Ethylene oxide monitor with part-per-trillion precision for in situ measurements

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Abstract. An Aerodyne tunable infrared laser direct absorption spectrometer with a multipass cell with a 413 m path-length for the detection of ethylene oxide (EtO) is presented (TILDAS-FD-EtO). This monitor achieves precisions of <75 ppt or <0.075 ppb s\(^{-1}\) and <20 ppt in 100 s (1\(\sigma\)). We demonstrate precisions averaging down to 4 ppt h\(^{-1}\) (1\(\sigma\) 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, SD). 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 to 700 ppb range depending on source identity and distance downwind.

1 Introduction

Ethylene oxide (EtO, also known as EO or oxirane) is a reactive compound with a strained three-member ether ring (\(\text{C}_2\text{H}_4\text{O}\), CAS no. 75-21-8, MW = 44.05 g mol\(^{-1}\)). It is commonly used in chemical manufacturing of polymers and glycols. It is also used to sterilize 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; US EPA, 2017), has set an inhalation unit risk (IUR) for EtO at 3.0 \(\times\) 10\(^{-3}\) \(\mu g\) m\(^{-3}\) in air (US EPA, 2022b). An IUR for EtO of 3.0 \(\times\) 10\(^{-3}\) \(\mu g\) m\(^{-3}\) implies that three excess cancer cases are expected to develop in 1000 people if exposed to 1 \(\mu g\) m\(^{-3}\) (0.55 ppb) of EtO over a lifetime. Other risk estimates for different populations are included in the EPA source material (US EPA, 2016). Workplace limits for 8 h 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.

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 parts per trillion. 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 cleanliness/cleaning protocol (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 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 Station (NATTS) monitoring sites for the October 2018–March 2019 period average 0.297 \(\mu g\) m\(^{-3}\) and range between 0.185 and 0.397 \(\mu g\) m\(^{-3}\) (103 to 220 ppt) (US EPA, 2019). More recent EPA data from 2022 at Massachusetts measurement sites show 24 h concentrations between 0 and 0.270 \(\mu g\) m\(^{-3}\) (0–150 ppt) (US EPA, 2022c). Olaguer et al. (2020) report near-source 24 h aver-
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 \( < 1 \text{ ppb} \) (1σ, 60 s) and 0.5 ppb (1σ, 15 min). Picarro, Inc. (2021) has publicized cavity ring-down spectroscopy (CRDS) instruments with detection limits of 0.1–0.25 ppb (3σ, 300 s) depending on the instrument model. Entanglement Technologies (2022) lists a CRDS instrument with EtO detection at the part-per-billion level in 5 s with other volatile organic compounds (VOCs) detected and at the part-per-trillion-level in 15 min in “lab-scan” mode. Aeris Technologies (2022) describes a laser-based EtO with 0.5 ppb sensitivity (1σ, 1 s). Here, we describe a commercially available Aerodyne EtO monitor (Aerodyne Research Inc., 2022a) based on direct-absorption spectroscopy that is capable of \( < 0.075 \text{ ppb} \) precision at 1 s (1σ) and 0.020 ppb precision at 100 s (1σ). With frequent zeroing and data averaging we demonstrate a precision of \( < 4 \text{ ppb} \) (1σ, 1 h). Instrument performance and calibration are described. A months-long ambient EtO record at a site in Billerica, Massachusetts, United States, 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

2.1 Instrument description

The basis of our EtO monitor is our commercially available dual-laser tunable infrared laser 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 a 413 m optical path length and an active volume of 1.8 L 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 Supplement.

We measure EtO in a narrow wavelength window near 3065 cm\(^{-1}\) (3.26 µm); see Fig. 1. This figure fits an ambient spectrum divided by a scrubber-zeroed spectrum, such that all species except EtO are near zero (see Sect. 2.2).

![Figure 1. Spectrum of EtO and other gaseous absorbers in the spectral window that is included in the spectroscopic fit. A measured spectrum (green diamonds, 24 h average ambient spectrum, humidity-matched scrubber zeroes) is shown overlaid with the final fit (black trace). Individual fit components include water (H\(_2\)O), formaldehyde (HCHO), ethylene (C\(_2\)H\(_4\)), methane (CH\(_4\)), 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 Sect. 2.2).](https://doi.org/10.5194/amt-16-1915-2023)
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 Fig. 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 $m = 0.981 ± 0.045$ (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 are of concern for accurate calibration of this and other EtO methods. A total of four 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 (Fig. 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 parts per billion). Indeed, mobile near-source measurements have shown such an 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 the background lasting typically 1–3 min) use a 5 to 15 min 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 part-per-trillion-level baseline drift during near-source measurements. Stationary sampling of background concentrations, on the other hand, yields the best long-term averaging with a 2 min cycle.

3 Results

3.1 Instrument performance

Precision for the TILDAS-FD-EtO monitor at 1 s is < 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 min for a 50 % duty cycle. The precision improves with averaging time from a base precision of 44 ppt ($1\sigma$ at 2 s), reaching 13 ppt at 2 min, 6.0 ppt at 15 min, and 4.1 ppt at 1 h (all precisions at $1\sigma$).

The TILDAS-FD-EtO monitor has also been used for near-source mobile monitoring, with less frequent autobackgrounds (5 to 10 min frequencies). The instrument shows sensitivity to truck motion, particularly quick turns or stops, which manifest as negative deviations in the mixing ratio on the order of 0.5 ppb. Optimizing optical alignment minimizes but does not eliminate these effects, which are largely at-
tributed 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 Fig. 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 min humidity-matched zeroing cycle. The 1 s precision of 50 ppt averages to 28 ppt in 2 min.

3.2 Ambient measurements

A months-long record of ambient EtO in Billerica, Massachusetts, United States, was acquired (Fig. 3), spanning the winter, spring, and summer of 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 concentrations are shown in Fig. S3. Hourly averages for summertime data are less noisy than wintertime data due to the more aggressive zeroing cycle (2 min vs. 30 min). Summertime concentrations (1 July–4 August) of 33 (13) ppt appear slightly elevated compared to winter averages (9 February–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 Table S3 in the Supplement). These data are consistent with recent data reported by the EPA for four Massachusetts sites (US EPA, 2022c): 2022 observations accessed on 20 August 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 27 March 2022 is shown in Fig. 4. This figure shows two plumes, the larger of the two reaching concentrations of 500 ppt and lasting 3–4 h near midnight local time. No EtO activity (e.g., calibrations) was occurring in the lab during this week. During these winter and spring rooftop measurements, the EtO monitor briefly switches to laboratory air prior to humidity-matched auto-backgrounds, providing several seconds of indoor air sampling. The laboratory air shows an “echo” of the outdoor EtO event ∼ 3 h delayed, and slightly broadened, with a maximum concentration of 168 ppt, which we attribute to the building’s ventilation system gradually mixing with 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 Figs. S4 and S5). These simulations suggest that regional transport was from the southwest 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, 2022a). 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 h) that would wash out brief events and are prone to sampling artifacts at hundreds of part-per-trillion 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, 2022a) were conducted in August 2022. The first source...
Figure 5. Summary of transects downwind of Facility A. Transects are plotted normal to the wind vector for paths driven along three roads approximately 1.4 km (a), 600 m (b), and 35 m (c) downwind of Facility A. The average of 600 m transects (dotted black line) is shown for panel (b). A map (d) shows the facility location (red square) with the three main transect roads labeled by distance downwind. The driven path is colored and sized by EtO concentration. Wind barbs (blue) are tethered to the truck path, with the feather end of the staff pointing into the wind.

visited, “Facility A”, was the facility identified through HYSPLIT-trajectory explorations of the 27 March 2022 event. Facility A was visited over the course of ~4 h, split between morning and afternoon. Average downwind concentrations are summarized in Fig. 5, showing clear enhancements above the 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 Supplement.

The second source measured, “Facility B”, is also a commercial sterilization facility (US EPA, 2022a) and is located 15 km 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, 2022a). Facility B also showed enhancements above the 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 Supplement.

4 Conclusions

The TILDAS-FD-EtO monitor achieves precisions of <75 ppt or <0.075 ppb in 1 s and <20 ppt in 100 s (1σ precisions), with averaging down to 4 ppt in an hour (1σ) when operated with frequent humidity-matched zeroes. Ambient measurements at a Massachusetts site reveal EtO concentrations on the order of 18 ppt (22 ppt SD). 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 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 are publicly and freely available at https://doi.org/10.17605/OSF.IO/JEWYD (Yacovitch et al., 2022).

Supplement. The supplement related to this article is available online at: https://doi.org/10.5194/amt-16-1915-2023-supplement.

Author contributions. TIY wrote over 50% of the manuscript and performed the laboratory calibrations. ChD wrote over 25% of the manuscript and led the phase 1 instrument development program. JRR identified the optimal spectral window, measured the spectroscopic line parameters, and developed the zeroing scheme. CoD led the field deployments of the instrument and optimized the zeroing scheme. JBM designed the optical system for the EtO instrument, including the 400 m path length optical cell. He was deeply involved with the tests and qualification of the instrument, including during hardware changes and spectral analysis. SCH performed time series analysis, wrote 25% of the manuscript, and led the phase 2 instrument development program.

Competing interests. The contact author has declared that none of the authors has any competing interests.

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**References**


