Final Report

Ethylene Oxide Monitoring –

Characterization of South Charleston and Institute, West Virginia and Surrounding Areas

February 21, 2023

West Virginia Department of Environmental Protection

Division of Air Quality

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Acronyms and Abbreviations

AQS - Air Quality System (EPA's Air database)
COC – Chain of Custody
DAQ – West Virginia Division of Air Quality
DEP – West Virginia Department of Environmental Protection
EPA - United States Environmental Protection Agency
ERG – Eastern Research Group
EtO – Ethylene Oxide
FSP – Field Sampling Plan
GA EPD - Georgia Department of Natural Resources Environmental Protection Division
GC-MS - Gas Chromatography-Mass Spectrometry
HEM - Human Exposure Model
ICAL - Initial Calibration
MDL – Method Detection Limit
NAAQS - National Ambient Air Quality Standards
NATA - National Air Toxics Assessment
NATTS - National Air Toxics Trends Stations
OAQPS - Office of Air Quality Planning and Standards
ppbv - Parts Per Billion by Volume
QAPP - Quality Assurance Project Plan
RFF - Relative Response Factor
SLAMS - State or Local Air Monitoring Stations
SOP - Standard Operating Procedure
SQL - Sample Quantification Limit
SSCV - Secondary Source Calibration Verification
UCC - Union Carbide Corporation
WVDHHR – West Virginia Department of Health and Human Resources

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Executive Summary

The U.S. Environmental Protection Agency (EPA) gathered emissions data of 2014 air toxic emissions across the United States. "Air toxics" are pollutants that at sufficient concentrations and exposure are known or suspected to cause cancer, other serious health problems, or damage to the environment. The EPA also reexamined the potential danger presented by a number of chemical compounds, one of which is called ethylene oxide, or EtO. In 2016 the EPA reclassified EtO as a "known human carcinogen" with an increased cancer risk. This cancer risk is based on continuous exposure to EtO emissions for 24 hours per day, seven days per week, 365 days per year, for 70 years.

In 2018, the EPA released a report called the National Air Toxics Assessment (NATA). The NATA was a broad overview of air emissions across the country – commonly referred to as a screening tool – and was designed to identify areas that may need further investigation. That 2018 report identified areas across the country that warranted further review, including two in West Virginia that were on the list due to EtO. These areas include the communities located around the chemical facilities in Institute and South Charleston.

In order to more accurately assess the potential problem, the West Virginia Department of Environmental Protection's (DEP) Division of Air Quality (DAQ) gathered more recent and detailed EtO emissions information and weather data. The DAQ performed long-term, EPA approved modeling around chemical facilities with EtO emissions located in South Charleston and Institute. The DAQ used this information to refine the potential areas of concern.

DAQ then conducted short-term EtO air monitoring to confirm its presence in the atmosphere. That process involved technical, mechanical monitoring (in the form of metal canisters) that were placed on-site around those chemical facilities, off-site but in close proximity to those facilities, and at locations that were intentionally selected because they were not near any facilities that use EtO.

More specifically, the DAQ conducted four monitoring events between January 25 and April 27, 2022. The DAQ placed seven canisters in and around the Institute and South Charleston sites. The DAQ also placed canisters in Guthrie and Buffalo, West Virginia, to obtain samples from areas not near any known EtO facilities.

Monitoring was conducted using a Silonite-coated canister with a manual regulator. Each sample was collected over a 24-hour period. After air samples were collected, the canisters were sent to a laboratory for analysis using Gas Chromatography-Mass Spectrometry (GC-MS) in accordance with method TO-15. The laboratory performed the analysis and returned the fourth and final set of results to DAQ on June 22, 2022.

In almost all cases, the monitoring results showed detectable levels of EtO, even at sites where there were no known EtO-related facilities. Comparing the results, one location from Institute showed relatively higher amounts than the other locations. This location is approximately 775 feet from where EtO rail cars are unloaded at Union Carbide Corporation (UCC) Institute.

The DAQ also performed short-term computer-assisted air dispersion modeling of the South Charleston and Institute areas for the sampling days. A comparison of the modeling to the monitoring results reinforced the modeling findings.

As a result of monitoring, the DAQ determined that EtO was present in the atmosphere at all locations sampled. In some cases, the levels obtained at locations far removed from facilities that use EtO were higher than levels at the sites monitored in Institute, North Charleston, and South Charleston.

It is important to note that the monitoring events performed for this study are **not** meant to be used to establish long term risk. Four snapshots in time **cannot** capture a representative 70-year lifetime cancer risk. The purpose of this study was to determine the presence of EtO in the atmosphere.

Summary of Recommendations

Based on the information obtained from air monitoring and computer modeling, the DAQ recommends the following actions:

1. The DAQ recommends that EPA develop more precise monitoring methods for EtO with lower detection limits, including the evaluation of enhanced cleaning practices for the canister and air sampling assembly.
2. The DAQ recommends EPA work to identify and quantify potentially naturally occurring EtO sources.
3. The DAQ recommends EPA use long-term dispersion modeling of EtO from known sources to better and more accurately understand concentrations in the community and for use in future rulemaking.
4. The DAQ work more closely with facilities that use EtO to improve how they monitor for EtO.
5. The DAQ requests companies to perform enhanced Leak Detection And Repair (LDAR) technology to track and reduce EtO emissions.
6. The DAQ recommends that all EtO emitting chemical facilities in the identified area enter into a voluntary agreement similar to the Collaborative Agreement reached with UCC Institute on January 18, 2023, which includes the following enforceable conditions:
    - Significantly reduce its potential emission limits for EtO.
    - Identify and fix leaks at levels 50 to 1,000 times lower than what is required by current regulations.
    - Continue working with DAQ and EPA to develop improved EtO monitoring.
    - That UCC Institute develop and implement a program for EtO rail cars to monitor them within 12 hours of arriving at the facility and take appropriate action if emissions are detected.

Background

The U.S. Environmental Protection Agency (EPA) conducted a study of air toxic emissions across the United States using data from 2014. While the assessment was being conducted, the EPA made a finding related to EtO and reclassified it from a probable human carcinogen to a known human carcinogen and increased the inhalation cancer risk. The screening modeling assessment was completed and released by the EPA in 2018 in a report called the National Air Toxics Assessment (NATA). The NATA was a broad overview of air emissions across the country – commonly referred to as a screening tool – and was designed to identify areas that may need further investigation.

The NATA identified four census tracts in West Virginia, all of which are nearby EtO-emitting facilities in Institute and South Charleston that warranted further review. DAQ performed a detailed site-specific modeling analysis which included obtaining more accurate emission locations and amounts, as well as on-site weather data, to more closely assess risk from EtO.

Known Sources of EtO in the Study Area

Site Name: South Charleston, WV, 437 MacCorkle Avenue SW, 25303

> *Union Carbide Corporation* (03-54-039-00003) - 440.026 km Easting, 4,246.927 km Northing, Zone 17
>
> *Covestro LLC* (03-54-039-00102) - 439.65 km Easting, 4,247.000 km Northing, Zone 17

Site Name: Institute, WV, 250 Carbide Road, Dunbar, WV 25064, ALTIVIA Institute Industrial Park

> *Union Carbide Corporation* (03-54-039-00005) – 432.189 km Easting, 4,248.754 km Northing, Zone 17
>
> *Specialty Products US, LLC* (03-54-039-00682) – 432.189 km Easting, 4,248.754 km Northing, Zone 17

All of these facilities have been subject to state and federal regulations of EtO emissions for decades. The facilities are currently in compliance with all state and federal regulations for EtO. The applicable regulations can be found in the associated Title V Permits which are available on the WV DAQ website. The West Virginia Department of Environmental Protection, Division of Air Quality (DAQ) conducted short-term Ethylene Oxide (EtO) air monitoring around facilities

located in South Charleston and Institute, West Virginia with subsequent laboratory analysis by Eastern Research Group, Inc. (ERG), a national contractor used by EPA to support the NATTS (National Air Toxics Trends Stations) network sampling to assess atmospheric concentrations. Monitoring was conducted at fenceline, on-site, and off-site locations of facilities with known EtO air emissions, as well as at two background locations. The background sites were chosen in areas where there were no known sources of EtO.

DAQ reviewed the monitoring results to determine the presence of EtO; performed short-term air dispersion modeling; and characterized the study area. The EPA provided funding for the lab analyses, and advisory assistance such as in technical matters and in quality review. Additional details on the review process and report content are contained in the Quality Assurance Project Plan (QAPP), as well as the Field Sampling Plan (FSP).

Risk

It is important to note that this report does **not** address long term risk. The project involved four (4) 24-hour sampling events. Four days of data **cannot** be used to calculate risk over a 70 year period.

EPA has indicated that modeling is the more accurate approach to determine potential risk associated with EtO. Regarding monitoring compared with modeling, EPA states

> A monitor tells us about EtO only in the area where the monitor is located. But computer models let us look at EtO across an entire community – not just at the monitor location. In addition, current monitoring methods cannot detect EtO down to all risk levels. For calculating risk across every part of a community, our experts believe that computer modeling gives us the best estimate possible of EtO concentrations in the air and the risks from breathing that air over many decades. Modeling also allows us to quickly examine how risks are expected to change when emission controls are installed, for example (https://www.epa.gov/hazardous-air-pollutants-ethylene-oxide/frequent-questions-about-ethylene-oxide-eto).

"EPA considers risk to be the chance of harmful effects to human health or to ecological systems resulting from exposure to an environmental stressor.

A stressor is any physical, chemical, or biological entity that can induce an adverse effect in humans or ecosystems. Stressors may adversely affect specific natural resources or entire ecosystems, including plants and animals, as well as the environment with which they interact." (https://www.epa.gov/risk/about-risk-assessment#whatisrisk).

The EPA has established a generally acceptable threshold of 100 in one million lifetime cancer risk (NATA FAQ: https://www.epa.gov/national-air-toxics-assessment/nata-frequent-questions).
The 100 in one million benchmark can be adjusted for smaller populations. For example, if there were a population of 10,000 residents, the benchmark would be 1 in 10,000. Meaning the risk would predict that over the course of 70 years, one individual would get cancer from that stressor.
EPA's approach to estimating cancer risk is intended to be health-protective and, therefore, uses conservative assumptions. For example, EPA assumes that a person is exposed continuously over a lifetime (i.e., 24 hours per day, 7 days per week, 52 weeks per year, 70 years). This approach to risk assessment is extremely conservative as people travel into and out of these areas for a variety of reasons including going to work, school, their homes, etc.
The potentially elevated risk from the 2018 NATA is not due to new emission sources or increased emissions from permit holders, but rather to the EPA's finding that long-term exposure to EtO may be more harmful than previously thought.
Reducing potential and actual emissions from the known sources of EtO in the study area will decrease exposure and therefore possible risk.
The South Charleston and Institute locations are in Kanawha County, WV. A report updated June 9, 2022 by the WV Division Health and Human Resources (WVDHHR) found no elevated levels of EtO related cancers (breast, lymphoma, or leukemia) in Kanawha County. Kanawha County does not rank in the top 10 counties in WV for any of the related cancers. Mapping the locations of people with EtO related cancers has not shown any clusters around the Institute or South Charleston areas. This report can be found at: https://dep.wv.gov/key-issues/Documents/EtO/Public-Meeting-8-18-2022/BPH.pdf.

Site Selection

The goal in selecting sampling locations was to sample at the locations with the highest concentration predicted by long-term modeling, while also ensuring sampling security and data integrity as described in the FSP in the Site Selection section. Therefore, sampling locations were selected on this basis and are a combination of fenceline, on-site, and off-site near facilities with known EtO emissions as well as background locations with no known nearby EtO emission sources. Monitoring was conducted at a combination of fenceline (hanging on the public side of the fence around the sites), on-site (within the Institute site), and off-site (a location not publicly accessible off site property) locations near facilities with known EtO air emissions, as well as at background locations not located near known sources of EtO emissions.

Due to EPA concerns with the use of automated canister timers, manual setup and takedown procedures were utilized for this limited sampling effort. This manual operation is resource and time intensive and was a consideration in site selection in order to ensure the 24 hr ±2hr timeline was met for each sample. Timely access to the sampling locations was important to maintain data integrity.

Figure 1 shows the monitoring locations, including the project background sites in Guthrie and Buffalo (Putnam County), WV. A scale is provided on the map which shows an area approximately 24 miles by 16 miles. Table 1 provides details on each of the EtO monitoring sites, including location and property ownership providing access to the site.

Figure 1 Short-term EtO monitoring locations including project background sites

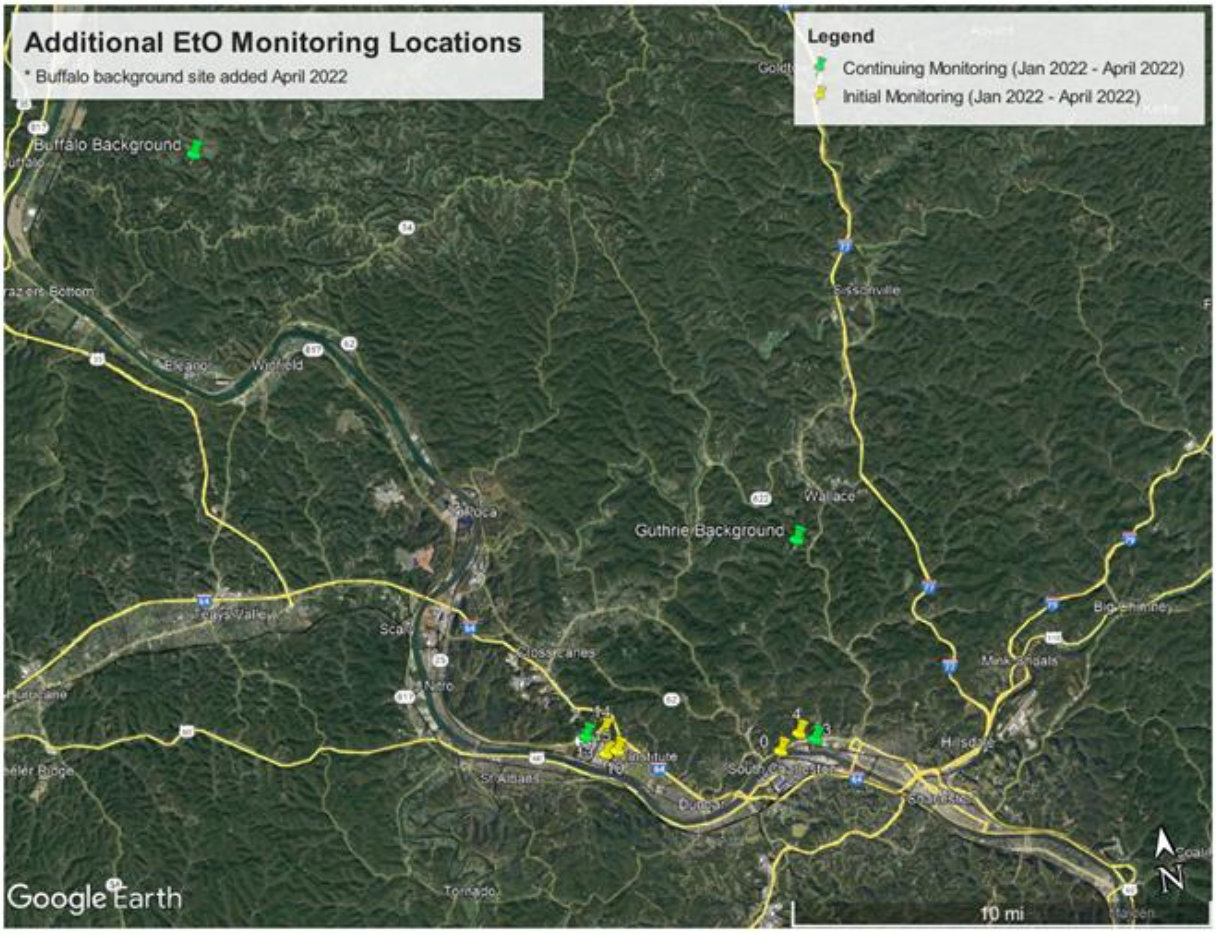


Table 1 EtO monitoring location details

ID Tag	Area	Latitute	Longitude	Onsite	Fenceline	Property Owner	Nominal Location
Project Background	Guthrie	38.4425	-81.680556	Yes	No	State of WV	367 Gus Douglas Lane, Charleston
0	SC	38.370984	-81.701646	Yes	No	DHHR Hygiene Lab	167 11th Ave, South Charleston
3	SC	38.373236	-81.685719	No	Yes	UCC	33rd Street W Blaine Blvd Charleston
4	SC	38.376072	-81.692346	No	Yes	UCC	37th Street 7th Avenue Charleston
10	I	38.379594	-81.771861	Yes	No	Altivia	250 Carbide Rd, Institute
13	I	38.378371	-81.778543	Yes	No	Altivia	250 Carbide Rd, Institute
14	I	38.387204	-81.777308	Yes	No	Altivia	250 Carbide Rd, Institute
15	I	38.386078	-81.785634	No	Yes	Altivia	1 road west of Malcolm Lane, Rt 25 Institute
16	B			No	No	Private Residence	Buffalo, WV

Figure 2 shows the EtO monitoring sites in South Charleston overlayed on the modeled concentration isopleths from UCC and Covestro's 2020 EtO emissions and 2019 meteorological data.

Figure 2 EtO monitoring sites in South Charleston shown with modeled concentration isopleths based on 2020 emissions and 2019 meteorological data

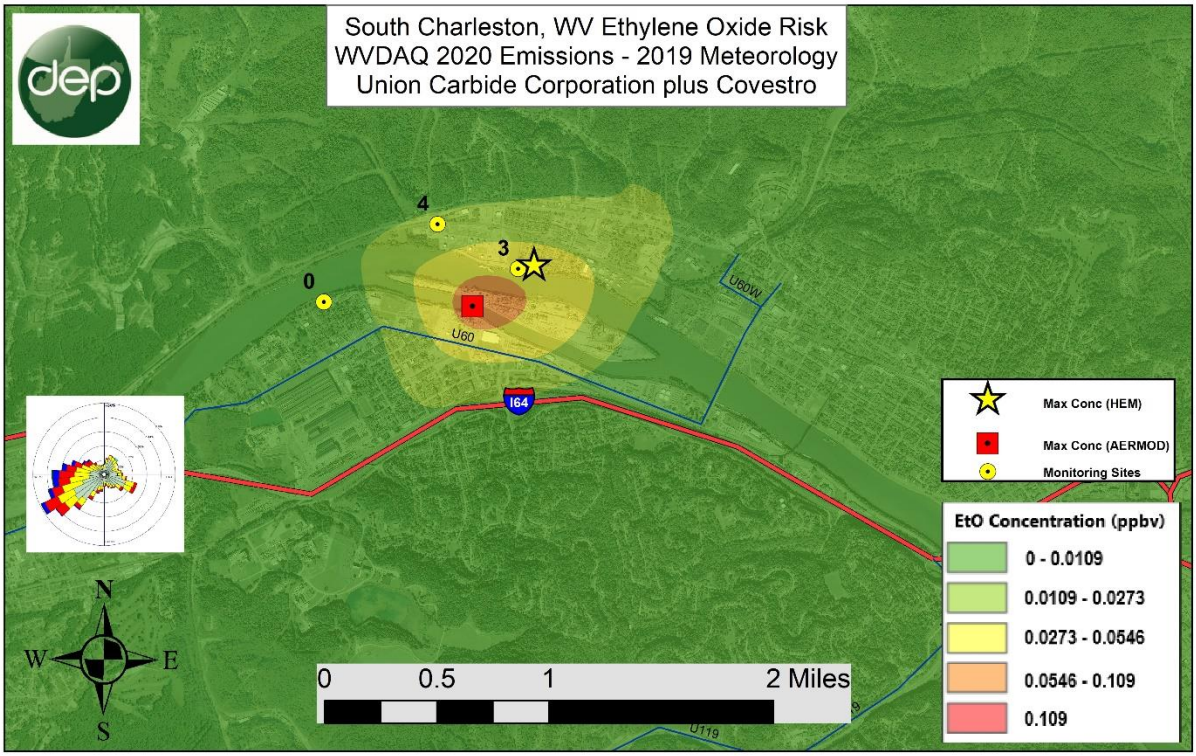


Figure 3 is a wind rose from the South Charleston facility indicating the wind generally comes from the North and North-Northeast at lower speeds, and higher wind speeds tend to come from the West-Southwest. Air dispersion modeling was performed using one year of meteorological data that was available at that time – the four months from the South Charleston site and the remainder of the data from the Institute site. While there are gaps in this meteorological data, it provides general information regarding this portion of the project area.

Figure 3 Wind rose from South Charleston facility

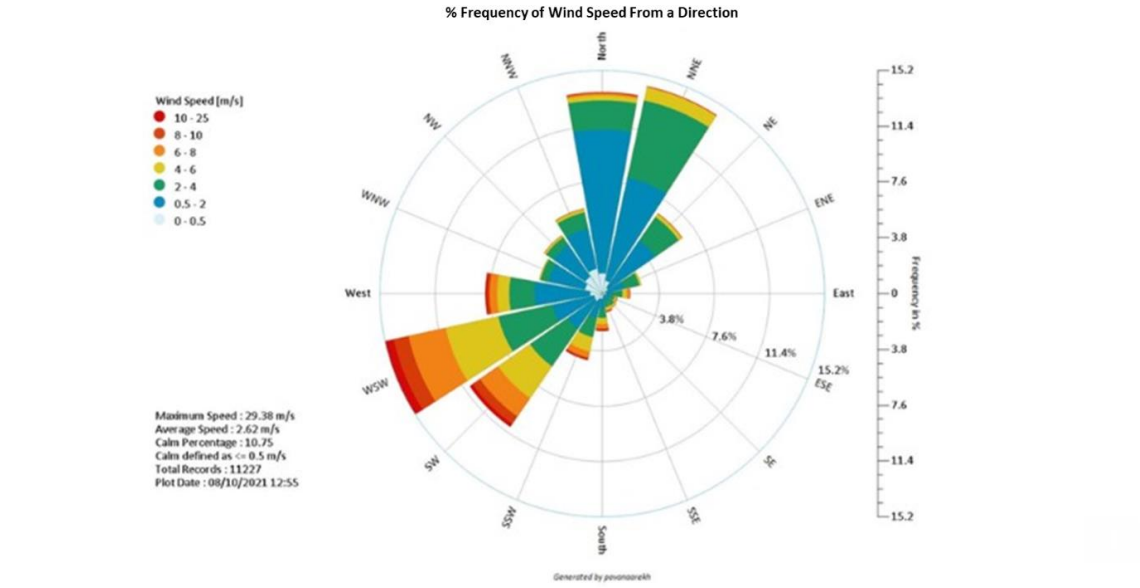


Figure 4 shows the EtO monitoring sites in Institute overlayed on the modeled concentration isopleths from UCC and Specialty Product's 2020 EtO emissions and 2019 meteorological data.

Figure 4 EtO monitoring sites in Institute shown with modeled concentration isopleths based on 2020 emissions and 2019 meteorological data

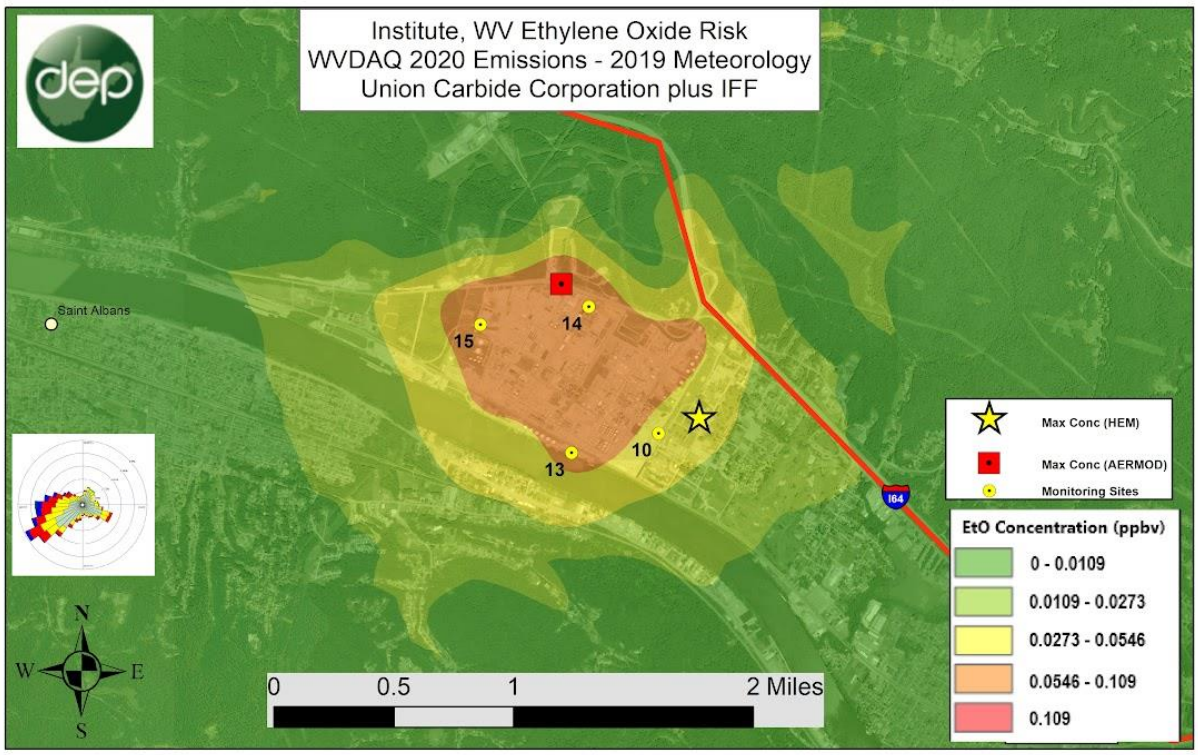
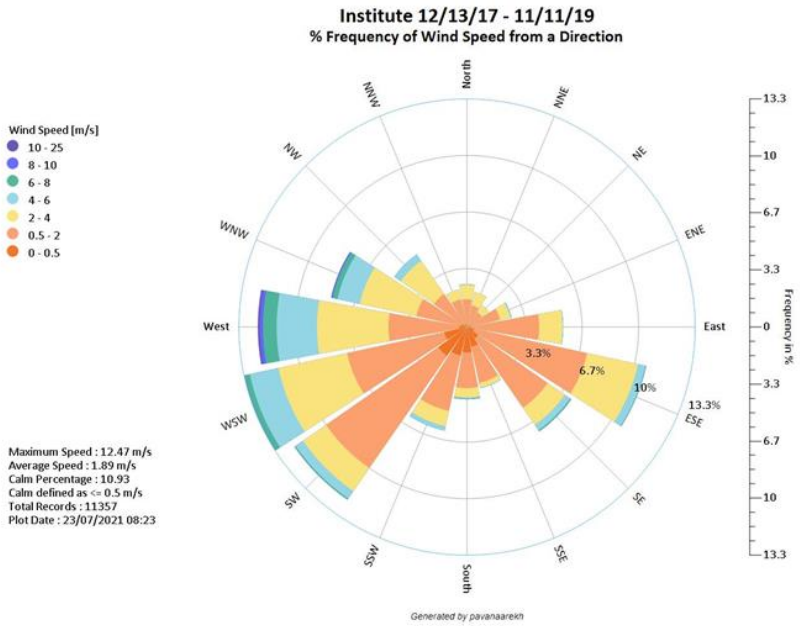


Figure 5 is a wind rose from the Institute facility indicating the majority of the wind comes *from* the westerly direction, and there is a portion of the time that wind comes *from* the East-Southeast.

Figure 5 Wind rose from Institute facility



Sampling

DAQ coordinated with the facilities to schedule sampling events while EtO emitting processes were operating. DAQ requested the facilities to operate at their maximum production levels, while staying in compliance with their permitted requirements.

The four (4) 24-hour sampling events occurred over an approximate 3-month period from January 25 through April 27, 2022. Monitoring was conducted using Silonite coated canister samplers. To the extent possible, the canisters were placed at an approximate breathing height (5-6 feet from the ground). Each sample was collected over a 24-hour period. Monitoring consisted of four (4) sets of 24-hour samples taken around each area. Each event consisted of a total of seven (7) canisters being placed in and around the Institute and South Charleston sites,

as well as a project background in Guthrie for the four sampling events and an additional project background site in Buffalo for the fourth sampling event (see Table 1 for a list of all sampling locations). The canisters were equipped with an air sampling assembly (supplied by ERG) consisting of a filter, sample tube, critical orifice, flow regulator and vacuum gauge. The exposed canisters were shipped to ERG Inc., for analysis using Gas Chromatography-Mass Spectrometry (GC-MS) as specified in Method TO-15. The GC-MS works as follows: Gas Chromatography separates the chemicals while Mass Spectrometry identifies and determines the concentrations of individual chemicals.

For all samples, ERG's chain of custody sheets were used to document sample custody. These sheets are attached in Appendix B. The DAQ was solely responsible for sampler operation and sample collection. ERG was responsible for canister and sample prep as per ERG's QAPP and SOP, as well as the analysis of the samples for EtO. The details of how the canisters were shipped from ERG to DEP, how they were stored, and shipped back to ERG are contained in the SOP Section 5.0 available on DAQ's EtO webpage.

Background Sites

A location in Guthrie, WV was chosen as the project background site since it is not near any known sources of EtO emissions (approximately 5 air miles from the South Charleston facility, and approximately 7 air miles from the Institute facility).

An additional background location in Buffalo (Putnam County), WV was added for the fourth round at the request of a citizen during a public meeting. It was located in a rural area further to the west (upwind) of the study area, and was not located near any known sources of EtO emissions. The Buffalo background site was approximately 20 air miles from the South Charleston facility and approximately 17 miles NW of the Institute facility as well as 19 miles SE of the ICL-IP Gallipolis Ferry facility which has EtO emissions.

Emissions and Modeling Characterization

Each of the four (4) facilities that emit EtO within the study area was sent a checklist to identify which processes operated during each sampling period, and provided air emissions estimates during this period. These checklists are provided in Appendix A and summarized in the Facility Emissions section. Meteorological data was provided by Union Carbide Corporation (UCC) South

Charleston for the South Charleston area and by ALTIVIA Services, LLC, for the Institute area. The DAQ used this information to perform short-term modeling over the period sampled. These modeled concentrations were used to characterize the study area. They are discussed in the Monitoring Event Modeling and Model Validation, Results, and Analysis sections below.

Sampling Challenges

Sampling Method Uncertainties

EPA's Method TO-15, which EPA approved for DAQ's QAPP and FSP and stated in the EPA NATTS Technical Assistance Document (TAD), is the required method for determining the concentration of EtO in ambient air. However, there are many challenges and uncertainties with this method. While there are other monitoring methods for EtO, these have higher MDLs, have their own associated uncertainties, and are not EPA approved methods.

Method Sensitivity

For this project, there is not a clear distinction in sampling results between background sites and sites near known sources of EtO. The sampling data can be found in Table 3 of this report. This can be attributed in-part to the very low concentrations of EtO present in ambient air relative to the ability of Method TO-15 to detect it. Additional discussion on method sensitivity and canister effect can be found in the MDL discussion below.

Method Detection Limit (MDL)

The method detection limit (MDL) is defined as the minimum measured concentration of a substance that can be reported with 99% confidence that the measured concentration is distinguishable from method blank results (https://www.epa.gov/cwa-methods/method-detection-limit-frequent-questions).

The MDL varies by laboratory, and each laboratory may revise their MDL through testing, new technology, or other reasons. The MDLs for this project can be found in Table 3 of this report.

EPA's updated lifetime inhalation cancer risk threshold for EtO for one-in-one million risk is 0.00011 ppbv. EPA's updated lifetime inhalation cancer risk threshold for EtO for 100-in-one million risk is 0.011 ppbv.

At this time, the analytical MDL for TO-15 is not low enough to measure EtO at the level that equates to a 100-in-one million cancer risk (0.011 ppbv). MDLs are necessary to properly assess data. Ambient air concentration data must be qualified according to the relationship with MDL and sample quantification limit (SQL) so data users can assign proper confidence. The SQL is defined at 3.18xMDL in Section 2.1.5 in the NATTS TAD. The NATTS TAD establishes a 5xMDL threshold for precision used to characterize data quality. DAQ had understood, based on discussions with EPA, that for EtO a 10xMDL internal threshold was used to offset method uncertainties that are not yet fully understood.

Over the past few years, the EPA has been working to develop methods that can reliably detect the very low EtO concentrations in ambient air, but there is no timeline for when these methods may be available.

In addition to the sensitivity of the analytical method, a presentation by Sara Waterson of EPA Region 4, at the National Ambient Air Monitoring Conference in Pittsburgh, PA in September 2022 (https://www.epa.gov/system/files/documents/2022-10/Waterson_Sara_for%20posting.pdf), provided a summary of known issues with monitoring in ambient air for EtO, including the canister effect, co-elution interference, degradation of calibration standards, and variations in GC/MS systems.

Canister Effect

The canister effect adds positive measurement bias and uncertainty to the values measured. The chemical mechanism of EtO formation and growth in a subset of canisters remains unclear. EPA is working to better understand and address these issues, including the development of Method TO-15A, which addresses enhanced canister cleaning protocols as well as canister lining materials.

EPA's Ambient Air Monitoring Group notes in their "Technical Note: The Ethylene Oxide (EtO) Canister Effect", posted at https://www.epa.gov/sites/default/files/2021-05/documents/technical-note-on-eto-canister-effect-052521.pdf:

> "...certain aspects (e.g., canister blank certification) in method TO-15 might not be sufficient in identifying problematic canisters which are not appropriate for low

concentration EtO sampling. However, the newly released TO-15A[1] method has updated requirements which are more relevant by using humidified zero air rather than nitrogen for canister zero certifications, as well as a more stringent cleanliness criterion (≤0.02 ppbv per target VOC when a canister is filled to standard ambient pressure (101.3 kPa absolute or 14.7 psia)). Most importantly, appropriate and sufficient canister cleaning and canister blank certification processes will be necessary before any canisters should be put in use for ambient EtO sampling. Such processes will allow for a better understanding of representative EtO concentrations in ambient air using the canister-based GC/MS measurement technique."

Another EPA memo "Effect of Canister Type on Background Ethylene Oxide Concentrations" can be found at https://www.epa.gov/sites/default/files/2021-05/documents/ord-eto-canister-background-memo-05072021.pdf.

The DAQ notes the air sampling assemblies (supplied by ERG) consisting of a filter, sample tube, critical orifice, flow regulator and vacuum gauge, used for this project, were not cleaned between sampling events. Given the canister effect observed for EtO sampling using Method TO-15, not cleaning the air sampling assembly in between uses could have introduced a source of error into the sampling results. Prior to initiating sampling for this project, DAQ clarified with EPA and ERG that regulator cleaning is not the norm for Method TO-15, and is not performed by ERG in between sampling during the same project ,nor is it recommended by EPA. The Standard Operating Procedure (SOP) used for this project did not include cleaning the air sampling assemblies in between uses. The SOP was reviewed by EPA prior to the start of the project. The Quality Assurance Project Plan (QAPP) and Field Sampling Plan (FSP), which references the SOP, were reviewed, and approved by EPA for this project.

Co-elution Interference:

There can be potential interference with certain compounds such as acetaldehyde, methanol, trans-2-butene, 2,2 dimethyl propane, and ethyl nitrite as specified in the TO-15 that leave a chromatographic column at the same time, making compound separation and identification difficult. This is a known issue, and ERG follows the quality control procedures of Method TO-15

[1] Determination of Volatile Organic Compounds (VOCs) in Air Collected in Specially Prepared Canisters and Analyzed by Gas Chromatography–Mass Spectrometry (GC-MS) https://www.epa.gov/sites/production/files/2019-12/documents/to-15a vocs.pdf

to eliminate potential interferences during analysis. An EPA presentation describing more about EtO co-elution issue can be found at https://www.epa.gov/sites/default/files/2021-05/documents/eto-technical-webinar-041521-w-gandas.pdf.

Degradation of Calibration Standards

EPA has noted a concern regarding the stability of EtO standards in cylinders to be used as primary or secondary source standards for Method TO-15 in an August 2019 technical note (Secondary Calibration Source Use for Ethylene Oxide Analysis in the National Air Toxics Trends Stations Network (epa.gov)), stating

> "there may be varying degrees of degradation inside the cylinder creating difficulty in meeting the secondary source calibration verification (SSCV) of ±30% recovery of the nominal or mean initial calibration (ICAL) relative response factor (RFF). OAQPS has developed this memo to provide clarification and guidance on the procurement and use of the primary and secondary source standards in supporting the EtO monitoring work in the NATTS."

An EPA presentation from August 2022 provided data showing improved stability and gas vendors improving precision and accuracy of gas standards (https://www.epa.gov/system/files/documents/2022-10/Kariher_Peter_Thurs_0900.pdf).

Leaks in Passive Field Sampling Timers

EPA discussed potential leaks in using stand-alone timers with canisters in a memo (https://www.epa.gov/sites/default/files/2021-04/documents/use_of_stand-alone_timer_timer_guidance_for_voc_sampling.pdf). This memo states:

> EPA has received reports of issues with the use of stand-alone timers used for VOC subambient sample collection. The issues involve potential leaks in the timer and/or sample flow controller that allow the sample canisters to drop to ambient pressure (0"Hg) during sampling and results in the invalidation of the sample.

DAQ was aware of EPA's concern regarding the use of stand-alone timers, therefore manual regulators were used to eliminate this possible source of error. The specific procedures used for the manual regulators are listed in Section 6 of the EPA reviewed SOP.

Variations in GC/MS Systems

Variations in GC/MS systems can introduce differences in MDLs. Variation in the MDL for EtO is observed in the national ambient air monitoring dataset maintained in EPA's AQS system. For this project ERG was used throughout, thereby removing the uncertainty of using different labs. As discussed below under "West Virginia Challenges", the MDL changed during the project sampling period due to standard equipment and sampling methodology changes at ERG during the period, and as captured by the annual MDL update. However, when comparing EtO results across labs, the differing MDLs should be taken into account.

West Virginia Challenges

ERG laboratories, which DAQ used, had an EtO MDL of 0.0261 ppbv (parts per billion by volume) for the first three sampling events, and an EtO MDL of 0.048 ppbv for the fourth set of DAQ samples processed by the lab.

EPA's current canister method for measuring ethylene oxide cannot detect EtO at extremely low levels. When ethylene oxide measurements are near the detection limits, there is greater uncertainty in the results and EPA is less confident in the accuracy of these values. The laboratory DAQ used, ERG, has indicated that there is increased confidence in the precision of the results at 5 times the MDL consistent with QA requirements in EPA's NATTS TAD . Figures 6 and 7 below show the results of the four monitoring events as compared to 5 and 10 times the MDL. For the first three rounds of sampling, the MDL was 0.0261 ppbv. For the fourth round of sampling ERG changed their MDL to 0.048 ppbv.

Figure 6 First three sampling event monitoring results compared to 5 and 10 times the MDL

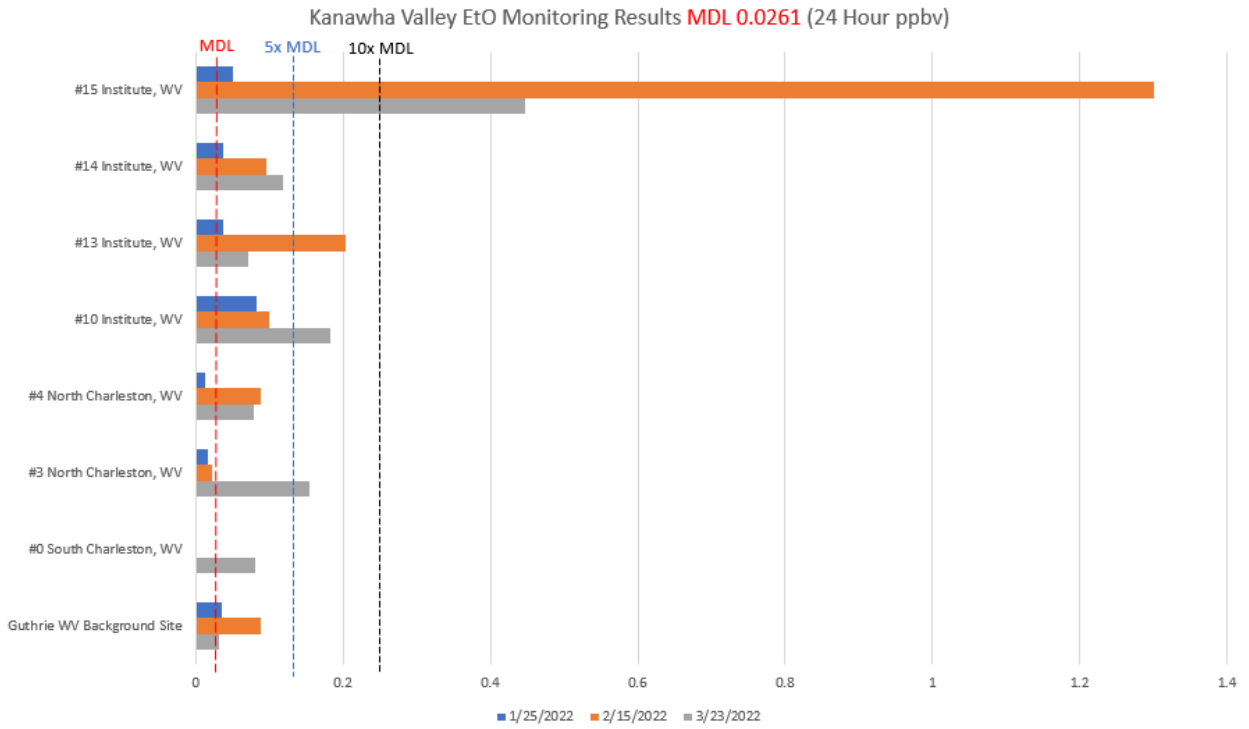
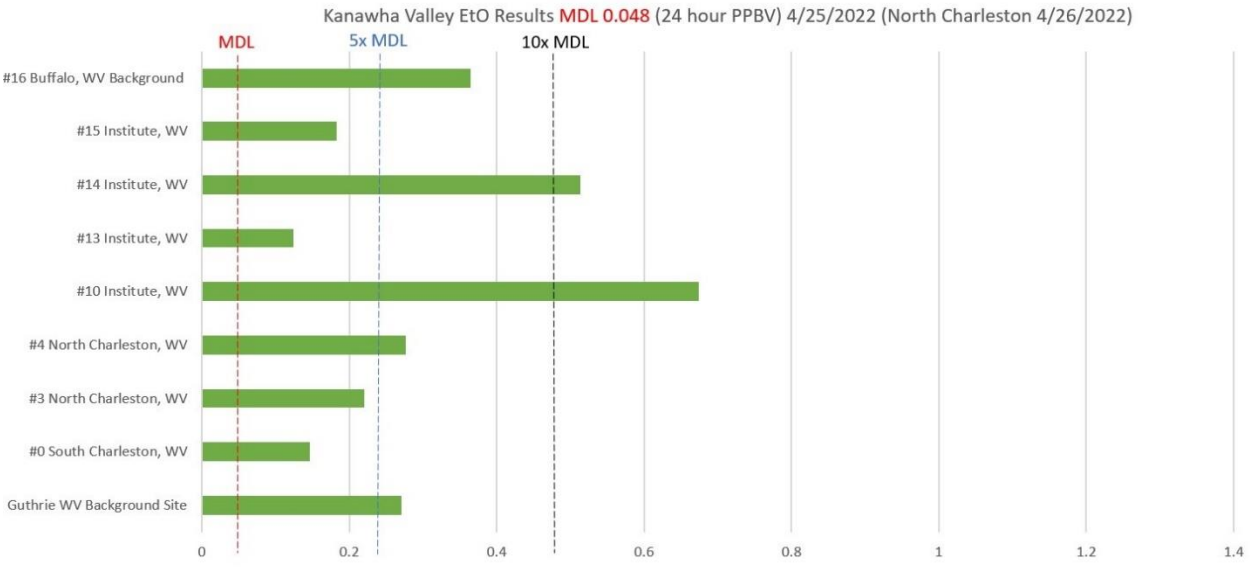


Figure 7 Fourth sampling event monitoring results compared to 5 and 10 times the MDL



For the first three samples, the background site in Guthrie, an area with no known EtO sources, had higher concentrations than some of the onsite locations. However, if 5 times MDL is used as the threshold for precision determination, as per the NATTS TAD, the data quality of these values

fall into question. The fourth background sample at Guthrie, was above five times the MDL, but less than ten times the MDL. A new background site was added in Buffalo for the fourth event; this remote rural site with no known sources of EtO approximately 17 to 20 miles northwest of the facilities, was also above five times the MDL but below ten times the MDL of 0.0261 ppbv for the first three sampling events and 0.048 ppbv for the fourth.

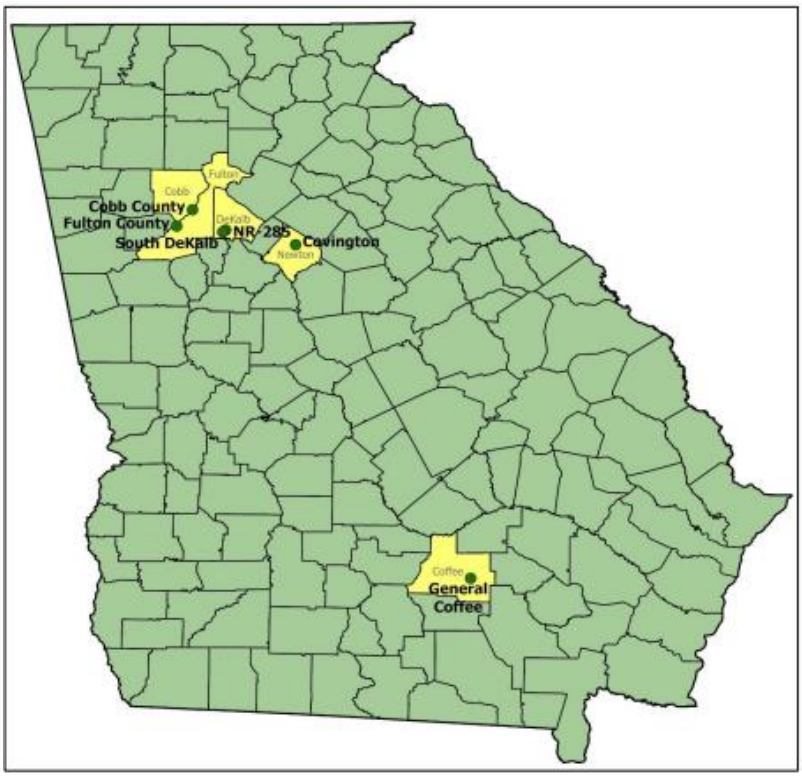
The QAPP stated that DAQ may subtract the background concentrations from the source-oriented monitoring results to determine the incremental contributions from the facilities. However, in several cases, the background concentrations were higher than the source-oriented monitoring concentrations, which would lead to negative numbers. These results where background concentrations were above source-oriented monitoring concentrations may be due to method uncertainties as has been discussed under “Sampling Challenges”. Therefore, background concentrations were not subtracted from source-oriented results for comparison with the 24 hour modeling results.

Georgia Challenges

The Georgia Department of Natural Resources Environmental Protection Division (GA EPD) released an Ethylene Oxide Monitoring Report on May 12, 2022, which can be found here: https://epd.georgia.gov/ethylene-oxide-information.
GA EPD collected over 1,600 samples (with 1,345 of the samples considered valid) of EtO in locations including near EtO emitting sites, urban background sites, and rural background sites.

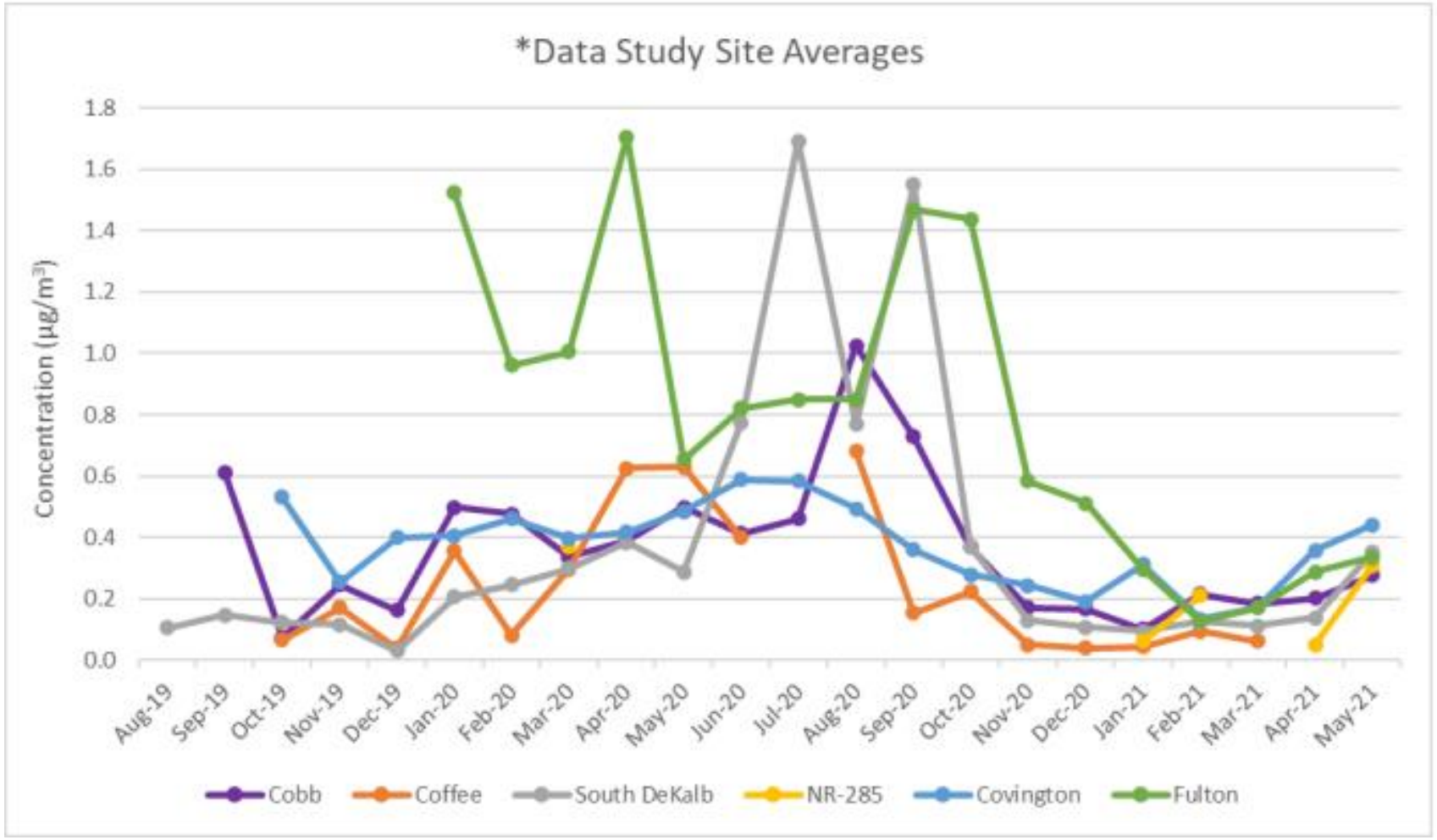
The Georgia sampling areas for near EtO emitting sites were located around 3 different EtO sterilizers, in Cobb County, Covington (Newton County), and Fulton County. The background areas with no known sources of EtO included South DeKalb, NR-285, and General Coffee. Of note, General Coffee is a 1,511-acre state park. Figures 8 and 9 show the locations of the sampling areas and the monthly EtO measured averages.

Figure 8 Areas with Ethylene Oxide Monitors in Georgia



Source: Ethylene Oxide Monitoring Report (https://epd.georgia.gov/ethylene-oxide-information) - Figure 12

Figure 9 GA EPD Monthly Averages for near-site and background levels of EtO without questionable canister data



Source: Ethylene Oxide Monitoring Report (https://epd.georgia.gov/ethylene-oxide-information) - Figure 21

The averages show that in some instances, the background levels are higher than near-site EtO emitting locations. In their report, GA EPD stated "The ethylene oxide concentrations measured at the background sites, far away from any known source of ethylene oxide emissions, suggest that there are other sources of the ethylene oxide."

GA EPD concluded in their EtO monitoring report that:
"Measuring the low concentrations of ethylene oxide present in ambient air is very challenging."
"More work needs to be done to improve the sensitivity and consistency of EPA's current method for analyzing for ethylene oxide." They also cautioned about canister effects, stating

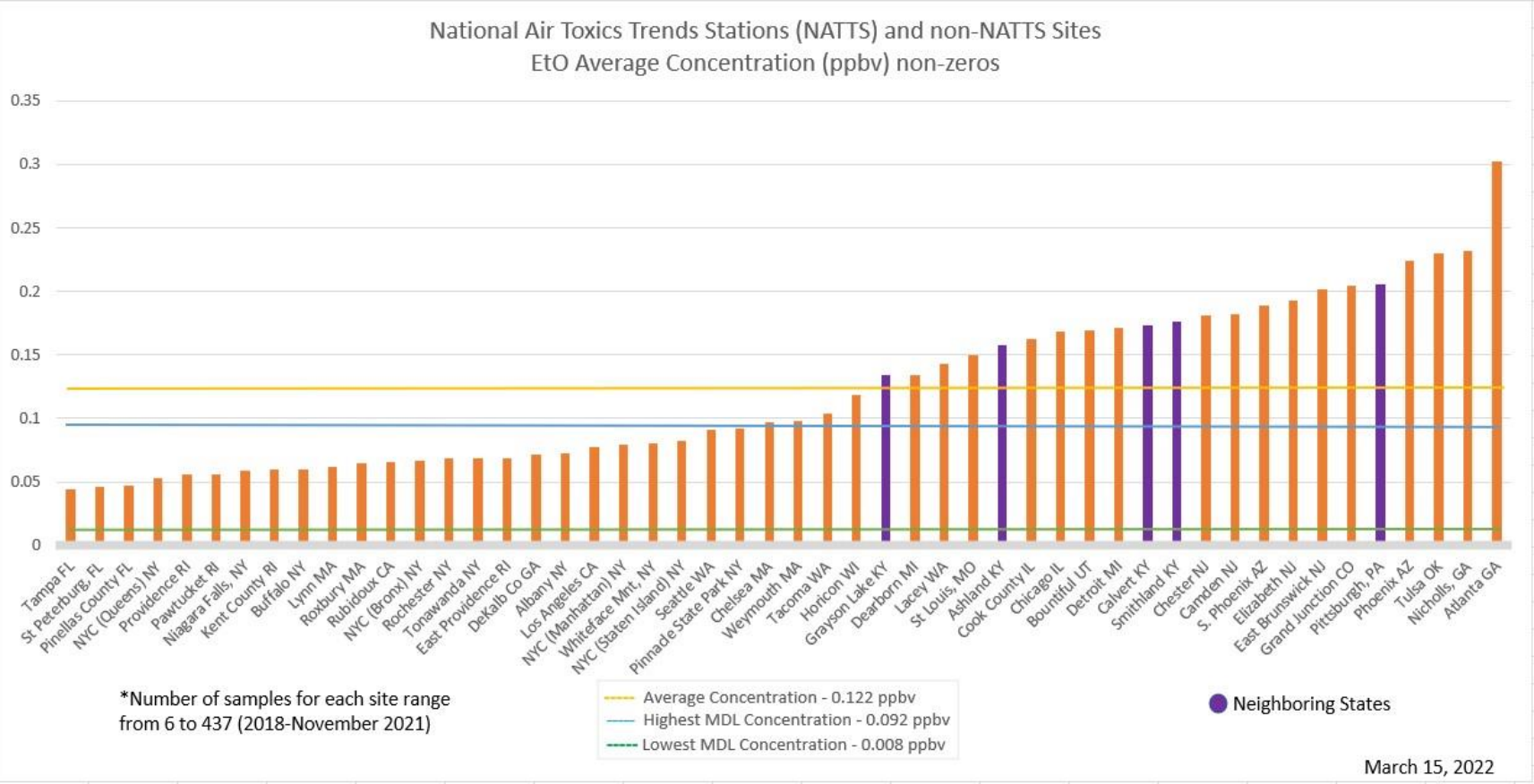
> "More research should be done to understand the canister effects on the measurement of ethylene oxide. For all sites, the number of samples that were impacted by the canister effects was significant. For the data presented, 31.4% of all samples collected, including quality assurance and field blanks, were impacted by this canister effect."

National Comparison

In 2018 EPA added EtO to the suite of pollutants to be monitored at NATTS sites as well as other locations. EPA established the NATTS network to obtain high-quality, long-term monitored air toxics trends data across the country. Based on data available in EPA's Air Quality System (AQS), EtO appears to be present across the country (sometimes at extremely low levels that challenge the MDL for TO-15 and TO-15A), even when no known sources of emissions are nearby. According to their website, "The Air Quality System (AQS) contains ambient air pollution data collected by EPA, state, local, and tribal air pollution control agencies from over thousands of monitors. AQS also contains meteorological data, descriptive information about each monitoring station (including its geographic location and its operator), and data quality assurance/quality control information." The AQS data is periodically updated and can be obtained at https://www.epa.gov/aqs.

Starting in 2018, EPA added a requirement that NATTS sites analyze and report EtO. Samples may be "flagged" for a variety of reasons, including: value is an estimate, value may be biased high, etc. All reported values (including some that were taken in 2018) were included in the following figures except as specified in this paragraph. Figure 10 shows the average EtO concentrations at various NATTS and non-NATTS sites across the country. Chemists may report less than MDL as zeros. However, it is reasonable to assume that there is some amount of EtO in the ambient atmosphere, so to be conservative, the zeros have been removed from the averages in Figure 11. While there are a range of concentrations and number of samples per site, the national average ambient concentration of EtO based on data currently available is 0.122 ppbv using this conservative approach.

Figure 10 National average EtO concentrations at various locations across the US in ppbv

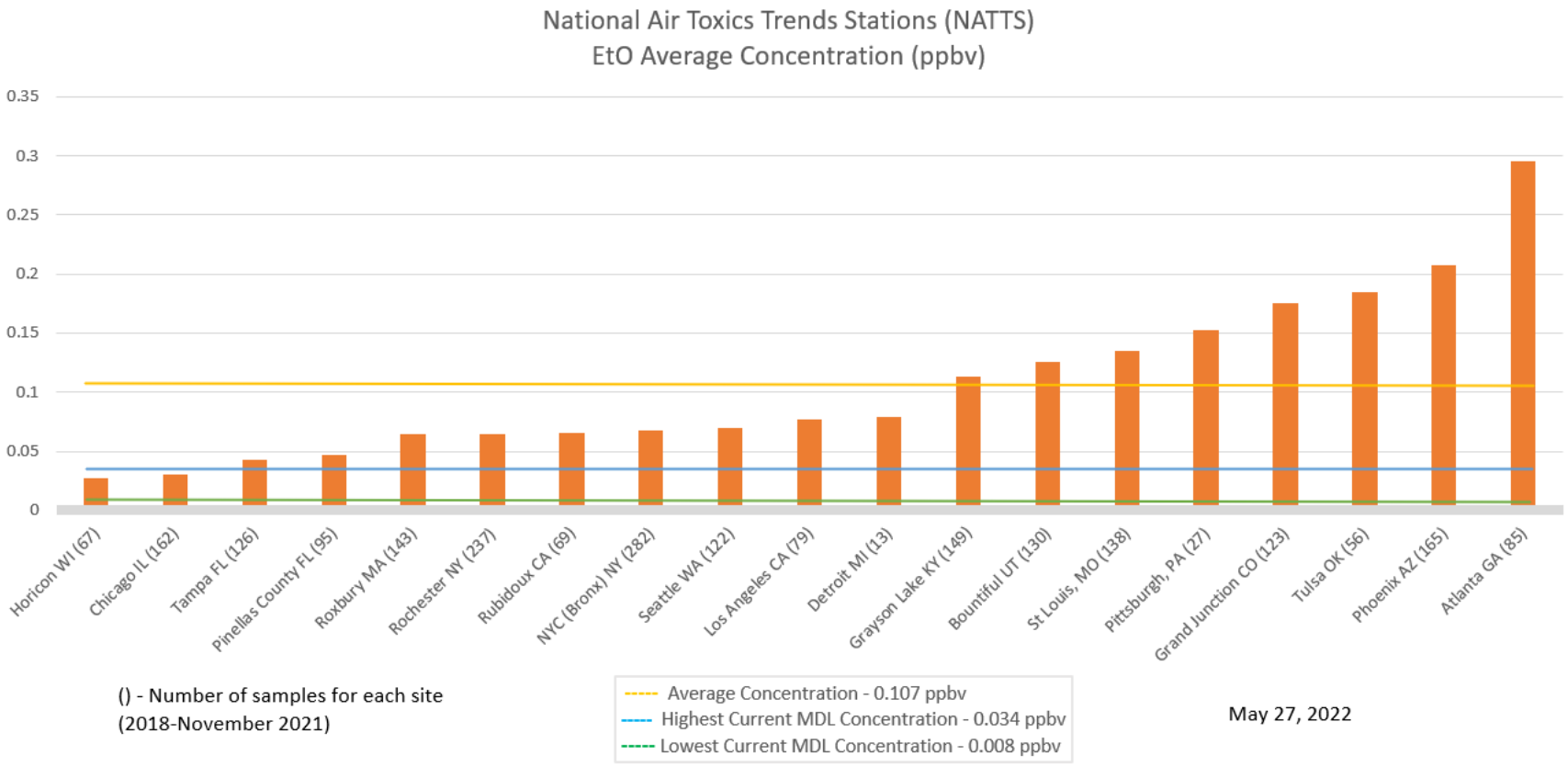


During discussions with DAQ staff, EPA questioned the accuracy of the previous graphs for the following reasons:

- The non-NATTS sites may not use EPA approved QAPPS
- Chemists may use zeros to report levels below the MDL
- Not including zeros in the average acknowledges possible concentrations below method of detection
- The number of samples at some of the non-NATTS sites were extremely low

To account for these issues, the non-NATTS sites were removed, zeros were added in the averaging, and the number of samples for each of the NATTS sites are identified. The updated graph is shown in Figure 11.

Figure 11 National average EtO concentrations at various National Air Toxics Trends Stations (NATTS) across the US in ppbv



As a result, the average concentration dropped from 0.122 ppb to 0.107 ppb.

The National Air Toxics Trends Station (NATTS) Network was developed to fulfill the need for long-term HAP monitoring data of consistent quality. Among the principal objectives are assessing trends and emission reduction program effectiveness, assessing and verifying air quality models (e.g., exposure assessments, emission control strategy development, etc.), and as direct input to source-receptor models (https://www3.epa.gov/ttnamti1/natts.html).

The NATTS site in Grayson Lake Kentucky is about 67 miles west of the Institute WV facilities. Grayson Lake is a recreational area with no known sources of EtO. This NATTS site recorded an average EtO concentration, with 149 samples taken, of 0.134 ppbv with zeros removed from the average; and 0.113 ppbv with zeros used in the average. The lab which does their testing has a current MDL of 0.026 ppbv. The average EtO concentration is over 5 times the current MDL for lab used by the Grayson Lake site without zeros and 4.4 times the current MDL with zeros.

Finding concentrations above 4-5 times the MDL in areas with no known sources of EtO emissions (Guthrie, Buffalo, and Grayson Lake Kentucky) is unexpected. Although there could be other explanations, two possibilities are that the technology and material to accurately detect EtO in the part per trillion range are insufficient, and/or there are naturally occurring sources of EtO.

Facility Emissions

The purpose of this study was to determine if EtO could be found in measurable amounts in the air. DAQ coordinated with the facilities to ensure that **all** EtO emitting processes were operating to the maximum extent possible while remaining within permitted limits. It is important to note that the facilities do not always operate at the same time, continuously, or at their maximum capacity. Due to this, concentrations may have been higher than typical.

During the fourth sampling event, Specialty Products experienced mechanical issues which did not allow them to operate their process, so they had no point source emissions. Fugitive emissions occurred, as the lines and connections still contained EtO.

DAQ met with the three companies (representing four facilities) to determine how they calculated the 24-hour period of emissions. The facilities based their four 24-hour point source emissions on the efficiencies of their control devices, multiplied by the amount of material sent to the control devices during each 24-hour period. A summary of the facilities' emissions is given in Table 2. To calculate short term fugitive emissions, the facility used their most recent year of annual calculated fugitive emissions and divided this number to get a representative daily average. While this is an estimate of fugitive emissions, there may be variability where actual amounts could be much higher or lower. These differences would show up in the comparison of the 24-hour monitored to 24-modeled data. Their reports are given in Appendix A.

Emissions from the EtO sampling events are given in the following Table:

Table 2 EtO 24-hour Facility Emissions

Facility	First Sampling Event	Second Sampling Event	Third Sampling Event	Fourth Sampling Event
	January 25-26, 2022	February 15-16, 2022	March 23-24, 2022	April 25-26, 2022**
	Emissions (pounds)	Emissions (pounds)	Emissions (pounds)	Emissions (pounds)
UCC SC	0.5242	1.9896	2.404	0.756
Covestro SC	0.3690	0.429	0.379	0.369
South Charleston Total	0.8932	2.419	2.783	1.125
UCC Institute	2.0056	2.3363	2.4316	2.3762
Specialty Products Institute	4.2988	4.4887	5.0621	0.0929*
Institute Total	6.3044	6.8250	7.4937	2.4691

* Production was down. Only fugitive emissions were reported

** The South Charleston emissions were for April 26-27 due to a different sampling day

Monitoring Results

The Analytical Results can be found in Appendix C. The monitoring results are summarized in the following Table.

Table 3 Ethylene Oxide Monitoring Results

Ethylene Oxide Monitoring Results

Sample Location	Jan. 25-26, 2022	Feb. 15-16, 2022	March 23-24, 2022	April 25-26, 2022***
	Results (ppbv)*	Results (ppbv)*	Results (ppbv)*	Results (ppbv)*
Guthrie Background **	0.0361	0.0884	0.0321	0.271
#0 South Charleston, WV	Nondetect	Not exposed	0.08	0.146
#3 North Charleston, WV	0.0165	0.0227	0.155	0.221
#4 North Charleston, WV	0.0121	0.088	0.0794	0.277
#10 Institute, WV	0.0821	0.0996	0.182	0.674
#13 Institute, WV	0.0375	0.204	0.0714 (co-located)	0.124
#14 Institute, WV	0.0376	0.0958	0.119	0.514
#15 Institute, WV	0.0505	1.3	0.447	0.183
#16 Buffalo, WV Background**	N/A	N/A	N/A	0.365

* Concentrations measured in parts per billion by volume (ppbv)
** Background site: This is an area with no known emitters of Ethylene Oxide
*** April 26-27, 2022 for #0 South Charleston, #3 North Charleston and #4 North Charleston
Method Detection Level (MDL) for the January through March sampling = 0.0261 ppb
Method Detection Level (MDL) for the June sampling = 0.048 ppb
MDL is the minimum concentration of a substance that can be measured and reported with 99% confidence that the concentration is greater than zero.

As discussed previously in the West Virginia Challenges Section, several data points have concentrations lower than the 5xMDL precision threshold consistent with QA requirements in EPA's NATTS TAD to characterize data quality. The background sites in some cases have higher concentrations than fenceline, on-site, or off-site.

Comparing the wind roses (showing the direction the wind is coming from) and concentrations in Figures 23-30 show a relationship between the direction of the wind and concentrations detected onsite.

Monitoring Event Modeling

Introduction

The DAQ performed air modeling for each of the 24-hour monitoring events in order to compare the results from monitoring against the modeled results. As defined by EPA, an air model is a mathematical simulation of how air pollutants disperse in the atmosphere to affect ambient air quality. DAQ used data provided by the four facilities which included the locations and amounts of EtO released for each of the four EtO emitting facilities in the Kanawha Valley during each sampling period, as well as weather (meteorological) data to perform these calculations. Weather data was provided by Altivia from its meteorological tower in Institute and by Union Carbide Corporation from its meteorological tower in South Charleston.

Model Selection

The DAQ used the EPA-recommended AERMOD Model (version 22112). AERMOD is a steady-state dispersion model designed for short-range (up to 50 kilometers) dispersion of direct air pollutant emissions primarily from stationary (non-moving) industrial sources. Steady-state models calculate concentrations for each hour from an emission rate and meteorological conditions that are uniform across the modelling domain. Thus, they simulate hourly-average concentrations. AERMOD is time-varying, changing from hour to hour.

The AERMOD atmospheric dispersion modeling system uses many preprocessors. In computer science, a preprocessor is a program that processes its input data to produce output that is used as input to another program. The output is said to be a preprocessed form of the input data, which is used by subsequent programs. In other words, the preprocessor takes input data and creates preprocessed data that can be used by AERMOD. The following preprocessors were used to prepare data for use in the AERMOD model:

- AERSURFACE (version 20060): a preprocessor that processes land cover data for use in AERMET.
- AERMET (version 22112): a meteorological data preprocessor that accepts AERSURFACE output, surface meteorological data, and upper air soundings. Optionally, data from on-site instrument, or meteorological, towers (Met Towers) can also be processed by AERMET. It then calculates atmospheric parameters needed by the dispersion model, such as atmospheric turbulence characteristics, mixing heights, friction velocity, Monin-Obukov length and surface heat flux.
- AERMAP (version 18081): a terrain preprocessor whose main purpose is to provide a physical relationship between terrain features and the behavior of air pollution plumes. It generates location and height data for a given physical location. It also provides information that allows the dispersion model to simulate the effects of air flowing over hills or splitting to flow around hills.

- BPIPRM (version 04274): an algorithm for modeling the effects of downwash created by the pollution plume flowing over nearby buildings. In addition to stack properties, BPIP-PRIME inputs include building parameters such as building corners, building elevation, and height.

Meteorological Data

For performing the modeling in AERMOD, meteorological data must be preprocessed into a format that AERMOD can use. EPA Region 3 was consulted to develop model control keywords to input site-specific meteorological data into AERMET. National Weather Service (NWS) data from surface and upper air stations in addition to onsite meteorological data provided by the facilities were input into AERMET. Onsite meteorological data was collected using onsite met towers (see figures below). The onsite meteorological data record includes wind speed, wind direction, temperature, relative humidity, and insolation (incoming solar radiation). The heights and coordinates for the onsite met towers is summarized in the table below.

Table 4 Met Tower Locations and Heights

Met Tower	Latitude	Longitude	Height (m)
Institute	38.38 N	81.79 W	7.9
South Charleston	38.37 N	81.69 W	7.9

Figure 12 Met Tower Locations

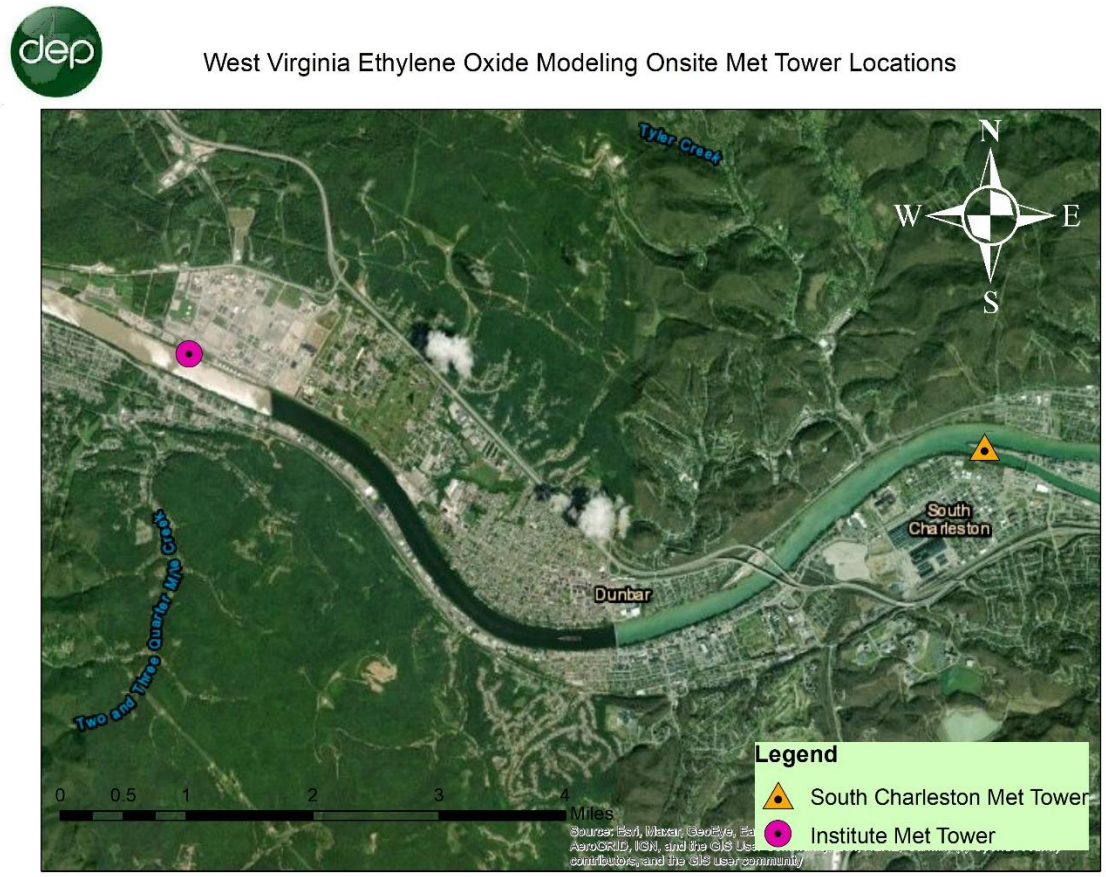


Figure 13 Institute Met Tower

Figure 14 South Charleston Met Tower

Note that the DAQ finalized modeling using a newer version of AERMET (Version 22112), which was unavailable during initial collaboration with the EPA. For the monitoring event modeling, the appropriate time-matching meteorological date for each monitoring event, was processed with AERMET.

The AERSURFACE program (Version 20060) was used to generate the three critical parameters used in AERMET: namely, albedo, Bowen Ratio (ratio of sensible heat to latent heat), and the surface roughness. 2016 National Land Cover Data (NCLD) along with the center-point coordinates for each facility were input into AERSURFACE.

The AERSURFACE user's manual indicates that different values are assigned to Bowen ratio based on surface moisture due to precipitation and whether the site has experienced wetter than normal, dryer than normal, or average (normal) conditions. The surface moisture condition for a site may vary depending on the meteorological data period for which the surface characteristics will be applied. AERSURFACE applies the surface moisture condition for the entire data period. Therefore, if the surface moisture condition varies significantly across the data period, then AERSURFACE may need to be applied multiple times to account for those variations. The surface moisture condition can be determined by comparing precipitation for the period of data to be processed to the 30-year climatological record. It is recommended the user specify "wet" conditions in AERSURFACE if precipitation is in the upper 30th-percentile, "dry" conditions if precipitation is in the lower 30th-percentile, and "average" conditions if precipitation is in the middle 40th-percentile.

Three outputs were generated for each facility for "wet", "normal", and "dry" conditions. Monthly precipitation levels for the Charleston, WV area were downloaded from the National Weather Service and a thirty-year baseline period was established, as recommended in the AERSURFACE user's manual. Monthly precipitation values for the periods being modeled by AERMOD were compared to this baseline. Based upon the percentile rank of each month compared to the baseline period, as explained in the previous paragraph, the AERSURFACE outputs for either "wet", "average", or "dry" conditions were input into AERMET. The following table summarizes the moisture conditions for each monitoring event:

Table 5 Moisture Conditions for Each Monitoring Event

Month	Precipitation (inches)	Percentile (Compared to 30 Yr Baseline[1])	Moisture Condition
Jan-22	5.85	0.98	Wet
Feb-22	4.42	0.85	Wet
Mar-22	3.69	0.69	Average
Apr-22	3.51	0.65	Average

[1]1990-2020

Coordinate System

In all EtO modeling analyses conducted by the DAQ, the location of emission sources, structures, and receptors were represented in the Universal Transverse Mercator (UTM) coordinate system. The UTM grid divides the world into coordinates that are measured in north meters (measured from the equator) and east meters (measured from the central 500 km meridian of each UTM zone, where the world is divided into 36 north-south zones). The datum for the EtO modeling analysis was based on North American Datum 1983 (NAD 83). UTM coordinates for this analysis all resided within UTM Zone 17 which will served as the reference point for all data as well as all regional receptors and sources.

Elevated Terrain

Terrain elevations were considered in the modeling analysis. The elevations of receptors, buildings, and sources will refine the modeling impacts between the sources at one elevation and receptor locations at various other elevations at the fence line and beyond. This was accomplished using the AERMOD terrain preprocessor called AERMAP (latest version 18081), which generates base elevations above mean sea level for sources, buildings, and/or receptors as specified by the user. For all receptors, AERMAP will determine the base elevation of each and an effective hill height scale that determines the magnitude of each source plume-elevated terrain feature interaction. AERMOD uses both receptor-related values to calculate the effect of terrain on each plume. Base elevations for select sources and buildings, terrain elevations for receptors, and other regional source base elevations input to the model will be read and interpolated from 1 arc second (approximately 30 meter resolution) National Elevation Dataset (NED) data obtained from the U.S. Geological Survey (USGS). The NED data will extend well beyond the extent of the modeled receptor grids to properly calculate the receptor elevations and hill-height scales.

Building Downwash

The Guideline[2] requires the evaluation of the potential for physical structures to affect the dispersion of emissions from stack sources. The exhaust from stacks that are located within specified distances of buildings may be subject to “aerodynamic building downwash” under certain meteorological conditions. This determination is made by comparing actual stack height

[2] U.S. Environmental Protection Agency. (EPA 2017) Appendix W to 40 CFR 51, Published January 17, 2017 Federal Register Volume 82 No. 10, Revisions to the Guideline on Air Quality Models: Enhancements to the AERMOD Dispersion Modeling System and Incorporation of Approaches to Address Ozone and Fine Particulate Matter; Final Rule.

to the Good Engineering Practice (GEP) stack height. The modeled emission units will be evaluated in terms of their proximity to nearby structures.
In accordance with recent AERMOD updates, an emission point is assumed to be subject to the effects of downwash at all release heights even if the stack height is above the EPA formula height, which is defined by the following formula:

$$H_{GEP} = H + 1.5L, \text{ where:}$$

H_{GEP} = GEP stack height,
H = structure height, and
L = lesser dimension of the structure (height or maximum projected width)

This equation is limited to stacks located within 5L of a structure. Stacks located at a distance greater than 5L are not subject to the wake effects of the structure.

Direction-specific equivalent building dimensions used as input to the AERMOD model to simulate the impacts of downwash will be calculated using the EPA-sanctioned Building Profile Input Program (BPIP-PRIME), version 04274 and used in the AERMOD Model. BPIP-PRIME is designed to incorporate the concepts and procedures expressed in the GEP Technical Support document, the Building Downwash Guidance document, and other related documents and has been adapted to incorporate the PRIME downwash algorithms.

The following parameters are input into the BPIP-PRIME program:

- For each building, the coordinates of each building corner, the height of the building, and the elevation of the building
- For each stack, the stack elevation, the stack height, and stack coordinates

The figures below, show locations of the coordinates entered into BPIP-PRIME.

Figure 15 BPIP-PRIME Coordinates (Institute Area)

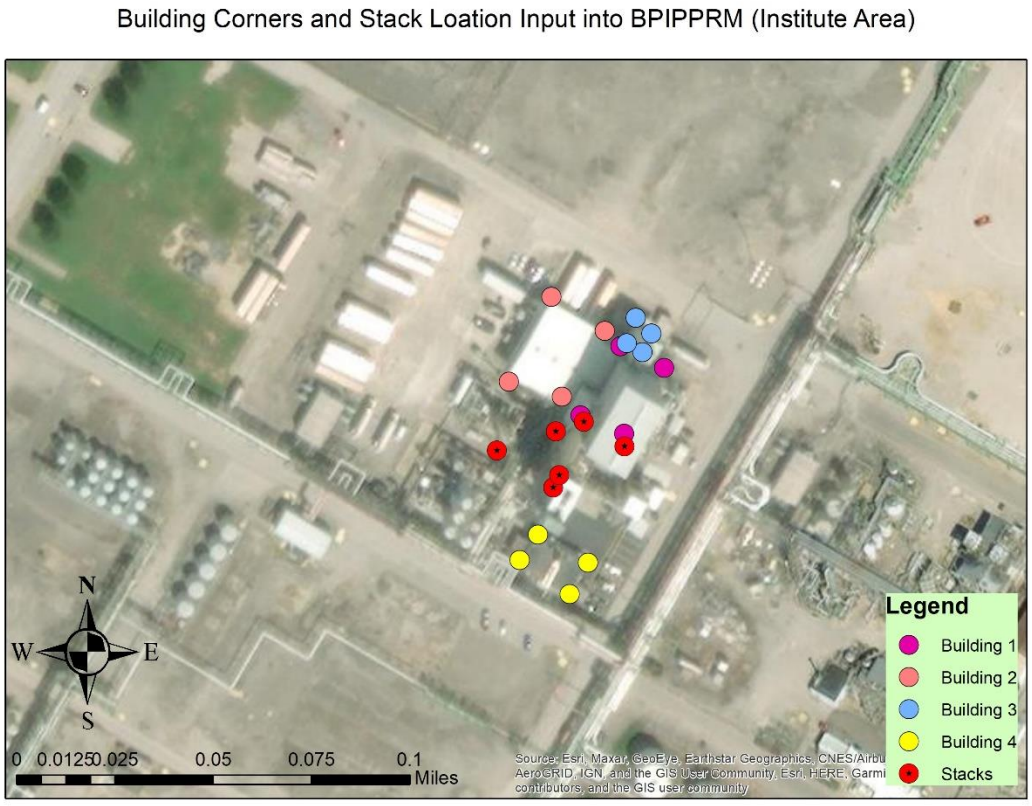
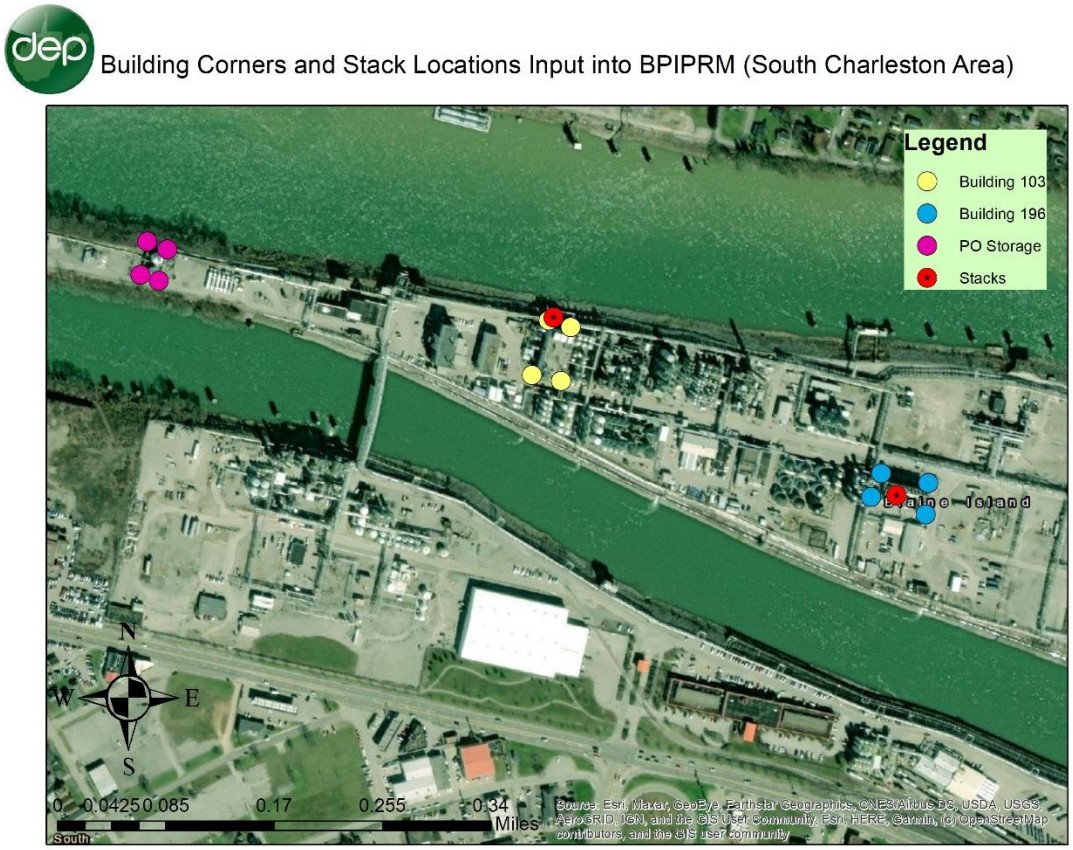


Figure 16 BPIP-PRIME Coordinates (South Charleston Area)



Receptor Grids

AERMOD calculates pollutant impacts, or concentrations, at discreet locations, referred to as receptors. AERMAP is used to generate the receptors which can be input into AERMOD.

For the EtO air dispersion modeling analyses, ground-level concentrations were calculated from the fence line of both the Institute and South Charleston facilities out to approximately 12 km from the centerline of the facilities using a series of nested receptor grids. These receptors were used in the EtO modeling; AERMOD calculates air pollution concentrations at each receptor location.

The following nested grids were created using AERMAP and were used to determine the extent of significance:

- Fine Cartesian Grid: A “fine grid” containing 50-meter spaced receptors extending 1 km from the facility,

- Medium Cartesian Grid: A “medium grid” containing 100-meter spaced receptors extending 1 km to 3 km from the facility, exclusive of receptors on the fine grids, and
- Coarse Cartesian Grid: A “coarse grid” containing 250-meter spaced receptors extending 3 km to 5 km from the facility, exclusive of receptors on the fine and medium grids
- Very Coarse Cartesian Grid: A “very coarse grid” containing 500-meter spaced receptors extending 5 km to 10 km from the facility, exclusive of receptors on the fine, medium, and coarse grids
- Monitoring Station Locations: EtO monitors were set up by the DAQ for several monitoring events during 2022. The locations of these monitors were included during modeling for timeframes that corresponded to these monitoring events.

A separate receptor grid was generated for both the South Charleston and Institute facilities. Modeling was performed both separately for each facility and for both facilities combined. For the combined modeling, both receptor grids were combined. Below are images of the receptor grids.

Figure 17 Institute Receptor Grid (Excluding Buffalo Monitor Site)

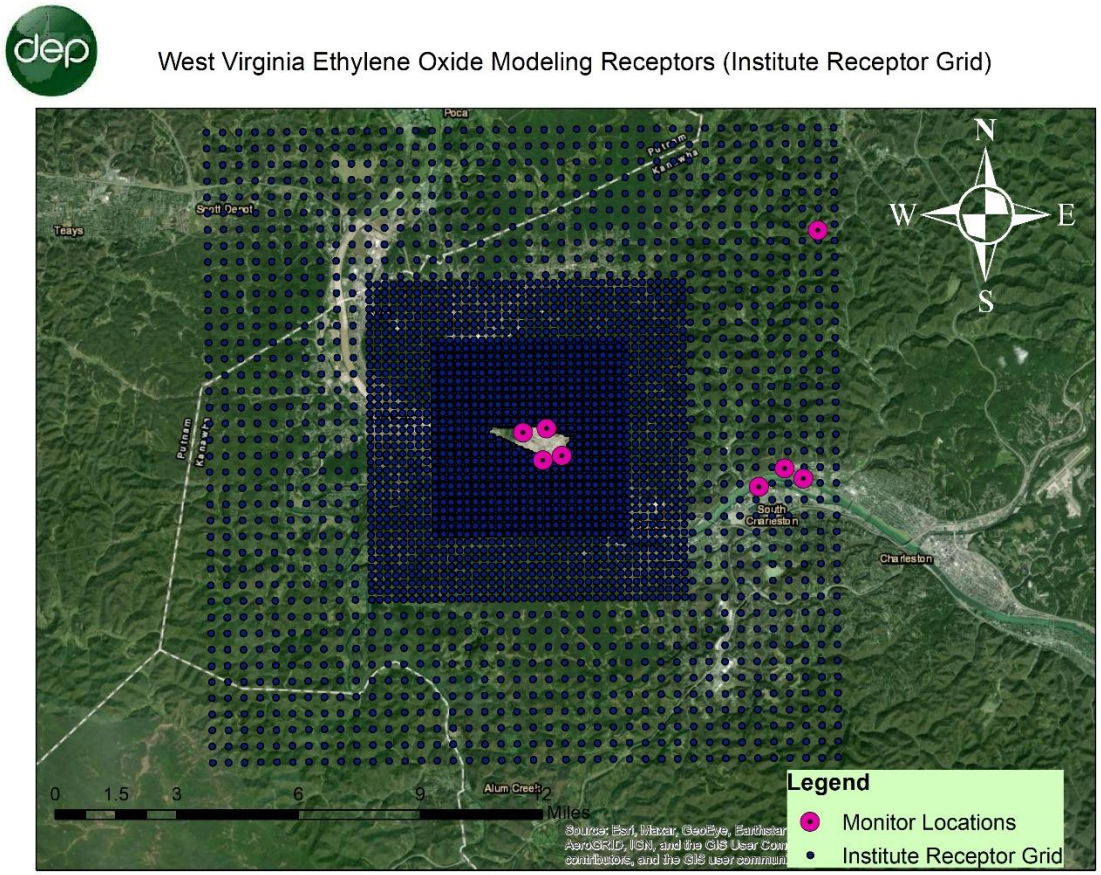


Figure 18 South Charleston Receptor Grid (Excluding Buffalo Monitor Site)

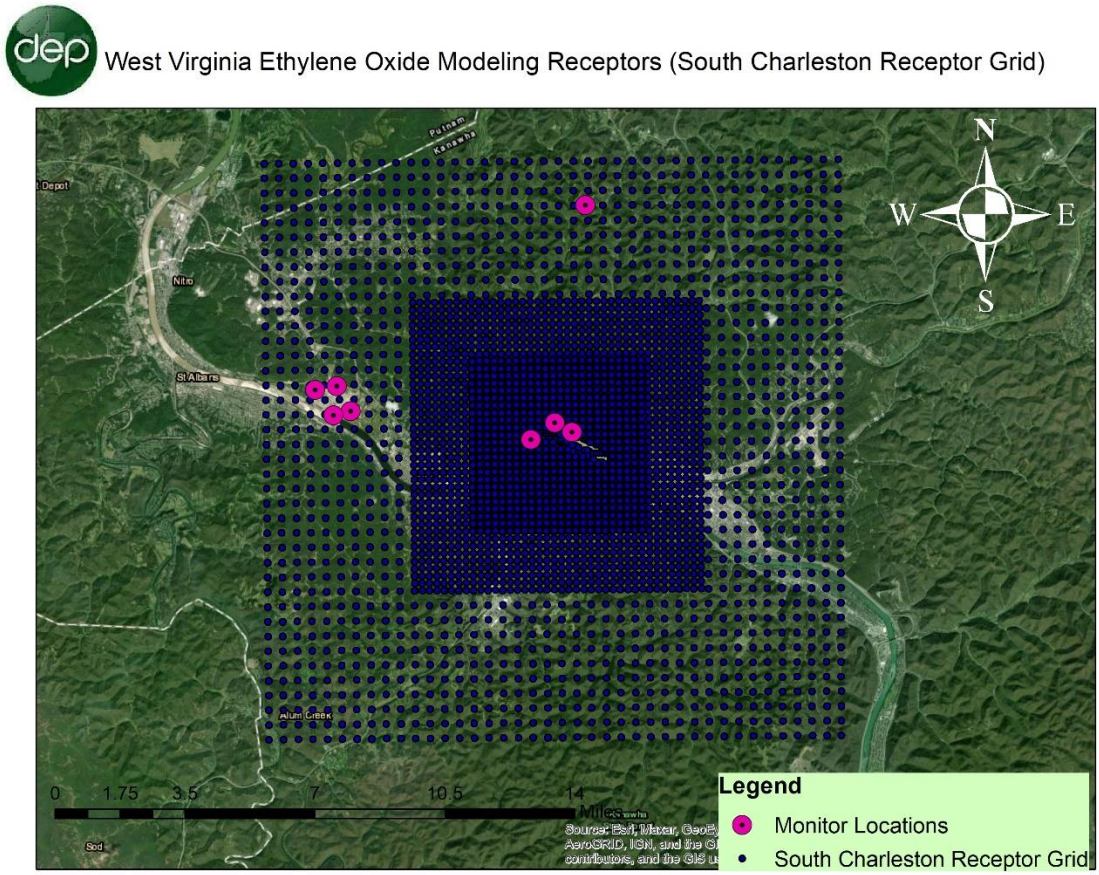
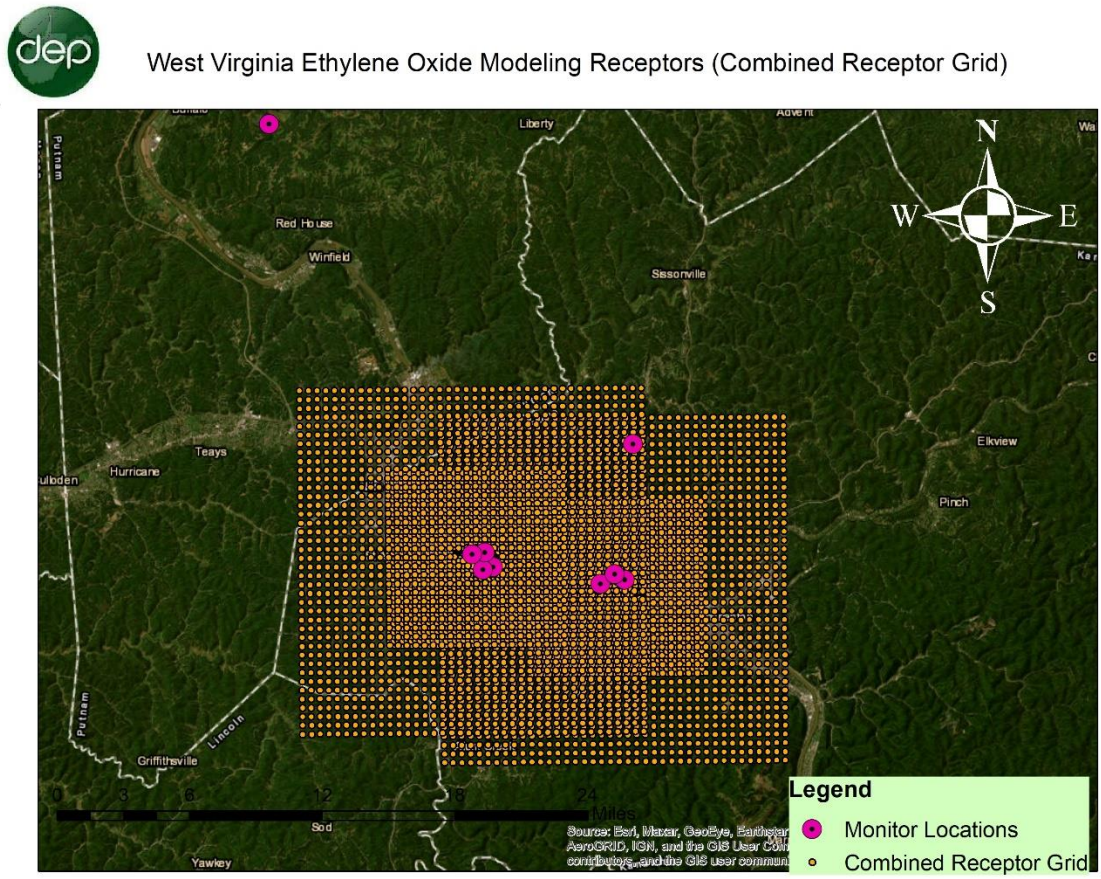


Figure 19 Combined Receptor Grid and All Monitoring Sites



Source Characterization

AERMOD allows an emissions source to be modeled several different ways. The following types of sources were used in the AERMOD modeling of EtO emissions from the Institute and South Charleston facilities:

- Point Sources: A point source injects emissions vertically into the atmosphere through a stack; it emits at a specific point. In addition to the emission rate (g/s), actual stack parameters (i.e., height, diameter, discharge gas temperature, and gas exit velocity) are input into AERMOD.
- Area Sources: An area source is meant to represent emissions from a flat surface (i.e. evaporative emissions from a flat surface such as a pond). The AERMOD area source inputs used for the DAQ's modeling efforts include the emission rate divided by that area of the source (g/s-m^2), release height above the ground (m), and length of the X side of

the area (m). The only EtO source modeled as an area source was the Chemical Mixing area at the South Charleston facility.

- Line Sources: A line source is a special case of the area source. It is an area that is narrow and elongated (i.e., a roadway). The AERMOD line source inputs used for the DAQ's modeling efforts include the emission rate divided by that area of the line source (g/s-m^2), release height above the ground (m), width of the source (m), and the optional input for initial vertical dimension of the line source (m). The only EtO source modeled as a line source was the Oxide Adducts' Western Tip of the Island at the South Charleston facility.
- Volume Sources: While area and line sources represent emissions on a two-dimensional surface, a volume source represents emissions from a three-dimensional area. A volume source can only be modeled as a square area with a specified height. An irregularly shaped volume source will be input into AERMOD as several, adjoining volume sources. To model a volume source, AERMOD requires inputs for the emissions rate (g/s), release height above the ground (m), initial lateral dimension of the volume (m), and initial vertical dimension of the volume (m). Volume sources were used to model the majority of fugitive EtO emissions. Fugitive emissions are those emissions that do not occur through a specific point such as a stack, chimney, vent, or other similar opening. Examples of fugitive emissions include equipment leaks, dust from haul roads, and emissions during transfer of material. Excluding, the Chemical Mixing Area and Western Tip of the Island at the South Charleston facility, all fugitive sources at both facilities were modeled as volume sources.

The Source Characterization Tables can be found in Appendix D. The following tables list the total number of each source type for the Institute and South Charleston areas.

Table 6 Total Number of Each Source Type (Institute Area)

Source Type	Total
Point	7
Volume	19

Table 7 Total Number of Each Source Type (South Charleston Area)

Source Type	Total
Point	99
Horizontal Point	3
Volume	15
Area	1
Line	1

The locations of the EtO sources for the Institute and South Charleston areas are provided in the following images:

Figure 20 Plot of EtO Sources (Institute Site)

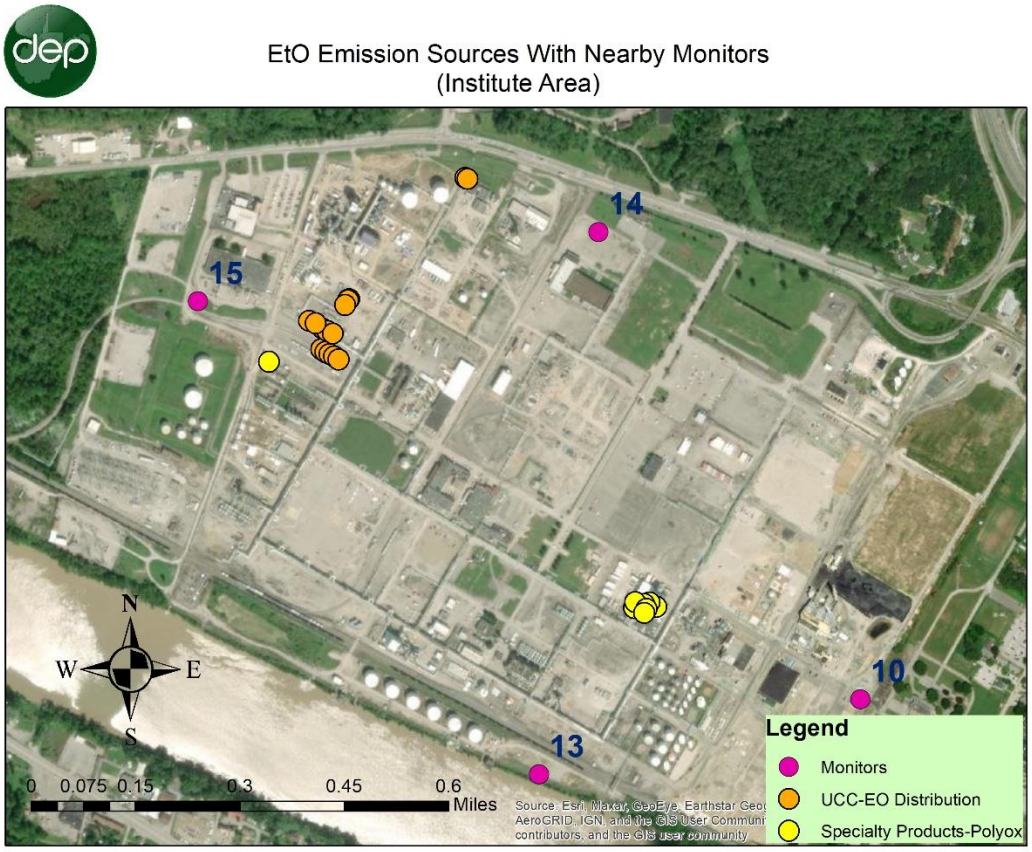
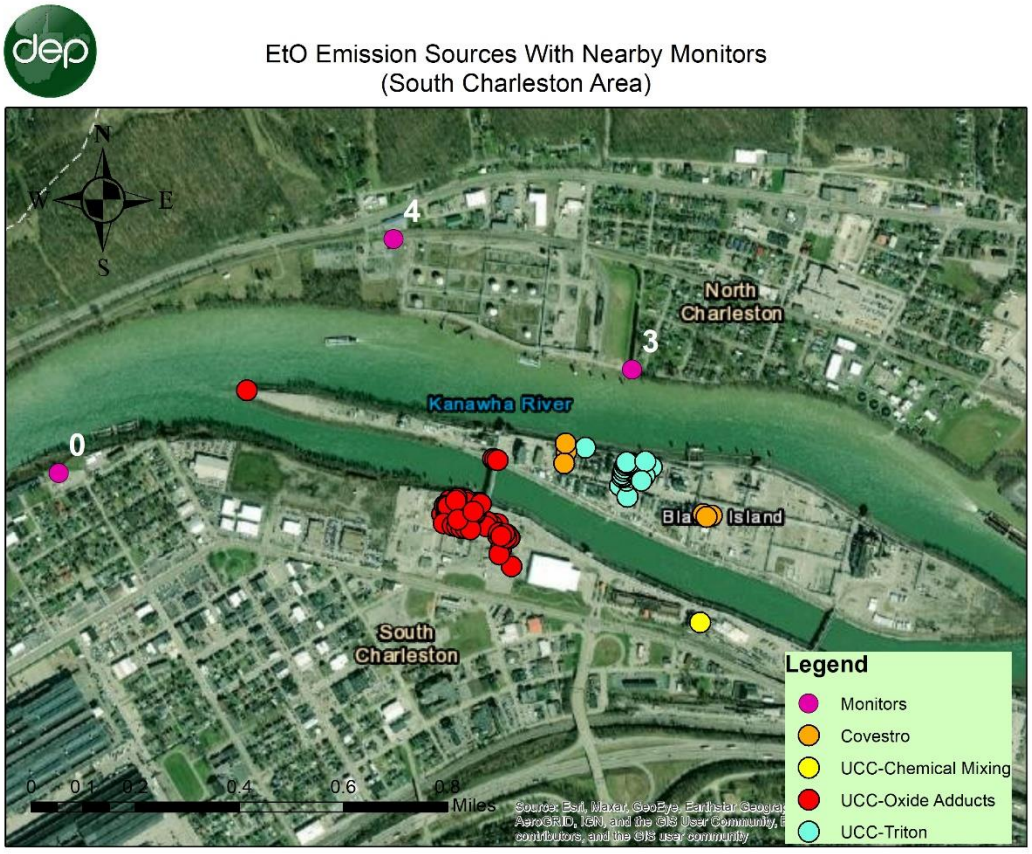


Figure 21 Plot of EtO Sources (South Charleston Site)



Appendix E has the AERMOD Source Files. Appendix F has the AERMOD Input Files. Appendix G has the AERMOD Summary Files. Appendix H has the Excerpts of Plot Files and Total EtO Concentrations for Monitoring Locations.

Model Validation, Results, and Analysis

Model Validation

EPA's *Guideline on Air Quality Models* (''Guideline'') addresses the regulatory application of air quality models for assessing criteria pollutants under the Clean Air Act. The Guideline provides air quality modeling techniques that should be applied to State Implementation Plan (SIP) submittals and revisions, and to New Source Review (NSR), including new or modifying sources under Prevention of Significant Deterioration (PSD). Although intended for criteria pollutants, it

is appropriate to apply many of the principles in the Guideline to air toxics modeling assessments. The Guideline identifies AERMOD as appropriate for use in evaluating air toxics in Appendix A.

> From Appendix A of the Guideline:
>
> a. Regulatory Use
> (1) AERMOD is appropriate for the following applications:
> • Point, volume, and area sources;
> • Buoyant, elevated line sources (*e.g.,* aluminum reduction plants);
> • Mobile sources;
> • Surface, near-surface, and elevated releases;
> • Rural or urban areas;
> • Simple and complex terrain;
> • Transport distances over which steady state assumptions are appropriate, up to 50km;
> • 1-hour to annual averaging times; and
> • Continuous toxic air emissions.

AERMOD is a steady-state plume dispersion model for assessment of pollutant concentrations from a variety of sources and has been the EPA regulatory-preferred model since promulgation in the Guideline on December 9, 2005. EPA conducted extensive performance evaluations of AERMOD to support designating the model as regulatory-preferred. The performance evaluation includes statistical evaluation of robust highest concentration (RHC), fractional bias (FB), and composite performance measure (CPM). The performance evaluations compare AERMOD's predicted concentrations to monitored concentrations, unpaired in space and time. In other words, AERMOD's performance at predicting concentrations depends on matching the highest monitored concentrations, regardless of where and when the monitored concentrations occur. AERMOD is not evaluated on its ability to predict concentrations at specific times and locations.

From EPA's *AERMOD Model Formulation and Evaluation* (EPA-454/R-19-014):

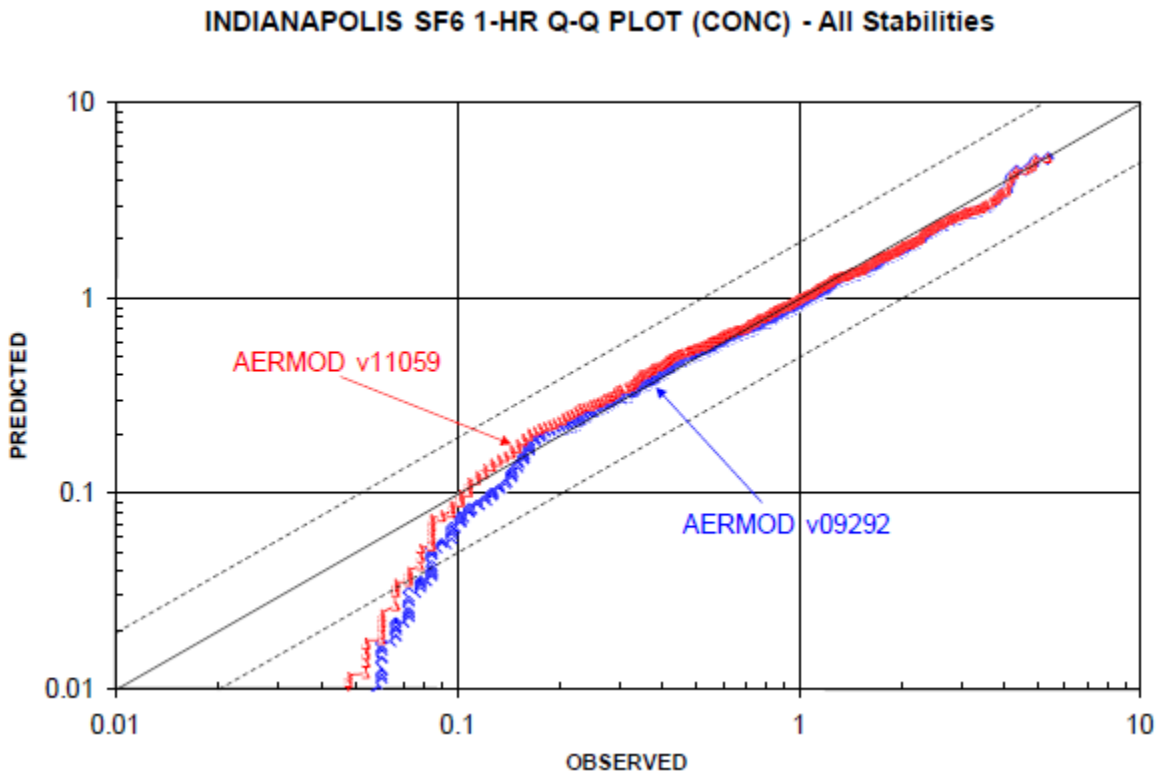
> For the 1-hour RHC, the RHC is calculated based on N=26 across all modeled and monitored values, i.e. not paired in time or space. (Page 128);
>
> and:
>
> The fractional bias is also calculated for the standard deviation where OB and PR refer to the standard deviation of the highest 25 observed and predicted concentrations

respectively. This is done across all monitors and modeled receptors, unpaired in time and space for the 3-hour and 24-hour averaging periods (Page 128)

These performance evaluations enable the EPA and model users to have confidence that model predictions are accurate for the right reasons. However, the comparison of modeled concentrations with observations provides only a part of the assessment of model performance. In addition to the performance evaluations, EPA relied on the conclusions reached in the science peer reviews and the supportive analyses in deciding whether a model will be useful for its intended purposes.

As part of the performance evaluation, EPA prepared plots (quantile-quantile, or Q-Q) comparing modeled and monitored values, unpaired in space and time. The highest modeled concentration is plotted against the highest monitored concentration, and the plot continues down through all other ranking concentrations. An example from Page 2 of Appendix C of EPA's *AERMOD Model Formulation and Evaluation* is in Figure 22. This figure illustrates very good agreement between AERMOD predicted concentrations and observed concentrations, unpaired in space and time.

Figure 22 1-hour Q-Q Plot for Indianapolis SF^6 Study for All Stabilities



Model Accuracy and Uncertainty

The formulation and application of air quality models are accompanied by several sources of uncertainty. ''Irreducible'' uncertainty stems from ''unknown'' conditions, which may not be explicitly accounted for in the model. There are likely to be deviations from the observed concentrations in individual events due to variations in the unknown conditions. ''Reducible'' uncertainties are caused by: (1) Uncertainties in the ''known'' input conditions (e.g., emission characteristics and meteorological data); (2) errors in the measured concentrations; and (3) inadequate model physics and formulation.

The ''irreducible'' uncertainty associated with Gaussian plume models may be responsible for variation in concentrations of as much as ± 50 percent and ''reducible'' uncertainties can be on a similar scale. Section 4 of the Guideline states that "Such uncertainties do not indicate that an estimated concentration does not occur, only that the precise time and locations are in doubt."

The Guideline also states in Section 4 that "Composite errors in highest estimated concentrations of 10 to 40 percent are found to be typical. However, estimates of concentrations paired in time and space with observed concentrations are less certain."

Percent Error vs Percent Difference

The Guideline discusses model performance in terms of percent error, which can be calculated with the following equation:

Percent Error = | (A – B) / (B) | x 100

Where A is a test value and B is the true, correct value.

Percent Difference, however, is calculated differently with the following equation:

Percent Difference = [| (A – B) | / (A+B)/2] x 100.

The central difference between percent difference and percent error is that a true, correct value is asserted to exist when applying the percent error method while percent difference evaluates the difference between two values without specifying that one value is the true and correct value.

The ambient measurement of EtO has significant uncertainties acknowledged by EPA and observed by DAQ. For example, the cause for EtO "background" measurements being higher than measurements near the EtO emitting sources is uncertain. Also, measurements taken close to one another have shown very poor agreement and leads to more uncertainty that the measurements are true and correct.

For these reasons, DAQ applied the percent difference formula to compare measured concentrations to modeled concentrations, since significant uncertainty exists to preclude identifying the measured concentrations as true, correct values. Finally, the percent difference formula provides a better indicator of the difference between two values without characterizing one value as a true, correct value.

Discussion of Results

Tables 8 through 13 provide a list of modeled results compared to monitored results for the same locations and time periods (paired in space and time) as well as the percent difference between the values. The comparison of modeled EtO results to monitored EtO results is not intended to validate AERMOD model performance, since the model has already been validated by EPA.

As discussed above, EPA's performance evaluation of AERMOD was not based on comparing modeled concentrations to monitored concentrations at specific times and locations, i.e., paired in space and time. Also as indicated previously, model prediction errors relative to monitored concentrations of 10 to 40 percent are typical. However, concentrations paired in space and time are less certain. No benchmarks exist for comparing model predictions to observations, paired in space (location) and time.

Uncertainties in the monitoring results also exist which present challenges when analyzing the comparison of modeled EtO concentrations to monitored EtO concentrations. Uncertainties also exist with the model inputs. Meteorological data accuracy has limitations for wind speed and wind direction and introduce further uncertainty. The emission estimates, although believed to be accurate, have limitations. The monitor will "see" the actual emissions from the facilities while the model will only "see" the best estimate based on calculations.

The percent differences between modeled and monitored concentrations range from 5.8% to 199.9%. Although a large range of percent differences is apparent, generally good agreement exists between the best performing comparisons.

Monitoring Event Modeling Results and Comparison to Monitoring Data

Modeling was performed for the January 2022, February 2022, March 2022, and April 2022 monitoring events. The maximum modeled EtO concentrations are compared to the maximum monitored EtO results for each monitoring event at each location in the following tables. The comparisons of modeled concentrations versus modeled concentrations, unpaired in space and time, are presented because these are the comparisons EPA makes as part of the performance evaluation for AERMOD (see prior section on Model Validation).

Table 8 Maximum Modeled EtO Concentrations Compared to Maximum Monitored EtO Concentrations for Institute Area (Unpaired in Space and Time)

Monitoring Event	Maximum Monitoring Results (ppb)	Maximum Monitoring Coordinates			Maximum Modeled Concentration (ppb)	Maximum Modeled Coordinates		Percent Difference (%)
		UTM Easting (m)	UTM Northing (m)	Site ID		UTM Easting (m)	UTM Northing (m)	
Jan-22	0.0821	432583.00	4248215.08	10	0.53669	432831.66	4248318.67	146.9
Feb-22	1.3000	431386.12	4248944.70	15	0.68392	431792.99	4248130.00	62.1
Mar-22	0.4470	431386.12	4248944.70	15	0.59515	439777.01	4247183.81	28.4
Apr-22	0.5140	432114.34	4249063.49	14	0.09147	432114.34	4249063.48	139.6

Table 9 Maximum Modeled EtO Concentrations Compared to Maximum Monitored EtO Concentrations for South Charleston Area (Unpaired in Space and Time)

Monitoring Event	Maximum Monitoring Results (ppb)	Maximum Monitoring Coordinates			Maximum Modeled Concentration (ppb)	Maximum Modeled Coordinates		Percent Difference (%)
		UTM Easting (m)	UTM Northing (m)	Site ID		UTM Easting (m)	UTM Northing (m)	
Jan-22	0.0165	440101.78	4247450.16	3	0.17460	439777.01	4247183.81	165.5
Feb-22	0.0880	439525.26	4247769.17	4	0.42210	439477.01	4246933.81	131.0
Mar-22	0.1550	440101.78	4247450.16	3	0.25011	439619.85	4247306.86	47.0
Apr-22	0.2770	439525.26	4247769.17	4	0.03744	439877.01	4246933.81	152.4

The modeled concentrations (EtO emissions both facilities combined) at the monitor locations are compared to the monitor values in the following tables.

Table 10 January 2022 Monitoring Event Modeling Results and Comparison to Monitor Values (Paired in Space and Time)

ID Tag	Area	Latitude	Longitude	UTM Easting (m)	UTM Northing (m)	Modeled Max Results (ug/m3)	Modeled Max Results (ppb)	Monitoring Results (ppb)	Percent Difference (%)
Project Background	Guthrie	38.4425	-81.6806	440609.50	4255132.47	0.00036	0.00020	0.0361	197.8
0	SC	38.3710	-81.7016	438708.63	4247210.74	0.06958	0.03802	NonDetect	N/A
3	SC	38.3732	-81.6857	440101.78	4247450.16	0.10219	0.05584	0.0165	108.8
4	SC	38.3761	-81.6923	439525.26	4247769.17	0.06271	0.03427	0.0121	95.6
10	I	38.3796	-81.7719	432583.00	4248215.08	0.51477	0.28130	0.0821	109.6
13	I	38.3784	-81.7785	431998.21	4248084.27	0.42838	0.23409	0.0375	144.8
14	I	38.3872	-81.7773	432114.34	4249063.49	0.37549	0.20519	0.0376	138.1
15	I	38.3861	-81.7856	431386.12	4248944.70	0.54703	0.29892	0.0505	142.2

Table 11 February 2022 Monitoring Event Modeling Results and Comparison to Monitor Values (Paired in Space and Time)

ID Tag	Area	Latitude	Longitude	UTM Easting (m)	UTM Northing (m)	Modeled Max Results (ug/m3)	Modeled Max Results (ppb)	Monitoring Results (ppb)	Percent Difference (%)
Project Background	Guthrie	38.4425	-81.6806	440609.50	4255132.47	0.00113	0.00062	0.0884	197.2
0	SC	38.3710	-81.7016	438708.63	4247210.74	0.03103	0.01696	VOID	N/A
3	SC	38.3732	-81.6857	440101.78	4247450.16	0.02599	0.01420	0.0227	46.1
4	SC	38.3761	-81.6923	439525.26	4247769.17	0.03902	0.02132	0.0880	122.0
10	I	38.3796	-81.7719	432583.00	4248215.08	0.15217	0.08315	0.0996	18.0
13	I	38.3784	-81.7785	431998.21	4248084.27	0.65232	0.35646	0.2040	54.4
14	I	38.3872	-81.7773	432114.34	4249063.49	0.11731	0.06410	0.0958	39.6
15	I	38.3861	-81.7856	431386.12	4248944.70	0.64425	0.35205	1.3000	114.8

Table 12 March 2022 Monitoring Event Modeling Results and Comparison to Monitor Values (Paired in Space and Time)

ID Tag	Area	Latitude	Longitude	UTM Easting (m)	UTM Northing (m)	Modeled Max Results (ug/m3)	Modeled Max Results (ppb)	Monitoring Results (ppb)	Percent Difference (%)
Project Background	Guthrie	38.4425	-81.6806	440609.50	4255132.47	0.00125	0.00068	0.0321	191.7
0	SC	38.3710	-81.7016	438708.63	4247210.74	0.06304	0.03445	0.0800	79.6
3	SC	38.3732	-81.6857	440101.78	4247450.16	0.14806	0.08091	0.1550	62.8
4	SC	38.3761	-81.6923	439525.26	4247769.17	0.09520	0.05202	0.0794	41.7
10	I	38.3796	-81.7719	432583.00	4248215.08	0.35301	0.19290	0.1820	5.8
13	I	38.3784	-81.7785	431998.21	4248084.27	0.33292	0.18192	0.0714	87.3
14	I	38.3872	-81.7773	432114.34	4249063.49	0.72832	0.39799	0.1190	107.9
15	I	38.3861	-81.7856	431386.12	4248944.70	0.58159	0.31781	0.4470	33.8

Table 13 April 2022 Monitoring Event Modeling Results and Comparison to Monitor Values (Paired in Space and Time)

ID Tag	Area	Latitude	Longitude	UTM Easting (m)	UTM Northing (m)	Modeled Max Results (ug/m3)	Modeled Max Results (ppb)	Monitoring Results (ppb)	Percent Difference (%)
Project Background	Guthrie	38.4425	-81.6806	440609.50	4255132.47	0.00013	0.00007	0.2710	199.9
0	SC	38.3710	-81.7016	438708.63	4247210.74	0.00340	0.00186	0.1460	195.0
3	SC	38.3732	-81.6857	440101.78	4247450.16	0.01740	0.00951	0.2210	183.5
4	SC	38.3761	-81.6923	439525.26	4247769.17	0.00685	0.00374	0.2770	194.7
10	I	38.3796	-81.7719	432583.00	4248215.08	0.14439	0.07890	0.6740	158.1
13	I	38.3784	-81.7785	431998.21	4248084.27	0.05384	0.02942	0.1240	123.3
14	I	38.3872	-81.7773	432114.34	4249063.49	0.16741	0.09148	0.5140	139.6
15	I	38.3861	-81.7856	431386.12	4248944.70	0.15174	0.08292	0.1830	75.3
Project Background	Buffalo	38.6061	-81.9184	420031.50	4273465.21	0.00029	0.00016	0.3650	199.8

Additionally, EtO concentrations for all receptors were plotted using ArcMap. Below are EtO concentration plots for the Institute and South Charleston facilities for each monitoring event. Each plot contains a wind rose for the monitoring event at the facility, monitor locations, monitored EtO concentrations, maximum modeled EtO concentration locations, and EtO concentration ranges labeled both in ppbv.

Figure 23 Plot of EtO Modeled Concentrations at Institute Site (January 2022 Monitoring Event)

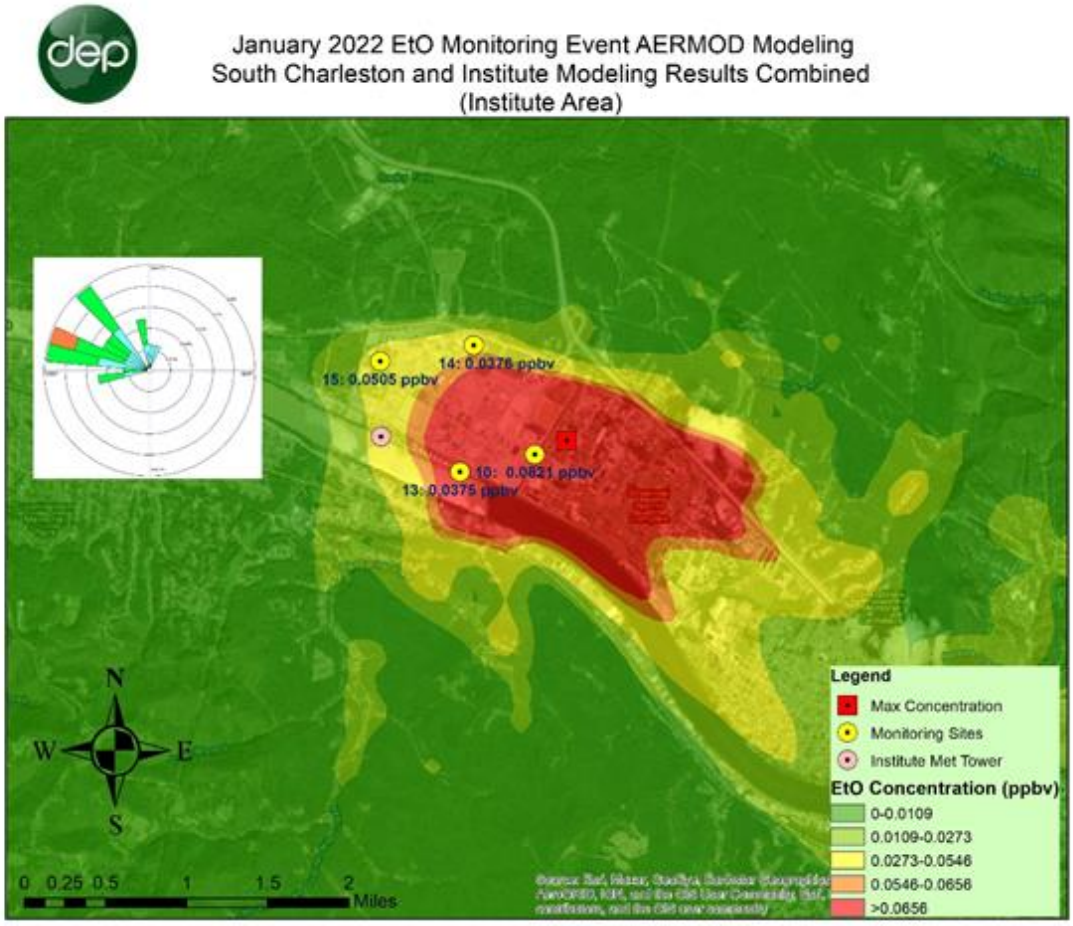


Figure 24 Plot of EtO Modeled Concentrations at South Charleston Site (January 2022 Monitoring Event)

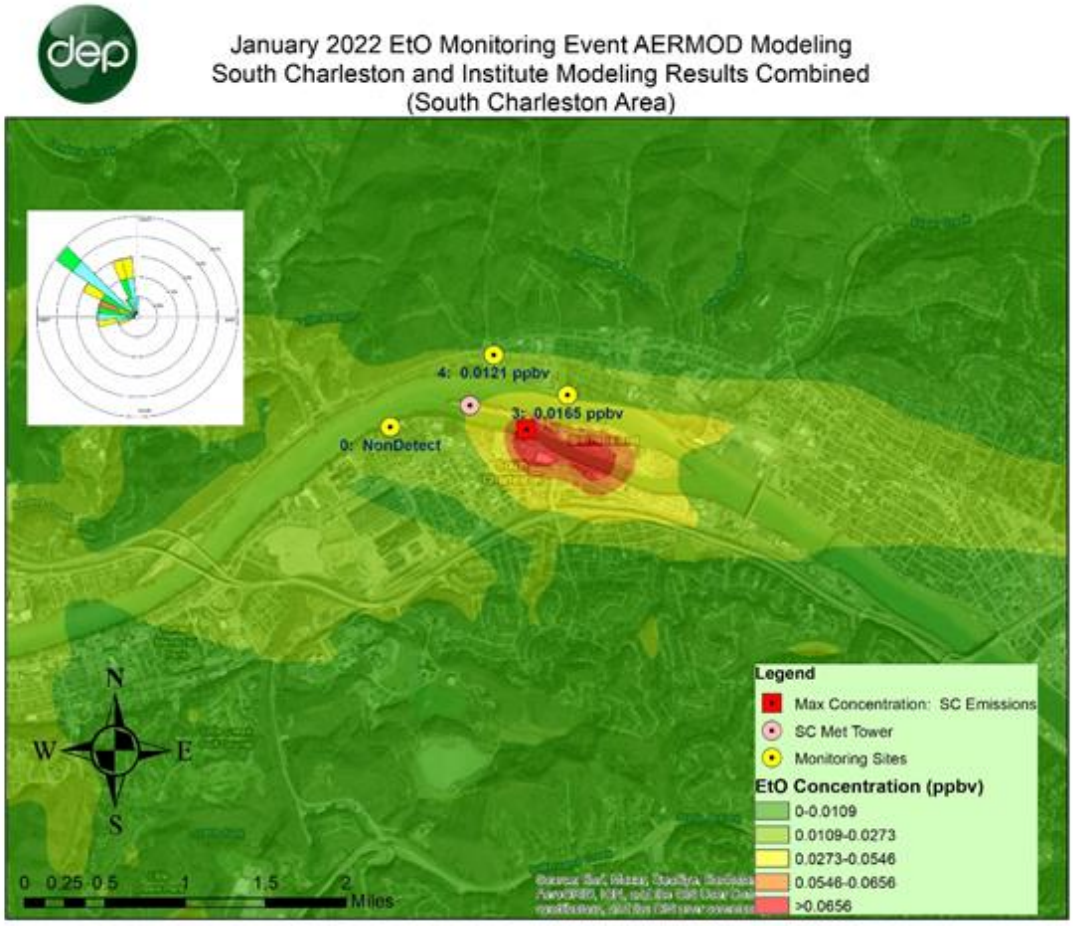


Figure 25 Plot of EtO Modeled Concentrations at Institute Site (February 2022 Monitoring Event)

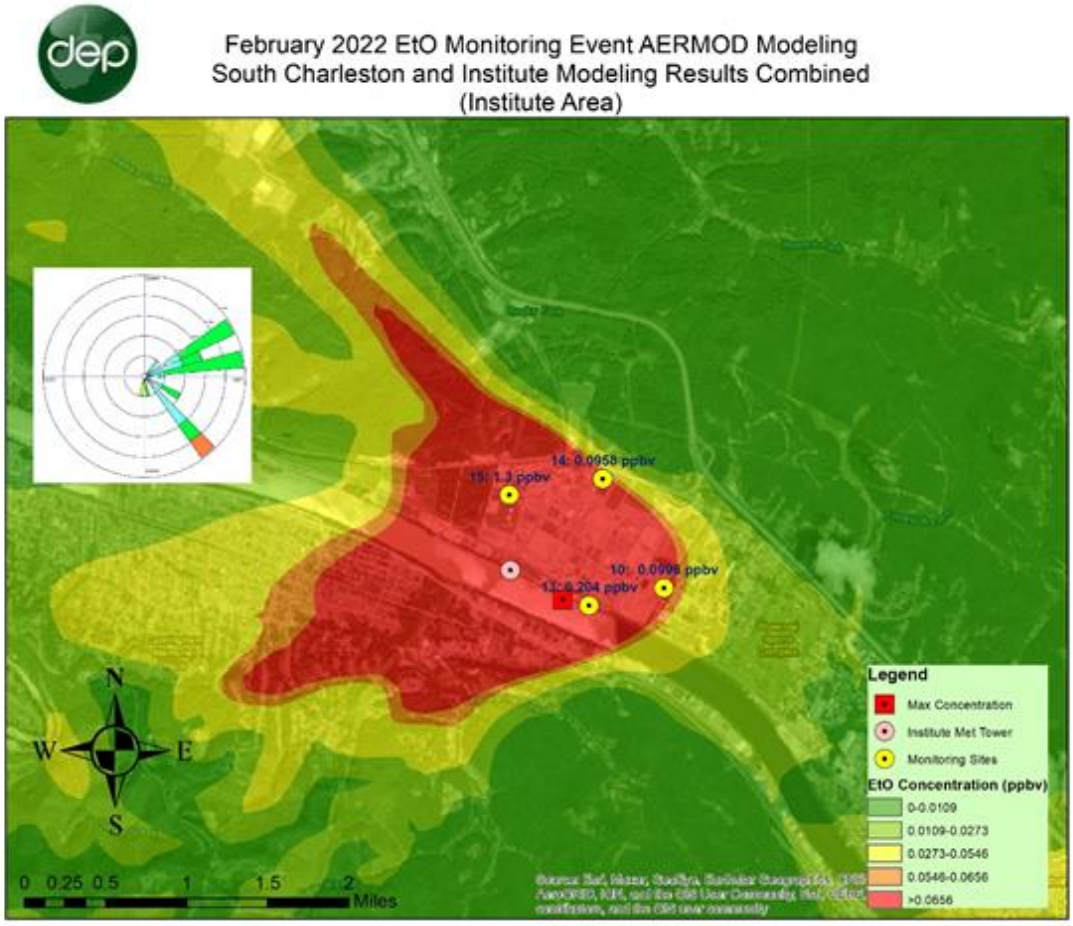


Figure 26 Plot of EtO Modeled Concentrations at South Charleston Site (February 2022 Monitoring Event)

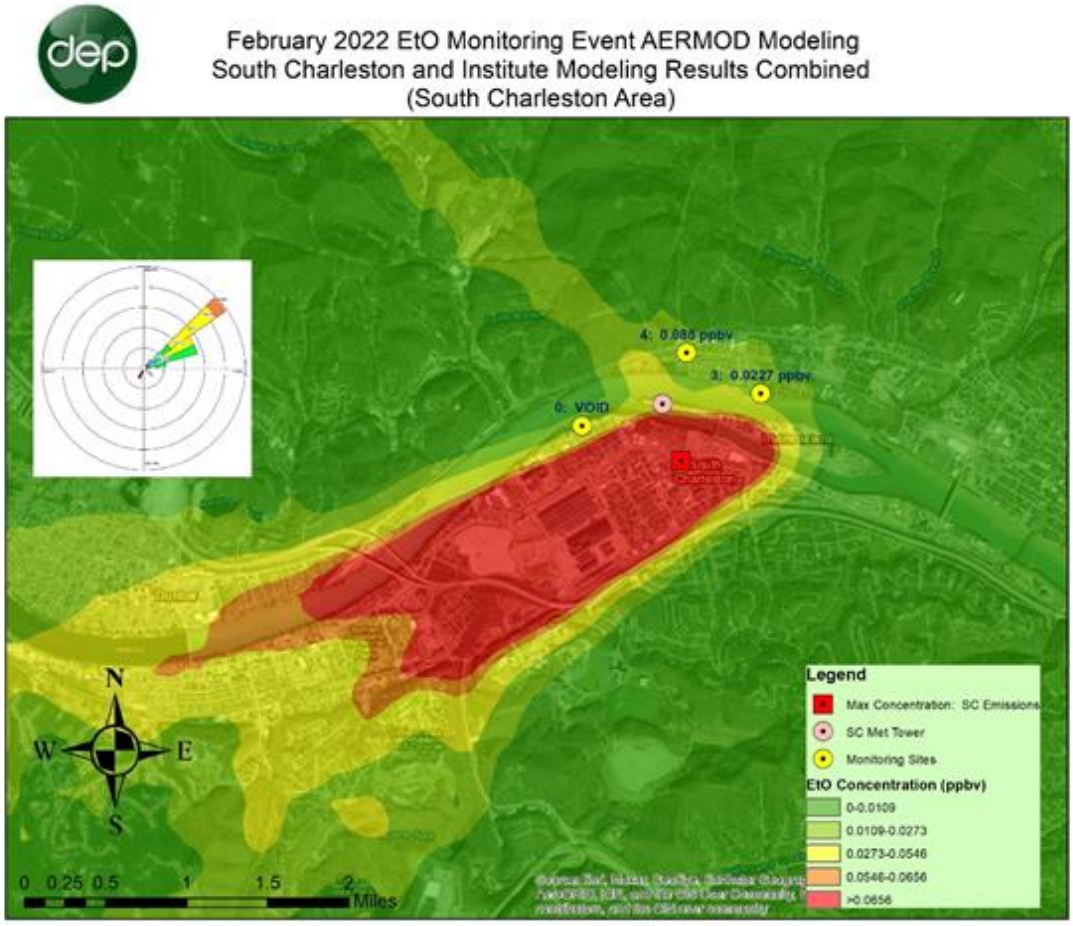


Figure 27 Plot of EtO Modeled Concentrations at Institute Site (March 2022 Monitoring Event)

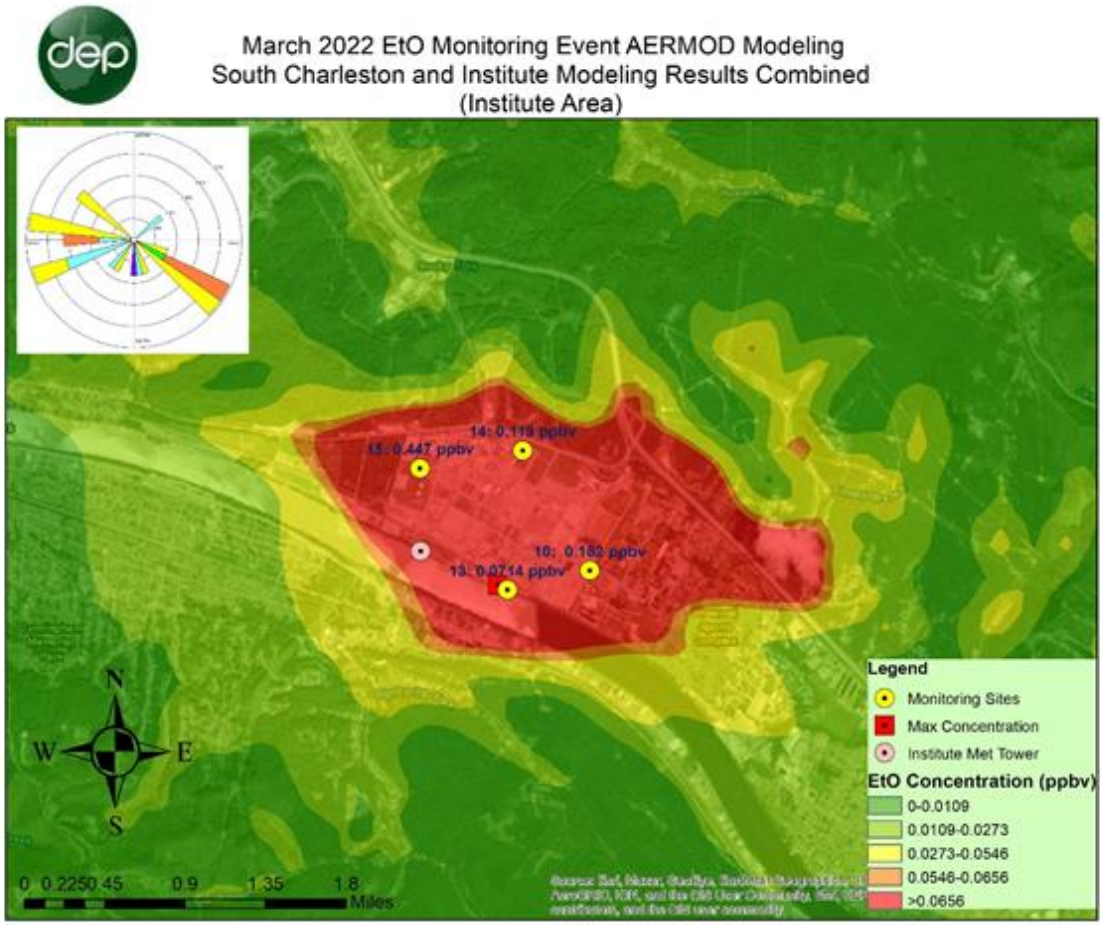


Figure 28 Plot of EtO Modeled Concentrations at South Charleston Site (March 2022 Monitoring Event)

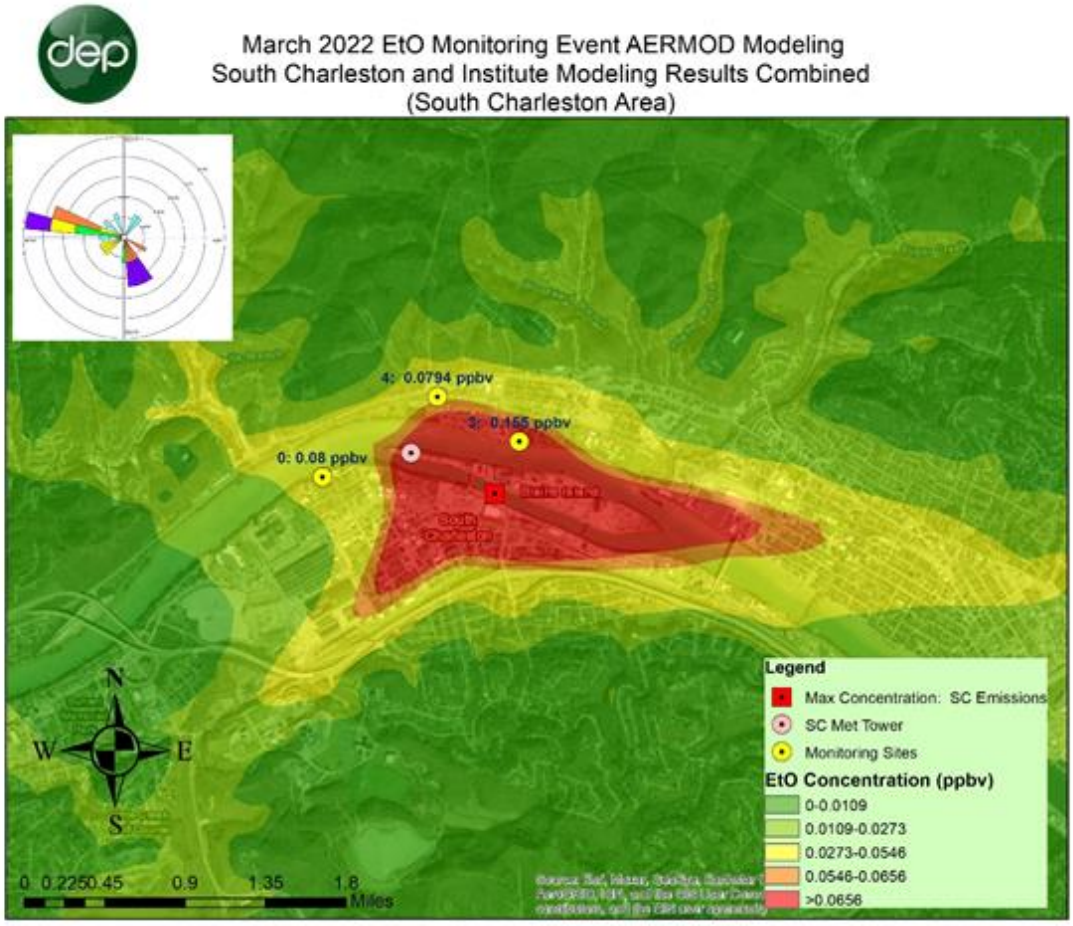


Figure 29 Plot of EtO Modeled Concentrations at Institute Site (April 2022 Monitoring Event)

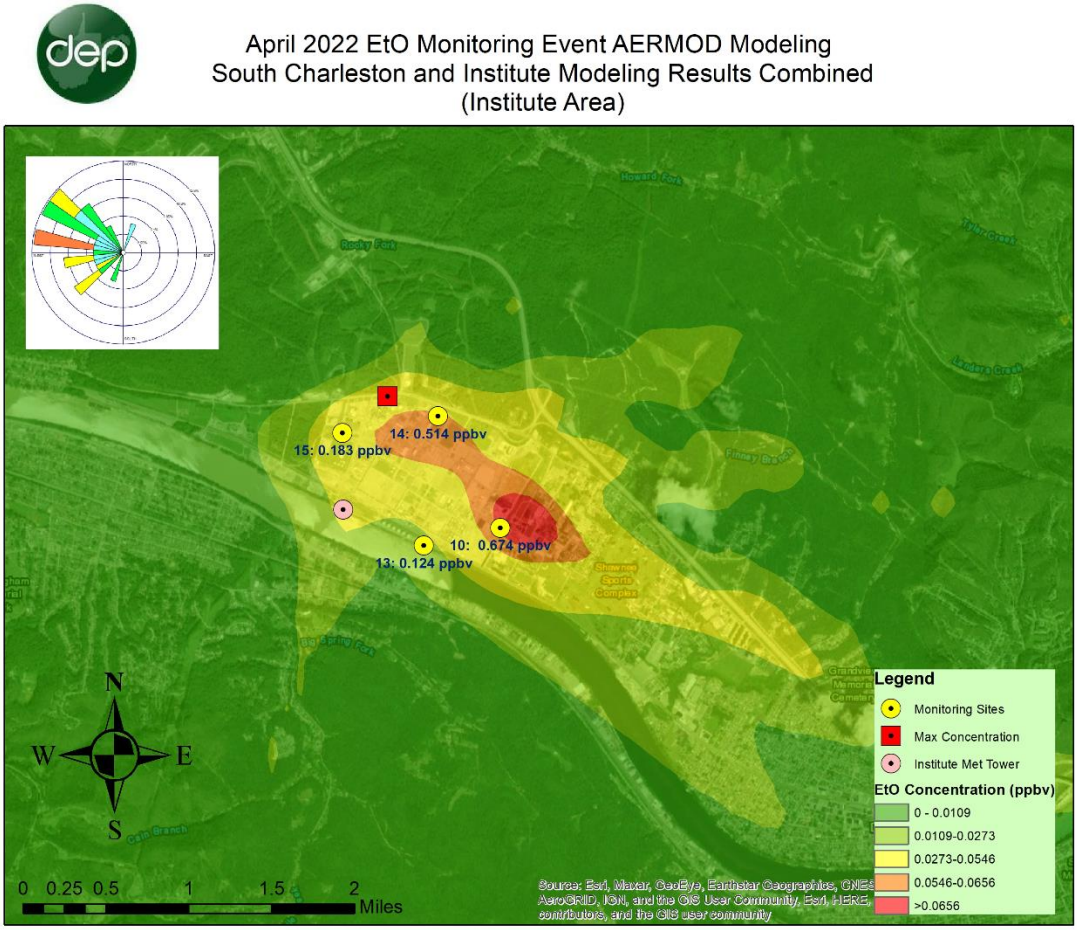
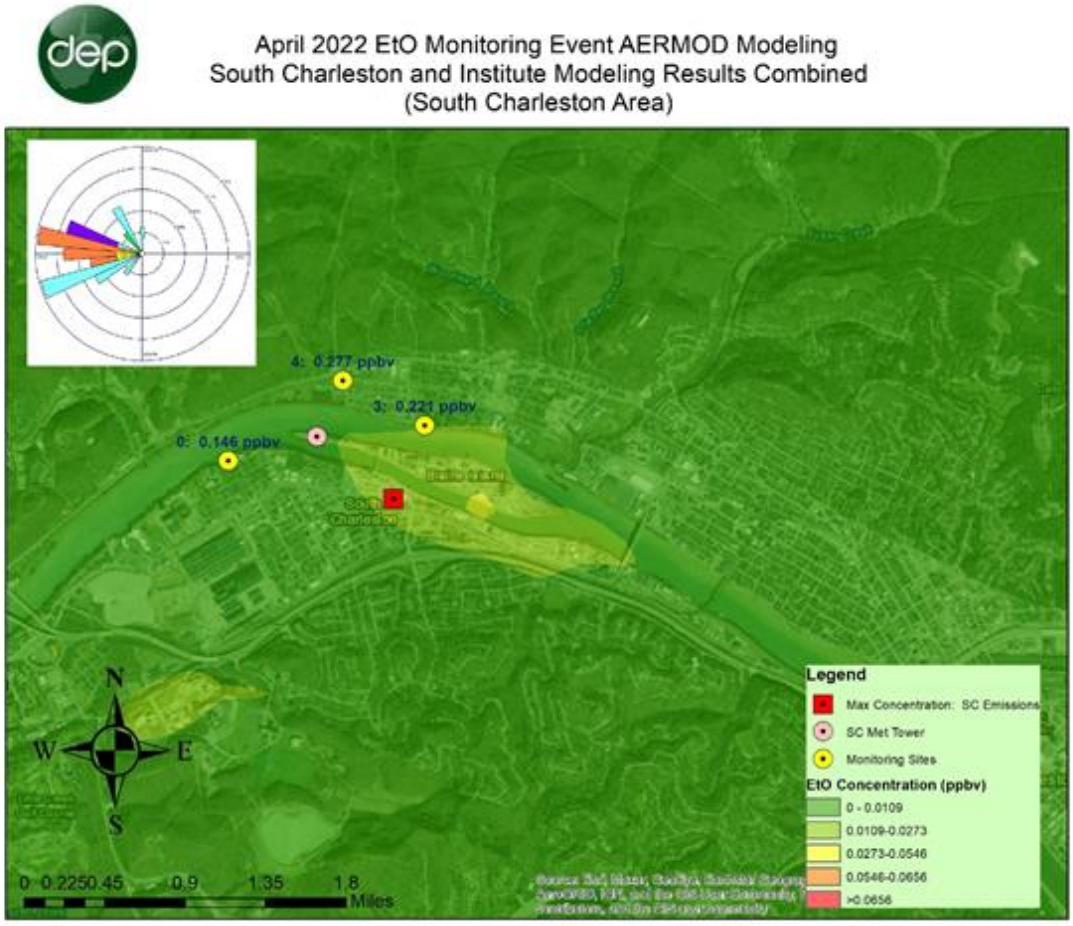


Figure 30 Plot of EtO Modeled Concentrations at South Charleston Site (April 2022 Monitoring Event)



Conclusions

Some of the samples had EtO concentrations below the 5xMDL precision threshold consistent with QA requirements in EPA's NATTS TAD to characterize data quality. Several of the background samples had higher concentrations than those taken onsite or around the facilities. Although there may be other explanations, these results could indicate that the monitoring method has precision issues at low concentration near the MDL (parts per trillion). Another possibility is that EtO is naturally occurring. Background areas with no known nearby emitters of EtO (ex: Guthrie, Buffalo, and Grayson Lake KY) showed measurable levels of EtO above 5 times MDL. Comparing the results at the different locations (see Figure 3), the Institute #15 location showed relatively higher amounts than any of the other locations. This location is approximately 775 feet from where the rail cars are unloaded.

DAQ agrees with EPA that modeling, while conservative, is an appropriate surrogate for monitoring, particularly for EtO. Long term modeling is able to calculate EtO concentrations, even at extremely low levels, but does not take into account background levels.

Recommendations

There is uncertainty surrounding monitoring method TO-15 used to detect EtO at such low concentrations near the MDL. There is additional uncertainty regarding the detection of EtO at background sites higher than near known sources of EtO. Based on this assessment, DAQ recommends the following:

- EPA continue to develop more precise monitoring methods with lower detection limits, including the evaluation of enhanced cleaning practices for the canister and air sampling assembly.
- EPA identify and quantify potentially naturally occurring EtO sources.
- DAQ recommends EPA use long-term dispersion modeling to characterize ambient concentrations of EtO from known sources in future rulemaking. This is the EPA-approved approach to determine the potential long-term risk associated with EtO.
- The following recommendations for each facility should be incorporated into enforceable limits, including monitoring, recordkeeping, and reporting similar to the Collaborative Agreement reached with UCC Institute on January 18, 2023. This will allow DAQ to ensure these actions will lead to reductions in potential and actual emissions from the known sources of EtO in the study area, thereby decreasing exposure and therefore possible risk:
    - To improve the monitoring method, it is recommended that the facilities work with DAQ and EPA to develop a fenceline monitoring project to obtain greater accuracy, and more confidence, at the parts per trillion level.
    - To reduce potential long term risk in the Kanawha Valley, it is recommended that the facilities perform enhanced LDAR with lower action levels than the “leak” definition, and without skip periods in frequency. Enhanced LDAR will reduce EtO emissions.
    - The facilities should reduce their potential to emit to ensure that risk levels do not increase.
    - Regarding UCC’s Institute facility, a LDAR plan with action levels to address emissions from the railcars as they come on-site and are unloaded should be developed and implemented.