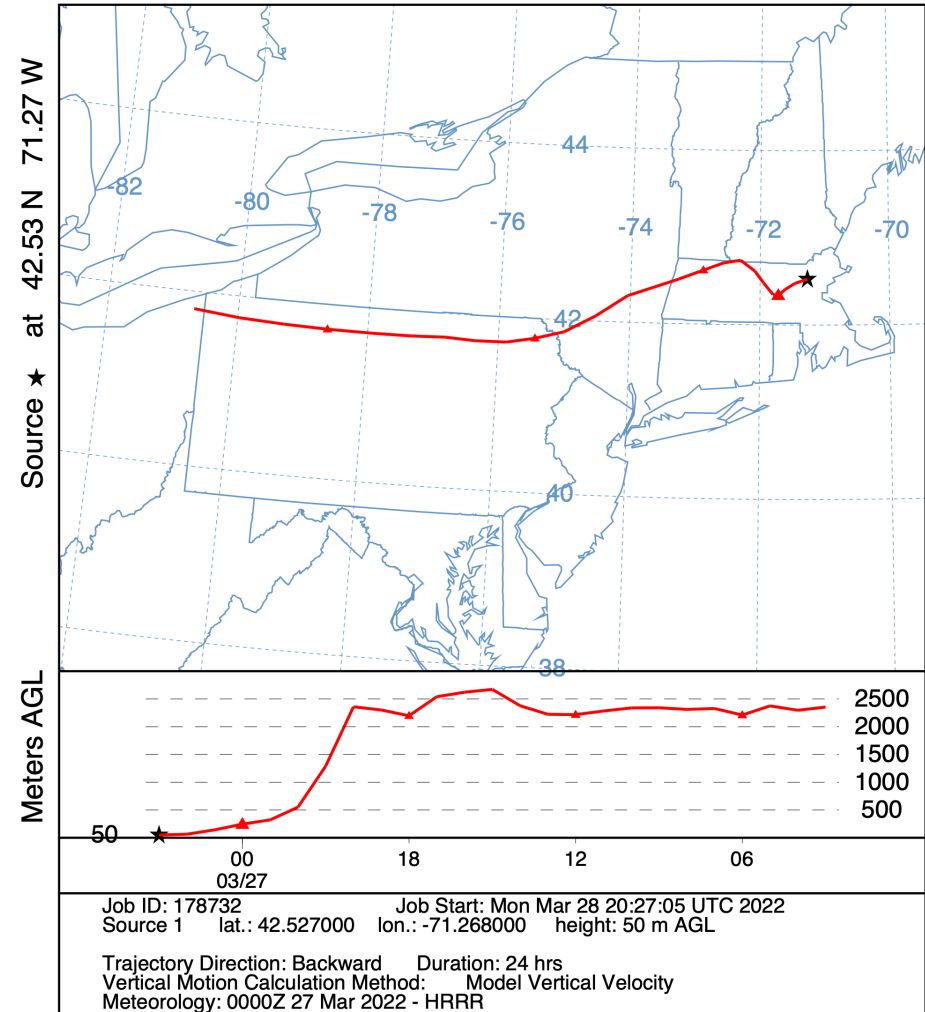


No clear diurnal trend
Feb-May 2022

Events



NOAA HYSPLIT MODEL
 Backward trajectory ending at 0300 UTC 27 Mar 22
 HRRR Meteorological Data



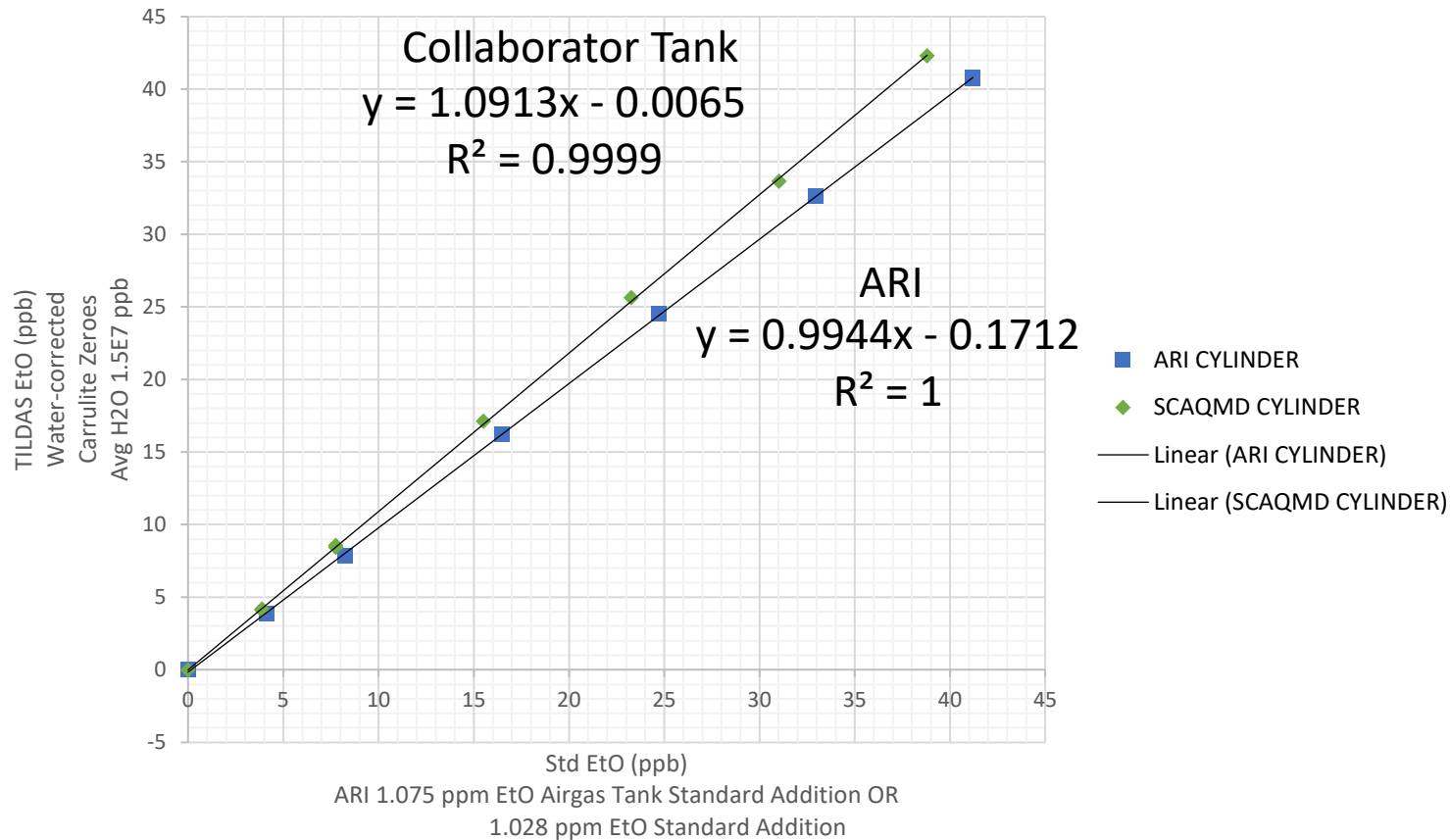
EtO Wind Rose and Hysplit trajectory for the 2022-03-27 plume. Sharp lines in the wind rose are artifacts from the anemometer posts. The hysplit trajectory is show to the right.

On the Road



Cal Factors using flows (divide by)

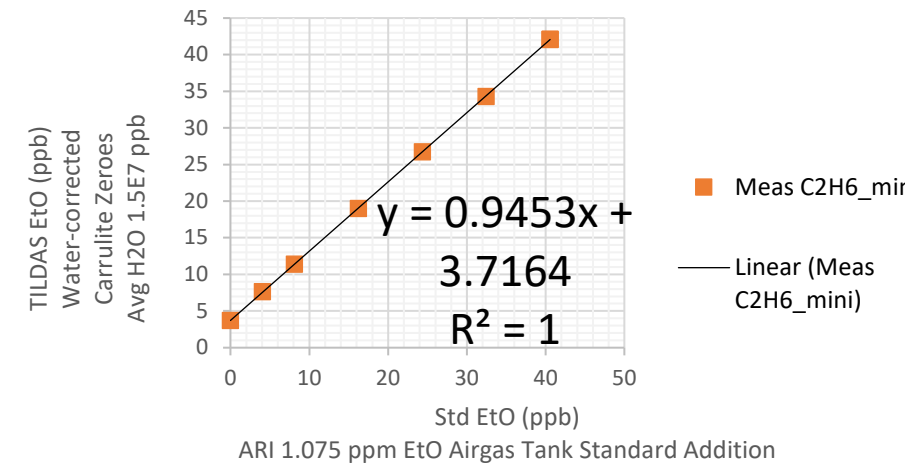
EtO Standard Addition
2 Tanks Attached to Same Flow Controller
6/16/22 16:50



During this calibration, we also get a cal factor for the Ethane-TILDAS-mini

Offset due to ambient ethane

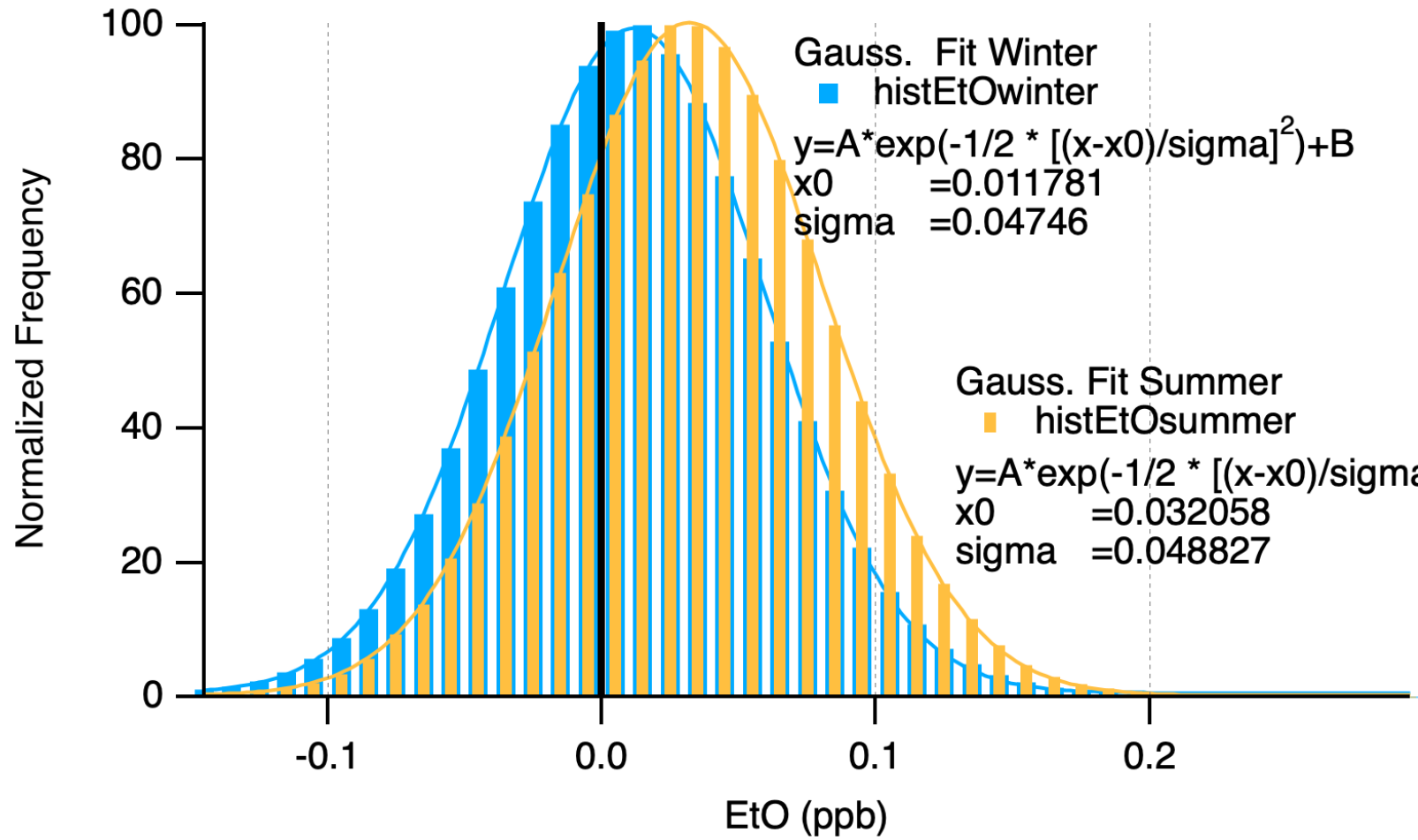
Ethane Standard Addition
2 Tanks Attached to Same Flow Controller
6/16/22 16:50



Comparison of analysis techniques for various standard addition calibrations using ARI's EtO calibration tank

Date/Time and Statistics	Humid Standard Additions (analysis by flows)	Humid by Ratio (C ₂ H ₆ calibrated separately for each cal)	Humid by ratio (single C ₂ H ₆ cal factor from "Ethane 3" tank)
6/10/22 15:30	0.990	0.958	0.957
6/12/22 15:25	0.976	0.976	0.943
6/12/22 16:10	0.963	0.963	0.929
6/15/22 16:50	0.994	0.994	0.938
Average	0.981	0.973	0.942
StdDev	0.014	0.016	0.012
95% error	0.045	0.052	0.037
95% error as % error	4.6%	5.3%	3.9%
1 ppb EtO would be corrected to	1.020	1.028	1.062

Flow uncertainties are not a major driver of error



Feb – April
12 ppt ± 92 ppt

July – August
32 ppt ± 96 ppt