Ethylene Oxide Measurements in Western Washington during June 2021

By

Beth Friedman

For the

Air Quality Program

Washington State Department of Ecology
Olympia, Washington

June 2022, Publication 22-02-020

Publication Information

This document is available on the Department of Ecology's website at:
https://apps.ecology.wa.gov/publications/summarypages/2202020.html

Contact Information

Air Quality Program

P.O. Box 47600
Olympia, WA 98504-7600
Phone: 360-407-6800
Website[1]: Washington State Department of Ecology

ADA Accessibility

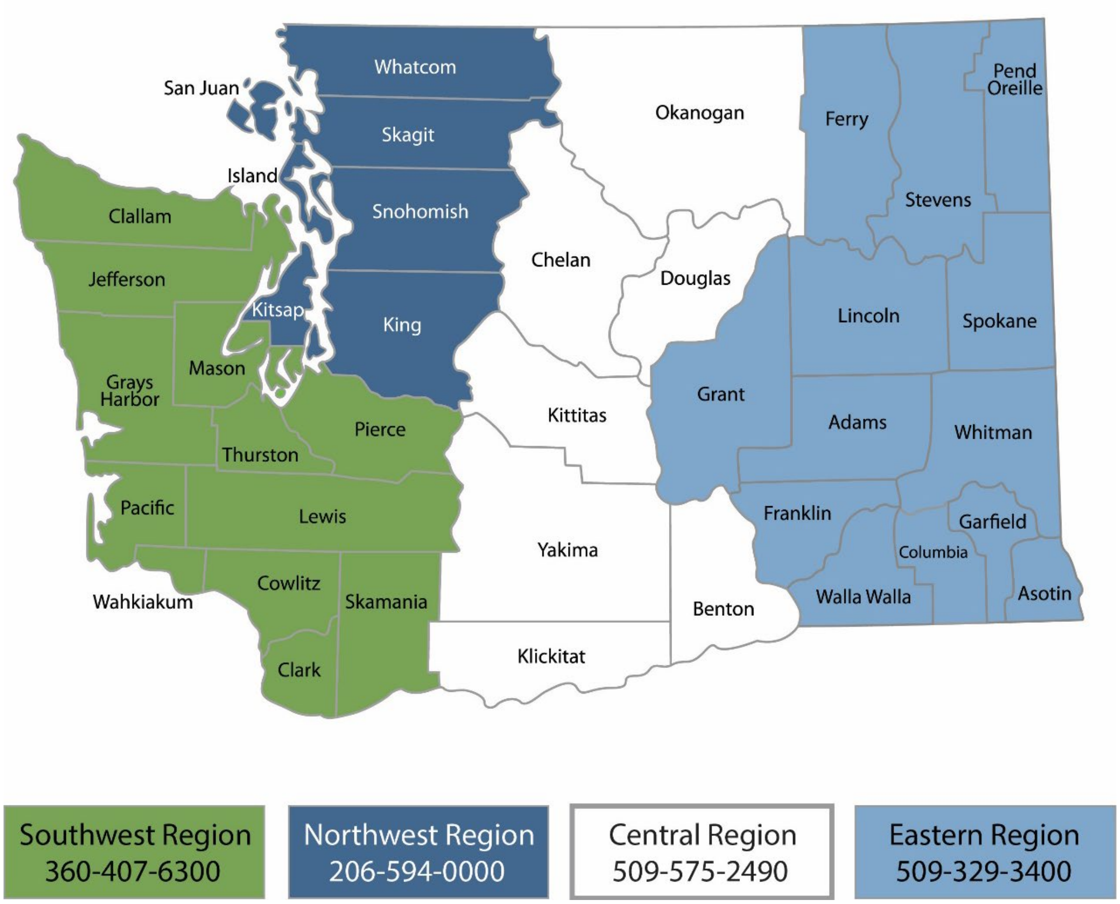
The Department of Ecology is committed to providing people with disabilities access to information and services by meeting or exceeding the requirements of the Americans with Disabilities Act (ADA), Section 504 and 508 of the Rehabilitation Act, and Washington State Policy #188.

To request an ADA accommodation, contact Ecology by phone at 360-407-6800 or email at melanie.forster@ecy.wa.gov. For Washington Relay Service or TTY call 711 or 877-833-6341. Visit Ecology's website for more information.

[1] www.ecology.wa.gov/contact

Department of Ecology's Regional Offices

Map of Counties Served



Region	Counties served	Mailing Address	Phone
Southwest	Clallam, Clark, Cowlitz, Grays Harbor, Jefferson, Mason, Lewis, Pacific, Pierce, Skamania, Thurston, Wahkiakum	P.O. Box 47775 Olympia, WA 98504	360-407-6300
Northwest	Island, King, Kitsap, San Juan, Skagit, Snohomish, Whatcom	P.O. Box 330316 Shoreline, WA 98133	206-594-0000
Central	Benton, Chelan, Douglas, Kittitas, Klickitat, Okanogan, Yakima	1250 West Alder Street Union Gap, WA 98903	509-575-2490
Eastern	Adams, Asotin, Columbia, Ferry, Franklin, Garfield, Grant, Lincoln, Pend Oreille, Spokane, Stevens, Walla Walla, Whitman	4601 North Monroe Spokane, WA 99205	509-329-3400
Headquarters	Statewide	P.O. Box 46700 Olympia, WA 98504	360-407-6000

Ethylene Oxide Measurements in Western Washington during June 2021

Air Quality Program
Washington State Department of Ecology
Olympia, WA

June 2022 | Publication 22-02-020

DEPARTMENT OF
ECOLOGY
State of Washington

Table of Contents

List of Figures and Tables

Figures

Tables

Acknowledgements

The authors of this report thank the following people for their contribution to this study:

- Odelle Hadley and Mike Shults, Olympic Region Clean Air Agency
- Ranil Dhammapala
- Picarro, Inc.

Executive Summary

Using cavity ringdown spectroscopy, EtO concentrations were determined at three different monitoring sites in Washington State in June 2021. Hourly EtO concentrations ranged from 0 to 272 ppt. Very little site to site, hourly, or day of week variability was observed. The measured low concentrations and lack of variability among monitoring sites suggests the presence of a regional background of EtO in Washington State. Extending these measurements to long-term health impacts suggests that the majority of measurements are below 11 ppt, the level at which lifetime exposure poses an increased cancer risk of 100-in-a-million.

Introduction

Ethylene oxide (EtO) is a colorless, water-soluble, odorless gas with an atmospheric lifetime of approximately 3-6 months. Used in solvents, as a chemical intermediate, and to sterilize surgical equipment, EPA updated their classification of EtO as "carcinogenic to humans" by the inhalation route of exposure in December 2016.[2,3]

Registered point source emissions of EtO in Washington State's emissions inventory include medical equipment sterilizers, paint spray booths, surface coatings, and fugitive emissions. However, Washington State's emissions inventory for ethylene oxide is not comprehensive, and potential missing sources include building and construction materials, manufacturing applications, transportation vehicle materials (such as antifreeze), and downstream products such as adhesives. An Ecology workgroup conducted an extensive literature search in 2019 regarding EtO sources. In addition to the sources listed above, EtO is used as a chemical intermediate in the production of ethylene and polyethylene glycols, surfactants, and other products. EtO is also used in pharmaceutical synthesis processes as well as a byproduct of various chemical manufacturing processes. Other potential identified sources include gasoline-powered engines, skin care product contamination, and tobacco smoke.[4]

Since October 2018, EtO monitoring in Washington State consists of a 24 hour sample collected every six days at the Seattle-Beacon Hill NATTS monitoring site with subsequent offline analysis by the TO-15 method. A special air toxics project by the Olympic Region Clean Air Agency at the Lacey monitoring site provided EtO data in 2018-2019 using the same TO-15 method.[5] Challenges of EtO measurements by TO-15 include method sensitivity, acquisition of standards, canister background, and interferences with other commonly observed atmospheric species. Current TO-15 EtO Method Detection Limits are also greater (ranging from 2-8 times higher) than the 100-in-1-million cancer risk level of 11 ppt.

Based in California, Picarro, Inc. recently developed a continuous instrument capable of measuring EtO at a higher time resolution than Method TO-15. In June 2021, Ecology contracted with Picarro to deploy their EtO analyzer at three monitoring sites in Western Washington. We report the resulting hourly concentrations of EtO as a function of site, day of week, and hour, and extend the results to compare to health metrics.

---

[2] https://www.epa.gov/hazardous-air-pollutants-ethylene-oxide
[3] The previous weight of evidence characterization of EtO was "probably carcinogenic to humans"
[4] Washington State Department of Ecology Air Quality Program Internal Document: Known and potential uses, production, and emissions of ethylene oxide (2020).
[5] O. Hadley, A. Cutler, R. Schumaker, R. Bond: Wildfires and wood stoves: Woodsmoke toxicity and chemical characterization study in the northwestern United States. *Atmospheric Environment*, 253, 15, 118347, doi: 10.1016/j.atmosenv.2021.118347 (2021).

Methods

Monitoring Sites and Study Timeline

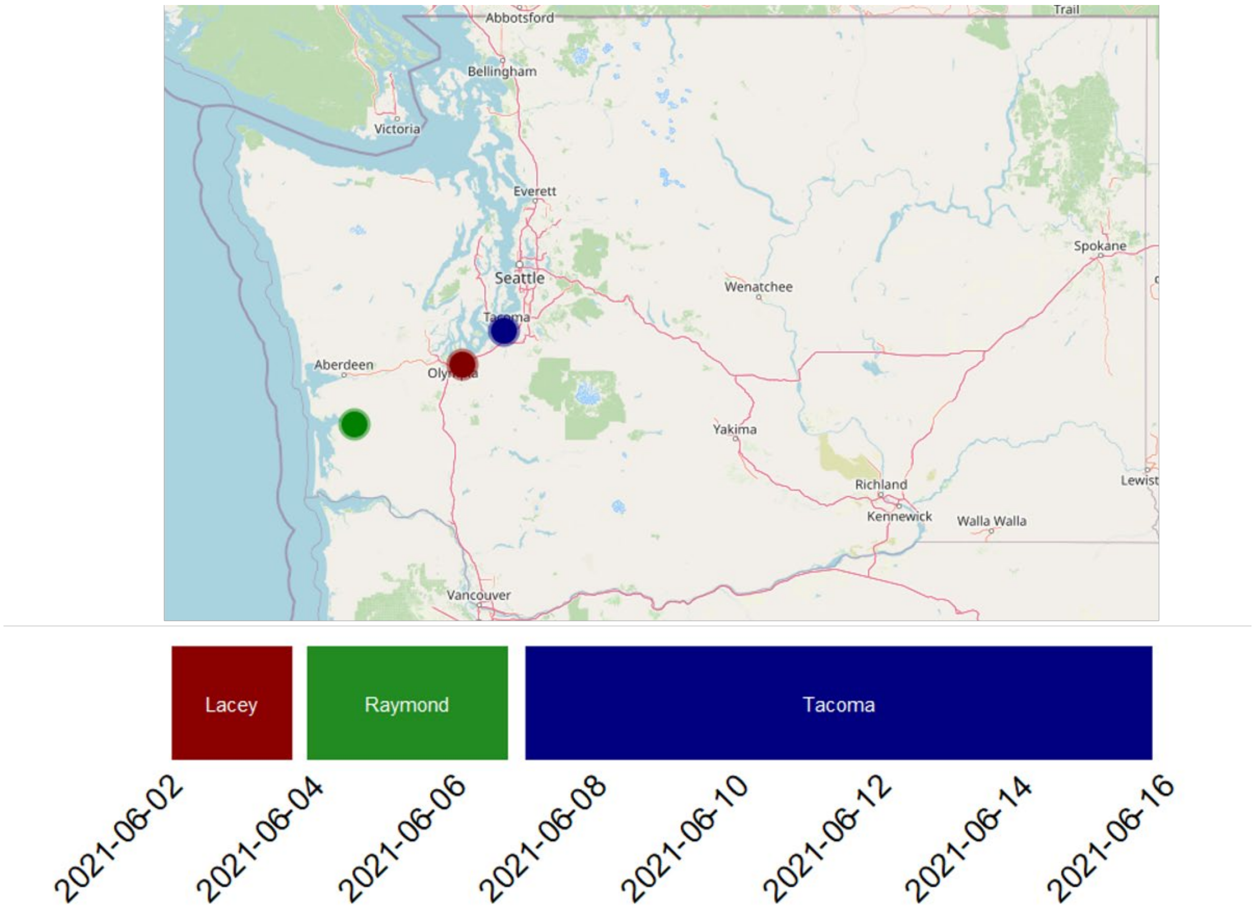


Figure 1. Monitoring site locations and the study timeline.

EtO measurements were conducted at Lacey, Raymond, and Tacoma monitoring sites in cooperation with the Olympic Region Clean Air Agency. The Lacey monitoring site is located at a school on a well-trafficked arterial corridor and provides an opportunity to compare to previous TO-15 measurements from a 2018-2019 special air toxics study. Located near the Washington coast, Raymond is representative of a rural background monitoring site. Designated a near-road monitoring site, Tacoma is located approximately 15 meters from Interstate-5 (annual average daily traffic is approximately 134,000). Other measurements available at these monitoring sites include $PM_{2.5}$, meteorology (at Tacoma and Lacey), and NO_x (at Tacoma). There are no known EtO sources in the vicinity of these monitoring sites, however small sources are not part of reported point source emissions and may not be known by Ecology or local air agencies.

Ethylene Oxide Measurements

The Picarro G2920 Gas Concentration Analyzer utilizes cavity ring-down spectroscopy (CRDS) to determine ambient EtO concentrations. Briefly, a laser beam enters a cavity defined by three mirrors and a fast photodetector senses the amount of light in the cavity. When the photodetector signal reaches a certain threshold, the laser beam turns off, and the light within the cavity bounces between the mirrors. Because the cavity mirrors have slightly less than 100% reflectivity, the cavity light intensity measured by the photodetector exponentially decays to zero. This decay is also known as "ring down". When ethylene oxide is introduced into the cavity and the laser is tuned to the characteristic wavelength at which ethylene oxide absorbs light, the ring down is impacted. The analyzer continuously determines the cavity ring down in an empty cavity and in a cavity where ethylene oxide is present. A mathematical fit to the laser absorption is used to calculate the concentration of ethylene oxide introduced into the cavity.[6]

The analyzer operationally measures EtO in the range of 0 - 10 ppm, specifies a 100 ppt lower limit of detection at 5 minutes (3σ), and does not require onsite calibration. The analyzer was calibrated prior to the measurement campaign to within 2% of the reference instrument and within standards put in place by the National Institute of Standards and Technology as well as the International Electrotechnical Commission. The analyzer was also equipped with an activated carbon scrubber that removed ambient EtO. An hourly measurement consisted of 50 minutes of ambient data, and 10 minutes of scrubbed data. To determine the hourly concentration, the average hourly scrubbed EtO value was subtracted from the corresponding average hourly ambient EtO value. The analyzer also reports measurements of water vapor, carbon dioxide, and methane.

[6] https://www.picarro.com/products/g2920_gas_concentration_analyzer

Results

Temporal Variability

Hourly timeseries of EtO at each monitoring site are shown in Figure 2. Aside from a few hourly concentration increases in Raymond, ambient EtO concentrations were fairly consistent at each monitoring site and did not vary significantly throughout the day. Averages, standard deviations, and maximum concentrations are shown in Table 1.

Table 1. EtO concentrations at each monitoring site.

Site	Number of hours of data	Average EtO [standard deviation] (ppt)	Maximum EtO (ppt)
Lacey	41	30.9 [17.9]	90.5
Raymond	68	30.3 [50.3]	272
Tacoma	212	15.9 [16.3]	57.3

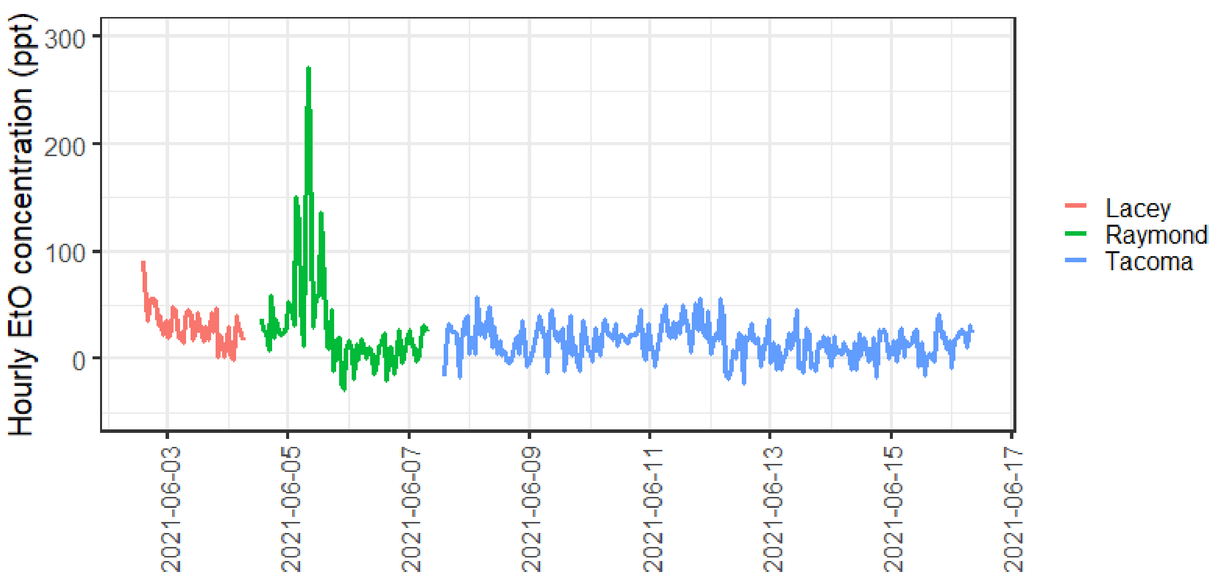


Figure 2. Hourly EtO concentrations during the campaign.

Diurnal cycles at each site are shown in Figure 3. With the most data (212 total hours), Tacoma shows very little diurnal variability. Figure 4 shows the diurnal cycle of NO_2 and EtO during the same time period at Tacoma. If EtO were associated with traffic-related emissions, it would likely show a similar pattern to the NO_2 data with corresponding concentration increases during the morning and evening rush hours (Figure 4).

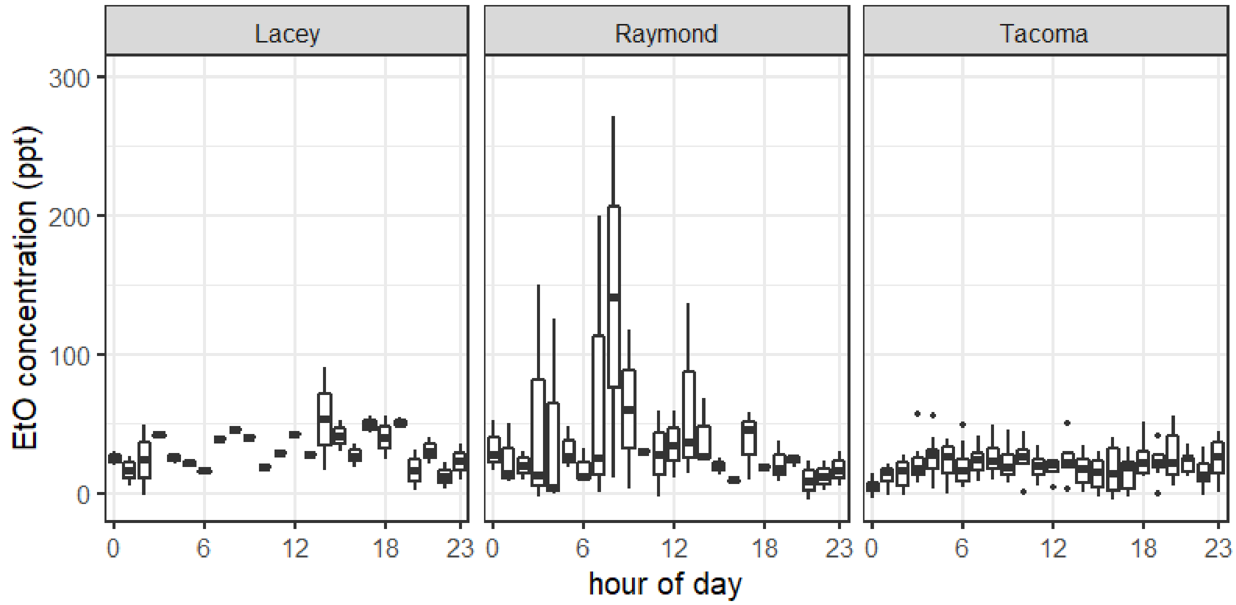


Figure 3. EtO concentrations at each monitoring site as a function of hour of day.

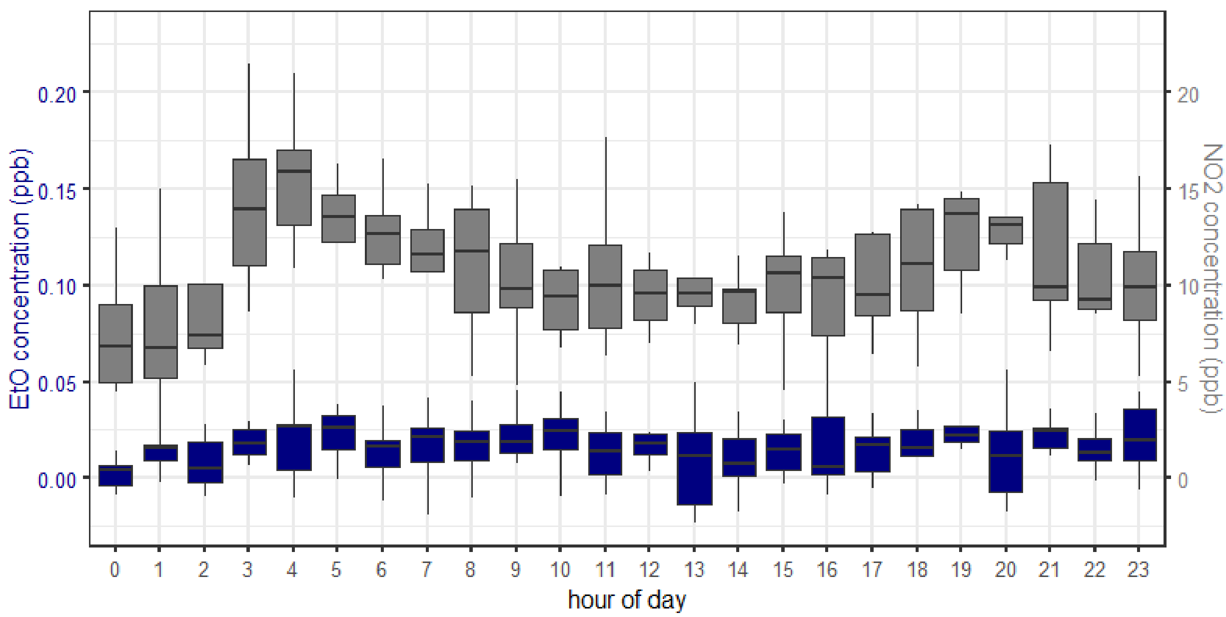


Figure 4. Hourly concentrations of EtO (left axis, blue boxplots) and NO_2 (right axis, grey boxplots) at the Tacoma monitoring site during the campaign.

EtO's inconsistency with traffic-related emissions is also reflected in comparing concentrations as a function of day of week at Tacoma (Figure 5). There was very little day-to-day variability exhibited between weekdays and weekends.

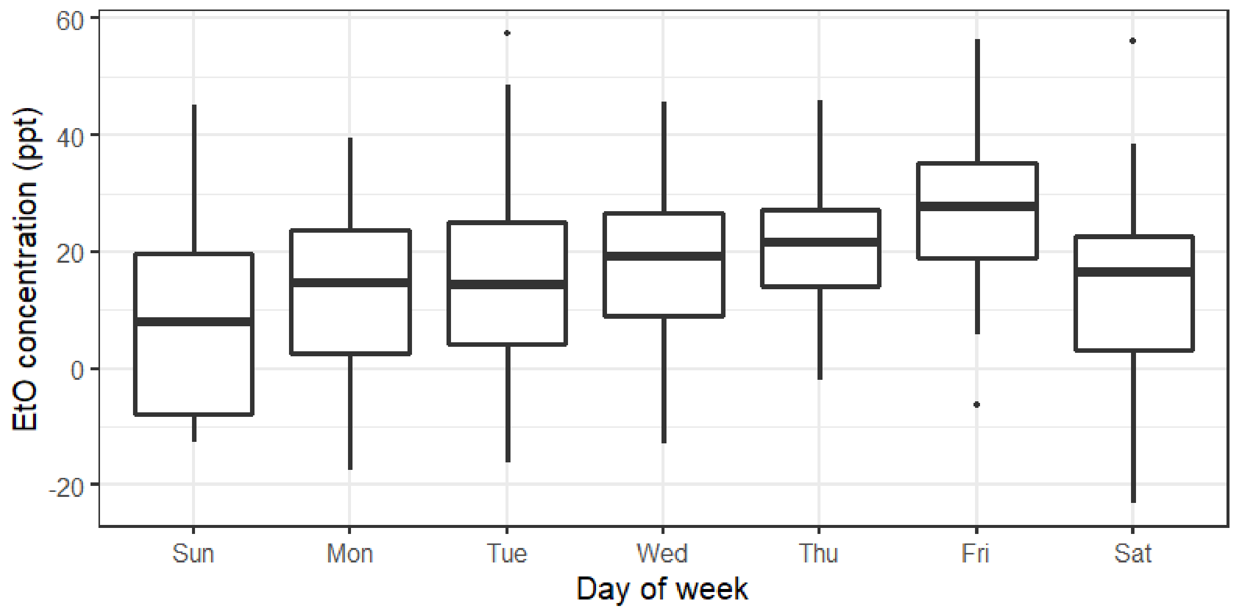


Figure 5. EtO concentrations as a function of day of week at the Tacoma monitoring site.

EtO Concentrations at Raymond

Given that the Raymond monitoring site is representative of a rural background site, and that monitoring at Raymond occurred over a weekend, the variability in EtO concentrations is surprising. It is also unlikely that any potential sources would be active on Saturday morning when the concentration increases occurred. Figure 6 shows an hourly timeseries of EtO at the Raymond monitoring site. EtO concentration increases occurred at 3-4am, as well as 7-9am on the morning of Saturday, June 5. Another sharp increase occurred at 1pm that same afternoon. Aside from 3am-1pm on June 5, EtO concentrations were below 100 ppt, averaging 16.9 ppt with a maximum of 68.6 ppt.

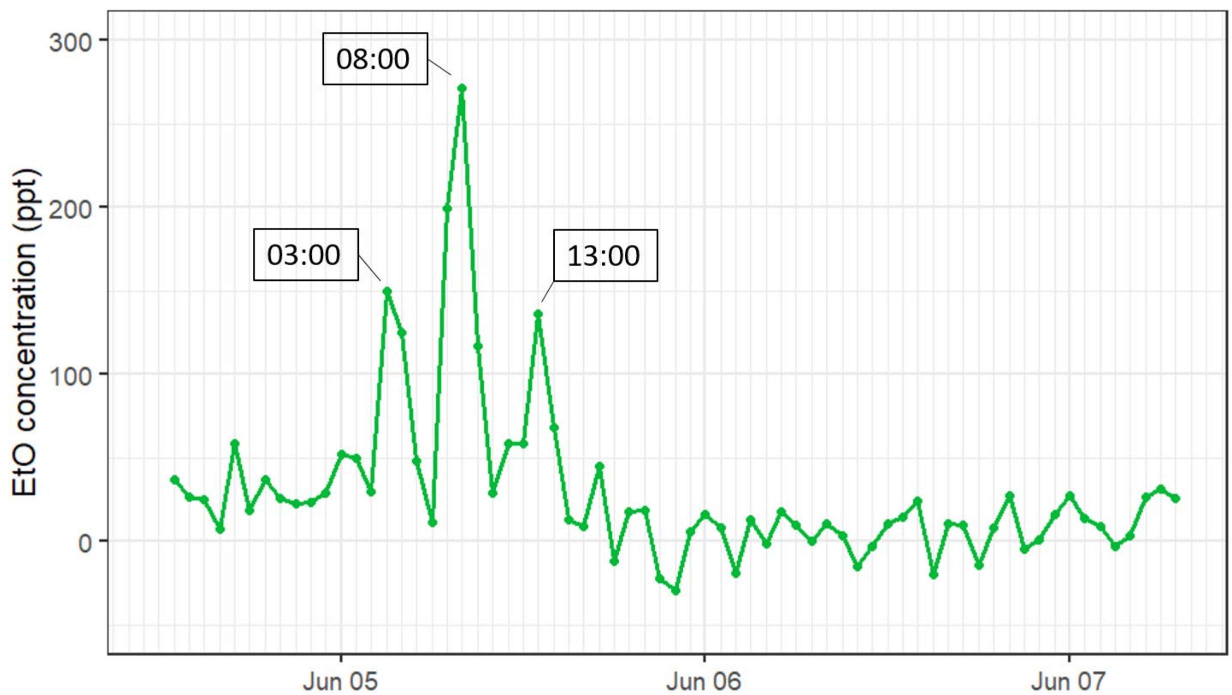


Figure 6. Hourly concentrations of EtO at Raymond.

Taking into account the lack of local sources as well as instrument diagnostics, we hypothesize that the increases in EtO concentrations are associated with an increase in precipitation and potential off-gassing from soils. While very little information exists regarding EtO and soils,[4] EtO could potentially volatilize given its high vapor pressure. The rain in Raymond on June 5 was the first rain in 8 days, and corresponds with the following hour's increase in EtO concentrations (Figure 7). During the concentration increases, the wind direction originated mostly from the northerly directions (NNW, N, NNE, WNW) as well as from the south (SE, ESE). However, wind speeds were all less than 4 mph, suggesting any EtO present was of local origin. The highest 5 minute EtO concentration observed on June 5 (624 ppt) corresponded to a wind direction from the northwest and a wind speed of 1.8 mph. However, seasonal patterns in EtO at Seattle-Beacon Hill do not show a strong association between precipitation and EtO concentrations, and no concentration increases were observed during precipitation events at Tacoma.

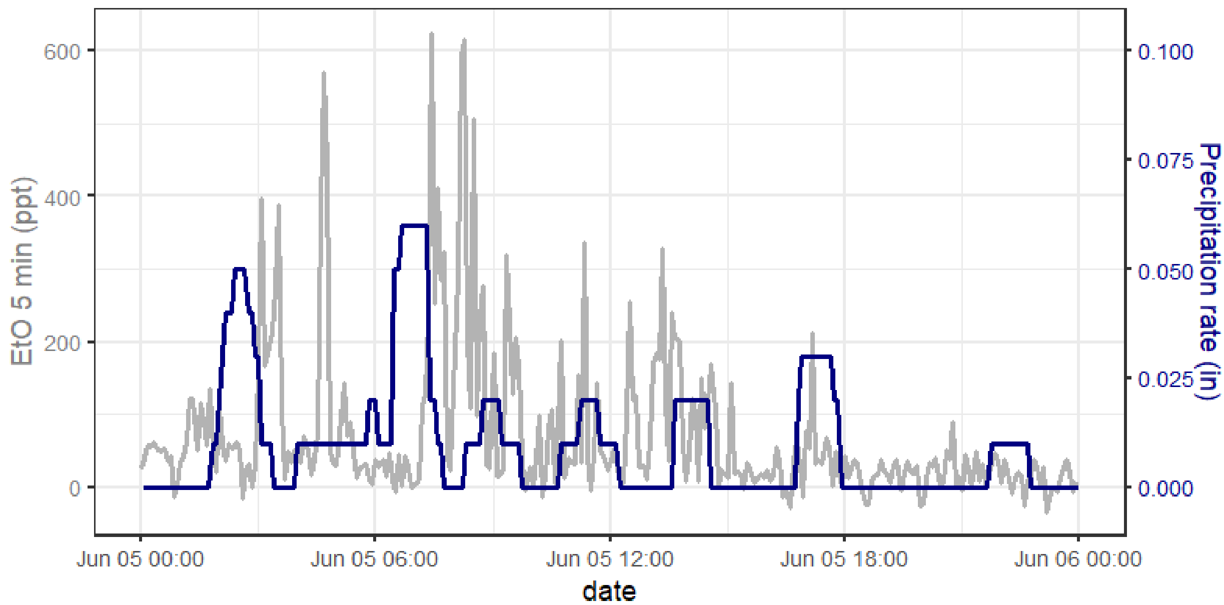


Figure 7. EtO concentrations (5 minute averages, left axis, gray line) and precipitation rate (blue line, right axis). Precipitation data is from a Wunderground station (Riverdale-KWARAYMO4) located approximately 4000 feet NW of the Raymond monitoring site.

Meteorology

During the sampling period, winds at Tacoma were mostly from the southwest, which is in the direction of Interstate-5 and residential areas. Downtown Tacoma and the Port of Tacoma are to the northwest of the site. Measureable precipitation also occurred on June 7 as well as June 12-15, and hourly wind speeds ranged from 0.9 to 10.7 mph during the sampling period. Daily high temperatures ranged from 57.0 – 70.8 °F. There were no characteristic wind directions associated with any high EtO concentrations, as shown in Figure 8.

Lacey winds were from the south/southwest as well as northwest, and wind speeds varied during the sampling period from 1.3 to 14.1 mph. No precipitation occurred while monitoring at Lacey, and daytime conditions were sunny with daily high temperatures of 82.9 and 74.3 °F on June 2 and June 3, respectively. Similar to Tacoma, there were no characteristic wind directions or conditions associated with higher-than-average EtO concentrations (Figure 8).

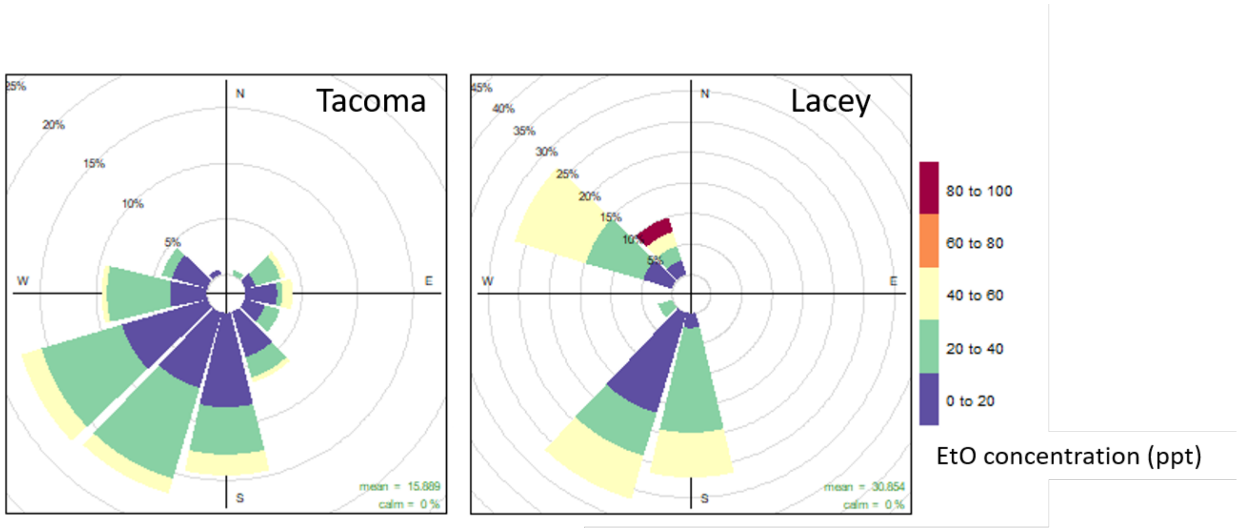


Figure 8. Pollution roses at the Tacoma monitoring site (left0 and the Lacey monitoring site (right).

Comparison to TO-15 Measurements Collected in June 2021

During the campaign, the Oregon Department of Environmental Quality collocated two silicon-ceramic canisters for TO-15 analysis—one canister at Lacey on June 3 and the other canister at Tacoma on June 15. EtO was not detected on June 3, and the Tacoma collocated canister on June 15 reported a 24-hour total of 138 ppt.

A comparison plot of the TO-15 and Picarro data collected during June 2021 is shown in Figure 9. Two TO-15 data points from the Seattle-Beacon Hill monitoring site are also included for comparison. Figure 9 illustrates the range of EtO concentrations observed during June 2021 in Western Washington for two different analytical methods. While the three TO-15 data points are higher than the measurements reported by the Picarro analyzer, generalizations due to three data points and the substantial differences between the two analytical methods should be interpreted with caution. EPA has recently reported potential TO-15 measurement bias due to canister age, materials, and cleaning processes, which adds additional uncertainty to the measurements shown in Figure 9.[7] The EtO measurements shown in Figure 9 are indicative of low EtO concentrations in multiple areas of Western Washington, indicating a lack of local sources.

[7] https://www.epa.gov/sites/default/files/2021-05/documents/ord-eto-canister-background-memo-05072021.pdf

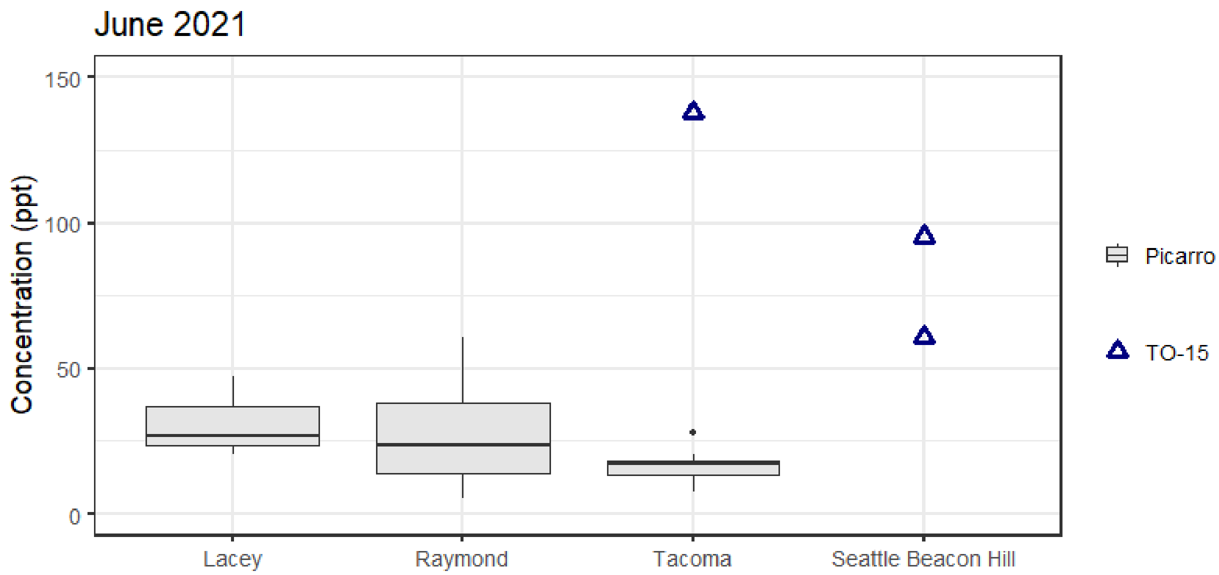


Figure 9. Comparison of EtO data collected during June 2021. Boxplots correspond to data collected with the Picarro Ethylene Oxide analyzer, and blue triangles correspond to TO-15 data.

Health Impacts

Levels of EtO in ambient air are expected to be much lower than those that may cause immediate noncancer health effects, but long-term exposure to EtO increases risk of cancers of the white blood cells.[8] Based on EPA's unit risk factor for EtO, Ecology derived the acceptable source impact level (ASIL) of 2.0E-04 µg m^{-3} (0.111 ppt – annual average concentration). This corresponds to a 1- in-a-million increased lifetime cancer risk, meaning that one person out of a million people who breathed air containing EtO at the ASIL for a lifetime could develop cancer.

Because the measurement campaign lasted only a few days at each location, the long-term (i.e., annual average) concentrations are not known. Using AERSCREEN's averaging time factors for worst-case annual averages,[9] the maximum hourly EtO concentrations were converted to annual averages to compare to the ASIL. All of the scaled annual average EtO concentrations from this measurement campaign are above the 1-in-a-million cancer risk level. However, current EtO measurement technology, including the analyzer deployed in this study, do not have the capability to measure such low concentrations. If a 100-in-a-million cancer risk[10] of 11 ppt is used for comparison instead, then both Lacey and Tacoma scaled annual averages fall

[8] Includes non-Hodgkin lymphoma, myeloma, and lymphocytic leukemia. Studies also show that long-term exposure to ethylene oxide increases the risk of breast cancer in females.
[9] U.S. EPA: AERSCREEN User's Guide (2021)
[10] The preamble to the benzene NESHAP stated that a 1 in 10,000 (or 100 in one million) risk is considered the upper end of the range of acceptability when setting air toxics emission standards. This is intended to apply to the maximum individual risk. EPA also considers the number of people exposed to levels resulting at a risk level of higher than 1 in one million when setting these emission standards.

below that level. If the uncertain data points at Raymond are excluded, then Raymond also falls below that risk level. However, further investigation is needed to understand the uncertainty of the high EtO concentrations in Raymond, as well as if other areas of Washington state also fall below the 100-in-a-million cancer risk value.

Table 2. Maximum hourly EtO concentrations and scaled annual average EtO concentrations at each monitoring site.

Site	Maximum hourly EtO (ppt)	Scaled annual average EtO (ppt)
Lacey	90.5	9.1
Raymond	272	27
Raymond (excluding uncertain data)	68.6	6.9
Tacoma	57.3	5.7

Conclusions and Future Work

Using cavity ringdown spectroscopy, EtO concentrations were determined at three different monitoring sites in Washington State in June 2021. Hourly EtO concentrations ranged from 0 to 272 ppt. Aside from a few hourly concentration increases observed at the Raymond monitoring site, there was very little site to site variability. At the Tacoma near-road site, there was very little diurnal or day of week variability. This lack of variability among monitoring sites, low EtO concentrations, as well as the lifetime of EtO suggests the presence of a regional background of EtO in Washington State. Extending these measurements to levels of health risk that are within EPA's acceptable risk range suggests that the majority of measurements are above the 1-in-a-million but below the 100-in-a-million cancer risk value.

Outstanding questions include the concentration spikes observed at Raymond. More investigation is needed to understand the uncertainty of those short-lived increases in EtO concentrations. Further, the three monitoring sites utilized during this campaign are all located in Western Washington. Further investigation is needed in other areas of the state to understand if these EtO concentrations truly reflect a regional background.

However, EtO data continues to be collected at the Seattle NATTS monitoring site with subsequent analysis by the TO-15 method. Ecology continues to compare this data to other sites in the country to better understand EtO concentrations in Washington State. Ecology will also continue to monitor improvements in analytical methods that provide lower EtO detection limits.