Ethylene Oxide Monitor with Part-per-Trillion Precision for In-Situ Measurements

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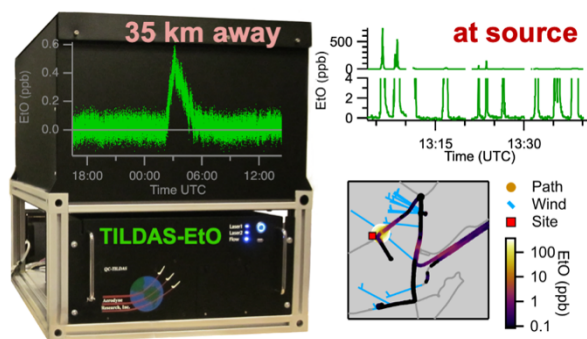
Abstract. An Aerodyne Tunable Infrared Direct Absorption Spectrometer with a multipass cell with 413 meter pathlength for the detection of ethylene oxide (EtO) is presented (TILDAS-FD-EtO). This monitor achieves precisions of <75 ppt or <0.075 ppb in 1 second and < 20 ppt in 100 seconds (1-sigma). We demonstrate precisions averaging down to 4 ppt in an hour (1-
10 sigma precision) when operated with frequent humidity-matched zeroes. A months-long record of 2022 ambient concentrations at a site in the Eastern United States is presented. Average ambient EtO concentration is on the order of 18 ppt (22 ppt standard deviation). Enhancement events of EtO lasting a few hours are observed, with peaks as high as 600 ppt. Back trajectory simulations suggest an EtO source nearly 35 km away. This source along with another are confirmed as emitters through mobile near-source measurements, with downwind concentrations in the 0.5 ppb to 700 ppb range depending on source identity
15 and distance downwind.

1 Introduction

Ethylene oxide (EtO, also known as EO or oxirane) is a reactive compound with a strained 3-member ether ring (C_2H_4O, CAS# 75-21-8, MW=44.05 g/mol). It is commonly used in chemical manufacturing of polymers and glycols. It is also used to sterilize
20 medical equipment (e.g. pacemakers, surgical kits) that cannot be exposed to heat or humidity. Due to its reactivity, ethylene oxide is a carcinogen. The United States Environmental Protection Agency (EPA), through its Integrated Risk Information System (IRIS), has set an inhalation unit risk (IUR) for EtO at 3.0×10^{-3} per $\mu g/m^3$ (5.5×10^{-3} per ppb), for adult increased cancer risk based on human data (US EPA, 2016). The IUR is an upper-bound estimate of excess cancer risk from continuous

exposure to a compound at 1 μg/m^3 in air (US EPA, 2022b). An IUR for EtO of 3.0×10^{-3} per μg/m^3 implies that 3 excess
25 cancer cases are expected to develop in 1000 people if exposed to 1 μg/m^3 (0.55 ppb) of EtO over a lifetime. Other risk
estimates for different populations are included in the source EPA material (US EPA, 2016). Workplace limits for 8-hour and
acute 5-min exposures are several orders of magnitude higher, on the order of 1 – 5 ppm (OSHA, 2002). The toxicity of this
chemical makes accurate, high precision measurements of ambient and near-source concentrations imperative; this advance is
described herein.

30 Background levels of EtO are challenging to measure via extractive methods such as canister sampling. EtO can be formed
during storage in the canisters used (Hoisington and Herrington, 2021; US EPA, 2019; Hasegawa, 2001). The levels of reported
EtO formation are on the order of hundreds of ppt. Hoisington and Herrington (2021) note EtO formation in blanks filled with
humidified air but not dry air or inert gas, and thus hypothesize the reaction to be between larger hydrocarbons and oxygen,
catalyzed by the presence of water and metal surfaces. Both canister type/coating (US EPA, 2019) and canister
35 cleanliness/cleaning protocol (Hoisington and Herrington, 2021) are thought to impact EtO formation.

Reported background concentrations of EtO at select US National Air Toxics Trends monitoring sites (NATTS) for the Oct
2018 – March 2019 period average 0.297 μg m^{-3} and range between 0.185 – 0.397 μg m^{-3} (103 to 220 ppt) (US EPA, 2019).
More recent EPA data from 2022 at Massachusetts measurement sites show 24-hour concentrations between 0 and 0.270 μg
m^{-3} (0 – 150 ppt) (US EPA, 2022a) (data accessed 2022/8/30). Olaguer et al. (2020) report near-source 24 hr average
40 concentrations in the 0.42 – 76.0 μg m^{-3} range (233 ppt – 42.2 ppb), the lower value representative of ambient background,
and the higher value sampled near a vent at a sterilization facility. These measurements all rely on canister sampling methods.
To date, this study is the first in-situ measurement of real EtO sources in the published literature.

Several additional in-situ instruments for the detection of EtO have been developed recently. Gupta et al. (2022) describe a
cavity-enhanced absorption spectrometry method with precision < 1 ppb (1 sigma, 60 seconds) and 0.5 ppb (1 sigma, 15
45 minutes). Picarro, Inc. (2021) has publicized cavity ringdown spectroscopy (CRDS) instruments with detection limits of 0.1 –
0.25 ppb (3 sigma, 300 seconds) depending on instrument model. Entanglement Technologies (2022) lists a CRDS instrument
with EtO detection at the ppb-level in 5 seconds with other VOCs detected, and at the ppt-level in 15 minutes in "lab-scan"
mode. Aeris Technologies (2022) describes a laser-based EtO with 0.5 ppb sensitivity (1 sigma, 1 second). Here, we describe
a commercially available Aerodyne EtO monitor (Aerodyne Research Inc., 2022b) based on direct-absorption spectroscopy
50 that is capable of < 0.075 ppb precision at 1-second (1 sigma) and 0.020 ppb precision at 100 seconds (1 sigma). With frequent
zeroing and data averaging we demonstrate a precision of < 4 ppt (1 sigma, 1 hr). Instrument performance and calibration is
described. A months-long ambient EtO record at a site in Billerica, Massachusetts, USA is described, and enhancements are
traced back to a potential inventory EtO source. This source, and another are confirmed via near-field mobile measurements.

2 Experimental

 2.2 Instrument Description

The basis of our EtO monitor is our commercially available dual-laser tunable infrared direct absorption spectrometer (TILDAS-FD) platform (Aerodyne Research Inc., 2022a), which in this case is equipped with a single mid-infrared interband-cascade laser (nanoplus GmbH). For the system described herein, we use a multipass cell with 413 m optical pathlength and an active volume of 1.8 liters for continuous flow applications. The sample pressure was maintained between 20 Torr (26 mbar) and 30 Torr (40 mbar) throughout the experiments described in this paper. Details of the optical setup and flow system are described in the SI.

We measure EtO in a narrow wavelength window near 3065 cm^{-1} (3.26 μm), Figure 1. This figure fits an ambient spectrum divided by a scrubber-zeroed spectrum, such that all species except for EtO are near-zero (see Section 2.3). In total, more than 250 individual absorption lines from 6 molecular absorbers are included in the spectroscopic fit: EtO (114 lines), water (H_2O, 18 lines), formaldehyde (HCHO, 23 lines), ethane (C_2H_6, 28 lines), methane (CH_4, 12 lines), ethylene (C_2H_4, 56 lines). Methanol can be included in the fit optionally (32 lines). Centre wavelengths, linestrengths, and broadening coefficients of all molecules except EtO, ethane and methanol are from the HITRAN database (Gordon et al., 2017). Ethane and methanol lines are based on experiments by Harrison et al. (2012). The high-resolution line parameters for EtO at 3065 cm^{-1} were derived at Aerodyne. Initial knowledge of absorption at this wavelength was gained from high-resolution Fourier transform spectra by Lafferty et al. (2013).

2.3 Calibration and Zeroing

The EtO measurement is based on a set of experimentally acquired absorption lines. These experiments were done on a prototype TILDAS instrument with 76 m pathlength absorption cell, operating at 30 Torr. The absorption linestrengths were calibrated in February 2020 using a certified EtO standard (Apel Riemer, certified value 0.1023 ppm, August 2019) determined by P. Kariher at the US EPA to show good relative agreement (within 7%) among 18 tanks from 5 vendors (Kariher, 2022). Pressure-dependent EtO line broadening and other changes in instrument setup such as the inlet may lead to additional uncertainty or bias when operating the 413 m instrument at 20 Torr, and so additional calibrations are done regularly for this instrument.

Calibrations are performed by quantitative dilution of high-concentration EtO standards, to achieve a multi-point calibration curve (see SI, Figure S1). We find dry calibrations prone to long time constants, which we tentatively attribute to surface effects. Humid standard additions are preferred, as they most closely resemble sampling conditions.

We use a 2021 Airgas calibration standard, containing EtO (1.092 ppm ± 5%) and ethane (1.075 ppm ± 5%) in a balance of nitrogen (see SI, Figure S2). The inclusion of ethane in the calibration tank provides a secondary known species measurable by the instrument and not prone to reactivity or inlet effects. The average calibration factor for a set of standard addition calibrations performed over a representative week-long period is $m = 0.981 \pm 0.045$ (95% error bars). This calibration factor

implies 1 ppb of measured EtO would be corrected to 1.02 ppb EtO. However, we do not apply this small 2% correction to the data, given a certified tank uncertainty of 5% and the 4.6% error bars on the average calibration factor.

Uncertainties in the certified values of commercially available calibration tanks is of concern for accurate calibration of this and other EtO methods. A total of 4 commercially available standards have been measured by the TILDAS-FD-EtO monitor described here, varying in vendors, and at nominal concentrations of 1 ppm except where noted. Their retrieved concentrations deviated from their certified values by -2% (the above EtO and ethane standard), +9%, -417% (standard at 0.5 ppm) and +18%. Spectral backgrounding (or autobackgrounding) is done by intermittently and regularly measuring air free of EtO. Each acquired background spectrum is used to divide sample spectra for the subsequent period, reducing the impact of drift due to instrumental effects like optical fringes and spectral baseline effects. The use of scrubbed air provides a near-humidity match between sample and background spectra, effectively flattening out the curvature of the baseline present under the EtO lines due to strong neighboring water absorptions. We have not extensively tested whether the scrubber decreases the other species measured in the fit (HCHO, C_2H_6, C_2H_4, CH_4, etc.), but they appear in the divided ambient spectra with near-zero concentrations (Figure 1). For species with significant ambient backgrounds like CH_4, this indicates that the scrubber is non-destructive to CH_4. Laboratory experiments suggest scrubber EtO breakthrough on the scale of 3% is possible (3-5 SLPM flow rates) at high mixing ratios (hundreds of ppb). Indeed, mobile near-source measurements have shown such EtO breakthrough when an autobackground occurs within a high-concentration plume. Correction of this data is possible after-the-fact by manually offsetting baselines or performing a spectral refit of the data.

The frequency of autobackgrounds is chosen to match the sampling strategy. Mobile measurements aimed at capturing plumes (enhancements over background lasting typically 1-3 minutes) use a 5- to 15-minute autobackground cycle. This is a practical decision that reduces the chance of a zero interfering with a plume during a downwind transect of a facility, and is defensible as we typically are less concerned with time averaging and ppt-level baseline drift during near-source measurements. Stationary sampling of background concentrations, on the other hand, yields best long-term averaging with a 2-minute cycle.

3 Results

3.1 Instrument Performance

Precision for the TILDAS-FD EtO monitor at 1-second are < 70 ppt (1-sigma), regardless of stationary or mobile measurements.

Figure 2 compares stationary and mobile ambient measurement Allan-Werle variance plots (Werle, 2011). Blue traces show stationary performance, with best precisions achieved when stationary by altering humidity-matched zeroes with ambient measurements every 2 minutes for a 50% duty cycle. The precision improves with averaging time, from a base precision of 44 ppt (1-sigma at 2-sec) reaching 13 ppt at 2-minutes, 6.0 ppt at 15 minutes and 4.1 ppt at 1 hour (all precisions at 1-sigma).

The TILDAS-EtO monitor has also been used for near-source mobile monitoring, with less frequent autobackgrounds (5- to 10-minute frequencies). The instrument shows sensitivity to truck motion, particularly quick turns or stops which manifest as

negative deviations in mixing ratio on the order of 0.5 ppb. Optimizing optical alignment minimizes but does not eliminate these effects, which are largely attributed to strain on the laser focusing objective. Continuous vibrations do not manifest as negative deviations, instead impacting the overall noise. Performance while in motion on the highway is shown in Figure 2 (red traces). For these measurements, the instrument was mounted in the Aerodyne Mobile Laboratory in a vibration-isolated rack and operated with a 10-minute humidity-matched zeroing cycle. The 1-second precision of 50 ppt averages to 28 ppt in 2 minutes.

3.2 Ambient Measurements

A months-long record of ambient EtO in Billerica, Massachusetts, USA was acquired (Figure 3), spanning winter, spring, and summer 2022. Averaging the hourly data for the entire period (with standard deviation in parentheses) yields Avg (SD) = 18 (22) ppt. The standard deviations given reflect the combination of instrument noise as described above and the variability of EtO in ambient air. Histograms comparing winter and summer concentraitions are shown in Figure S3. Hourly averages for summertime data are less noisy than wintertime data due to the more aggressive zeroing cycle (2 mins vs 30 mins). Summertime concentrations (1 July – 4 Aug) of 33 (13) ppt appear slightly elevated compared to winter averages (9 Feb – 30 April) 12 (23) ppt measurements. We exclude the intermediate spring data (May) from these averages. The averages are different at the 95% confidence level using Gaussian statistics and standard error of the mean (see SI, Table S3). These data are consistent with recent data reported by the EPA for 4 Massachusetts sites (US EPA, 2022a): 2022 observations accessed 8/20/2022 range between 0 and 0.270 μg m^{-3} (0 – 150 ppt) with a median of 0.090 μg m^{-3} (50 ppt); they are below 2019 levels shown for EPA NAATS sites in New York and Pennsylvania (US EPA, 2019) of 0.298 – 0.361 μg m^{-3} (165 – 201 ppt), though the EPA has since noted that true background concentrations are unknown due to the influence of canister artifacts (US EPA, 2021).

Several distinct EtO enhancement events are evident in the ambient record. One such event on 3/27/2022 is shown in Figure 4. This figure shows two plumes, the larger of the two reaching concentrations of 500 ppt, and lasting 3-4 hours near midnight local time. No EtO activity (e.g., calibrations) was occurring in the lab during this week. During these winter and spring roof-top measurements, the EtO monitor briefly switches to laboratory air prior to humidity-matched autobackgrounds, providing several seconds of indoor air sampling. The laboratory air shows an "echo" of the outdoor EtO event ~3 hours delayed, and slightly broadened, with a maximum concentration of 168 ppt, which we attribute to the building's ventilation system gradually mixing in outdoor air. This observation highlights the fact that indoor air quality is directly impacted by outdoor EtO concentrations.

Back-trajectory simulations for this event were performed using NOAA's HYSPLIT model (Rolph et al., 2017; Stein et al., 2015) (see Figures S4 – S5). These simulations suggest that regional transport was from the south-west during this time. This trajectory passes over a commercial sterilization facility approximately 35 km away that is known by the EPA to use EtO (US EPA, 2022c). In the following section, we describe near-field mobile measurements of this source showing clear EtO enhancements downwind. These ambient measurements highlight the benefits of the high-precision TILDAS-FD-EtO sensor

over alternative methods like canister sampling, which typically have long integration times (24 hours) that would wash out brief events and are prone to sampling artifacts at 100's of ppt levels (US EPA, 2021; Hoisington and Herrington, 2021).

3.3 Near-Field Mobile Measurements

Motivated by the sporadic enhancement events in the ambient measurement record, mobile measurements of two commercial sterilization facilities in Massachusetts (US EPA, 2022c) were conducted in August 2022. The first source visited, "Facility A", was the facility identified through Hysplit trajectory explorations of the 3/27/2022 event. Facility A was visited over the course of ~4 hours, split between morning and afternoon. Average downwind concentrations are summarized in Figure 5, showing clear enhancements above background downwind of the facility. Concentration enhancements ~600 m from the source were around 5 ppb, with enhancements as high as 300 ppb measured 35 m from the facility. Additional transects, time series and spatial averages are shown in the SI.

The second source measured, "Facility B", is also a commercial sterilization facility (US EPA, 2022c), and is located 15 km miles south of the Billerica MA stationary measurement site. The EPA has conducted a risk assessment of this facility and found enhanced cancer risk (US EPA, 2022c). Facility B also showed enhancements above background on this measurement day (maximum of 7.5 ppb 60 m downwind), though at far lesser concentrations than Facility A. Further details are presented in the SI.

4 Conclusions

The TILDAS-FD-EtO monitor achieves precisions of <75 ppt or <0.075 ppb in 1 second and < 20 ppt in 100 seconds (1-sigma precisions), with averaging down to 4 ppt in an hour (1-sigma) when operated with frequent humidity-matched zeroes. Ambient measurements at a Massachusetts site reveal EtO concentrations on the order of 18 ppt (22 ppt standard deviation). Distinct EtO events lasting a few hours are observed in the ambient record, with back trajectory simulations suggesting an EtO source nearly 35 km away. Mobile measurements directly downwind of this medical sterilization facility, as well as another sterilization facility in the state, confirm the presence of EtO emissions at both sites, with downwind concentrations in the 0.5 ppb to 700 ppb range depending on source identity and distance downwind. These measurements highlight how continuous in-situ EtO monitoring with a high-precision sensor can provide information leading directly to EtO point source identification.

Data availability

Ambient ethylene oxide dry air mixing ratios, hourly averages and mobile measurement data is publicly and freely available at https://osf.io/jeywd/?view_only=421c0d48e2d1449488c14f883a7859b6

Author Contribution

The manuscript was written through contributions of all authors.

Competing Interests

The authors declare no competing interests.

Disclaimer

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

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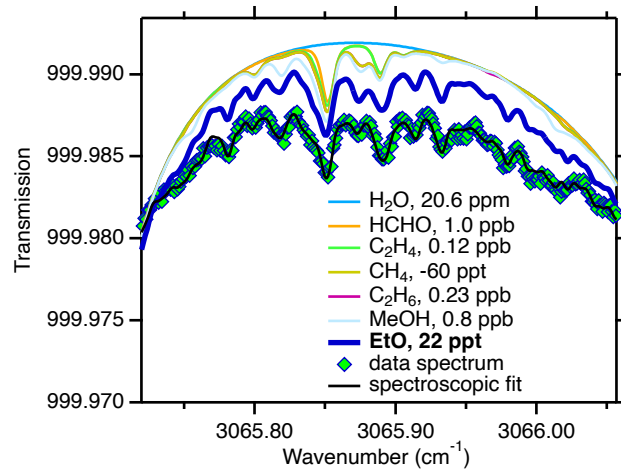
255 **Figure 1. Spectrum of EtO and other gaseous absorbers in the spectral window that are included in the spectroscopic fit. A measured spectrum (green diamonds, 24 hr average ambient spectrum, humidity-matched scrubber zeroes) is shown overlaid with the final fit (black trace). Individual fit components include water (H_2O), formaldehyde (HCHO), ethylene (C_2H_4), methane (CH_4), ethane (C_2H_6) and methanol (MeOH). This figure fits an ambient spectrum divided by a scrubber-zeroed spectrum, such that all species except for EtO are near-zero (see Section 2.3).**

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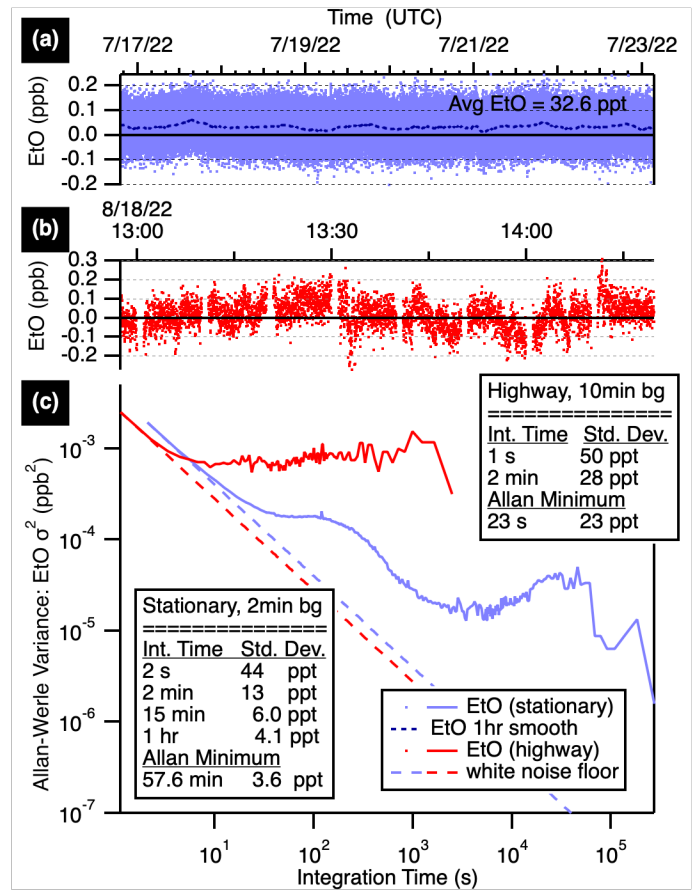
Figure 2. Time series (a, b) and Allan-Werle variance plots (c) showing EtO precisions at various averaging times while stationary with 2-min autobackgrounds (blue), and while mobile on the highway with 10-min backgrounds (red). The stationary data (a) averages to 32.6 ppt EtO, with a 1-hour smooth (dotted line) shown.

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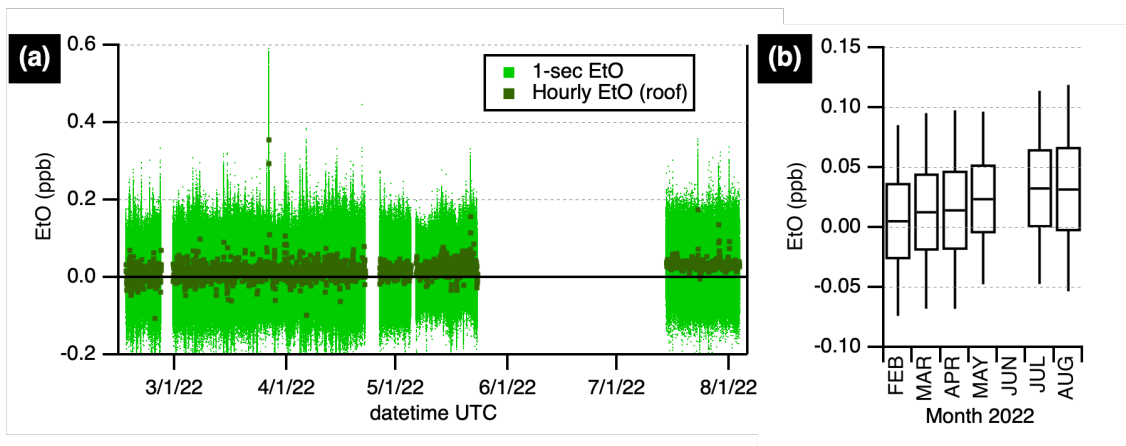
Figure 3. Ambient ethylene oxide at a site in Billerica, Massachusetts, USA. Panel (a): Data at 1-second (pale green) is shown alongside hourly averages (dark green squares). Panel (b): Monthly box plot showing the median, 25th and 75th quartiles, with whiskers extending to the 5th and 95th percentiles. Data prior to 6/2022 were acquired from a roof-top inlet with humidity-matched autobackgrounds every 30 minutes; data after 7/2022 were acquired from a 3-meter inlet with humidity-matched autobackgrounds every 2 minutes. Gaps in the time series are due to laboratory or field experiments.
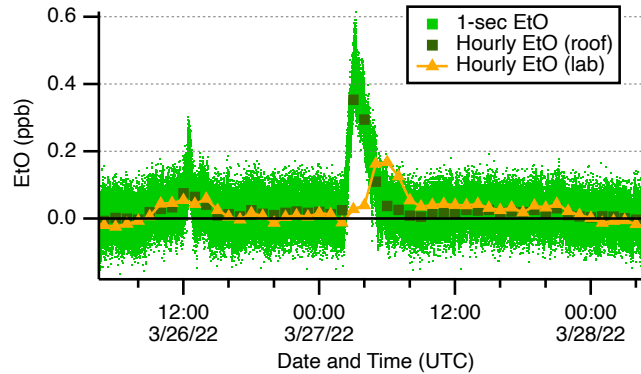
Figure 4. Ethylene oxide events measured on the roof-top inlet. Outdoor data at 1-second data (pale green) is shown alongside hourly averages (dark green squares) averages. Laboratory air sampled prior to autobackgrounds (orange triangles) is shown.
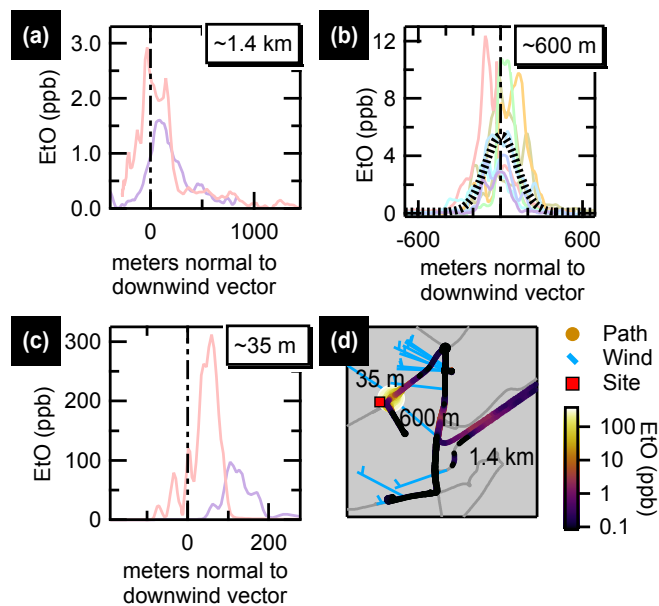
Figure 5. Summary of transects downwind of Facility A. Transects are plotted normal to the wind vector for paths driven along 3 roads approximately 35 m (a), 600 m (b) and 1.4 km (c) downwind of Facility A. The average of 600 m transects (black dotted line) is shown for Panel B. A map (d) shows the facility location (red square) with the three main transect roads labelled by distance downwind. The driven path is colored and sized by EtO concentration. Wind barbs (blue) are tethered to the truck path, with feather end of the staff pointing into the wind.

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