Characterizing VOC Emissions and Plume Dynamics from an Oakland, CA Recycling Fire

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ABSTRACT

Air pollution in urban areas remains a major health hazard despite decades of regulatory progress to reduce emissions. Majority black and Hispanic communities experience disproportionately higher concentrations of ambient air pollution than white communities, sometimes because they are located closer to industrial sources of pollution. This study examines emissions from fire at a metal recycling facility in Oakland, CA that released substantial amounts of hazardous VOCs and impacted air quality in the San Francisco Bay Area. We combined VOC measurements from a Vocus proton transfer reaction time-of-flight mass spectrometer (PTR-ToF-MS) located near the fire (in Berkeley, CA) with particulate matter with diameter smaller than 2.5 micrometers ($PM_{2.5}$) measurements from PurpleAir sensors located across the affected areas. The combination of data from higher-cost, low spatial-density instruments and lower-cost, high spatial-density sensors enabled the estimation of VOC concentrations in the immediate vicinity of the fire where direct measurements could not be collected. Source attribution of VOCs measured in Berkeley to the fire in Oakland was supported by model results from HYSPLIT. We estimated the 1-hour peak average concentration of multiple hazardous VOCs in the area nearest to the fire using the dilution factor (*0.07*) calculated from the $PM_{2.5}$ measurements in both locations (benzene: *4.2 ppb*, styrene: *4.8 ppb*). While measurements did not support the conclusion that either $PM_{2.5}$ or hazardous VOC regulatory standards were exceeded following the fire, the elevated concentrations of multiple pollutants concurrently could have led to adverse health effects for nearby residents.

KEYWORDS

environmental justice, air pollution, lower-cost sensor networks, particulate matter with diameter ≤ 2.5 micrometers ($PM_{2.5}$), proton transfer reaction time-of-flight mass spectrometer (PTR-ToF-MS), hazardous air pollutants (HAPs), benzene, styrene

INTRODUCTION

Despite decades of progress in environmental regulation, air pollution exposure remains a serious health concern in many parts of the United States (Mcdonald et al. 2018, Manisalidis et al. 2020). Due in part to improved regulations, vehicle emissions have steadily decreased, contributing to a shift in the constituents of urban air pollution, specifically volatile organic compounds (VOCs) (Warneke et al. 2012, Mcdonald et al. 2018). VOCs are emitted from a wide variety of sources including plants, combustion, consumer products, and evaporation of solvents. Given the myriad of potential emitters, VOC composition in urban environments is highly variable. Many VOCs are designated as hazardous air pollutants (HAPs) by the Environmental Protection Agency (EPA), and individual exposure to some VOCs has been linked to cancer (Jia and Foran 2013, U.S. EPA OAR 2015, Manisalidis et al. 2020). Additionally, emission of VOCs can lead to the formation of secondary pollutants, including the criteria air pollutants ozone and particulate matter (PM), exposure to which is known to lead to health complications (Manisalidis et al. 2020, Gu et al. 2021). Urban ozone levels in some areas have not improved to the extent that would be estimated based on reductions in vehicle emissions, indicating the increasing importance of other sources (Coggon et al. 2021). The decrease in the importance of vehicles as a source of urban VOC emissions motivates research into the plethora of other potential sources of secondary pollutants in urban areas.

Air pollutants are emitted as the direct result of a variety of economic activities, one being heavy industry. In some metropolitan areas, large portions of the population live within a few miles of major industrial centers; this proximity leads to higher incidence of exposure to harmful air pollutants (Perlin et al. 2001). Many industrial processes can contribute to the release of VOCs into the atmosphere, and highly concentrated industrial centers are known to be major sources of PM pollution in urban environments (Karagulian et al. 2015, Wang et al. 2023). In the United States, communities of color are more likely to be exposed to higher levels of pollution due to disparities in the spatial distribution of highly polluting industrial activity from historic redlining practices (Perlin et al. 2001, Jia and Foran 2013, Pais et al. 2014, Lane et al. 2022). Prolonged exposure to air pollutants in residential areas can have significant health effects for these communities.

In addition to emissions of air pollutants from regular industrial production, accidents, (such as leaks, spills and fires) can emit large amounts of VOCs and PM in a relatively short period of time. Following an industrial fire in Houston, TX, concentrations of hazardous VOCs in the ambient air increased, with some exceeding safety thresholds (Goldman et al. 2022). Firefighters have also been exposed to hazardous VOC concentrations while responding to industrial fires; this exposure has also been linked to cancer (Alharbi et al. 2021). While the smoke from wildfires has been a topic of rising concern in air pollution research due to climate change, emissions from structure fires, industrial fires, and waste fires have not been studied as thoroughly (Brilli et al. 2014, Koss et al. 2018, Holder et al. 2023). This paper will examine a case study of a fire at an industrial recycling facility in Oakland, CA that caused high concentrations of PM and VOCs.

Sensors that can detect and quantify many VOCs simultaneously are usually expensive and require maintenance by trained personnel. In contrast, lower-cost sensor networks include many individual sensors, and are able to capture relatively high spatial resolution, however, with lower chemical resolution. Currently, widespread lower-cost networks are not capable of accurately detecting and quantifying individual VOCs, and the most common use of these networks is for measuring PM (U. S. Government Accountability Office 2024). To estimate speciated VOC emissions from the fire in areas where there were no direct measurements, we combined VOC data from a high-cost sensor located approximately 6 miles from the fire with PM data from a lower-cost network across the region.

This study will attempt to answer the following: What were the levels of exposure to harmful pollutants, including VOCs and $PM_{2.5}$, originating from the recycling fire in West Oakland? What VOCs and other air pollutants were emitted from the fire, and what were the concentrations of these species measured in downtown Berkeley, California? What was the evolution and overall dispersion of the smoke plume from West Oakland to Berkeley? What do we estimate to be the concentrations of HAPs and other pollutants that people were exposed to across the region, and were there disparities in concentration that reflect known environmental justice concerns? This project will also demonstrate how lower-cost sensor networks can be utilized in combination with higher-cost methods to quantify industrial emissions at sites where emission events can be sporadic and difficult to measure.

Acronyms and Abbreviations

VOC	Volatile Organic Compound
HAPs	Hazardous Air Pollutants
EPA	United States Environmental Protection Agency
PM	Particulate Matter
$PM_{2.5}$	Particulate Matter with a diameter ≤ 2.5 μm
BWW	Berkeley Way West
BAAQMD	Bay Area Air Quality Management District
DTSC	California Department of Toxic Substances Control
WOEIP	West Oakland Environmental Indicators Project
PTR-ToF-MS	Proton Transfer Reaction Time-of-Flight Mass Spectrometer
m/z	exact mass to charge ratio
E/N	ratio of electric field strength to ion number concentration
ppb	part per billion
$BEACO_2N$	BErkeley Atmospheric CO_2 Observation Network
$\mu g/m^3$	microgram per cubic meter
NOAA	National Oceanic and Atmospheric Administration
HYSPLIT	formerly ‘HYbrid Single-Particle Lagrangian Integrated Trajectory’ model
HRRR	High Resolution Rapid Refresh model
GIS	Geographic Information System
READY	Real-time Environmental Applications and Display sYstem

METHODS

Site and Fire Description

Around 5:30 PM on August 9, 2023, a pile of waste caught fire at the Radius Recycling (formerly Schnitzer Steel) facility located near the Port of Oakland. The City of Oakland Fire Department managed to contain the blaze to the pile that initially ignited within an hour. However, the burning and the containment process resulted in the release of substantial amounts of smoke into the surrounding air, which led the Bay Area Air Quality Management District (BAAQMD) to issue an air quality advisory for the night of the fire (Hunt 2023). The smoke from the fire was detected by instruments located on the roof of Berkeley Way West (BWW) in downtown Berkeley, CA (roughly 6 miles away from Radius Recycling) during the night of the fire and the following morning. Due to the spread of the smoke, BAAQMD extended the advisory into the following day; a spokesperson for the agency claimed that smoke from the fire had dispersed across the wider region and impacts on visibility and health may have persisted into the following day (Madyun 2023).

The Radius Recycling facility (hereafter referred to as “the facility”) is located around half a mile from the West Oakland BART station and, along with the rest of the Port of Oakland, borders the residential West Oakland, CA neighborhood. Since 2009, there have been four fires that occurred (not including the most recent fire), spurring regulatory action by state and local governments to limit pollution generated by the facility (Madyun 2023). This includes investigations and sampling activities by the California Department of Toxic Substances Control (DTSC), Alameda County District Attorney’s Office, and the California Attorney General regarding emissions of toxic pollutants from the facility, which culminated in financial settlements and multiple enforcement actions (DTSC 2023). Despite the regulatory activities at the facility, release of pollutants has continued to be a concern for residents of West Oakland.

The West Oakland neighborhood is roughly four square miles in area and is bordered on all sides by highways built during the historic period of redlining, where white communities were segregated from communities of color via home loan discrimination and other economic methods. In the early 2000s, the EPA identified West Oakland as an area with significant environmental justice concerns, and partnered with community organizations such as the West

Oakland Environmental Indicators Project (WOEIP) to reduce the impacts of toxic pollutants in the neighborhood (Fisher et al. 2006, Grow and Beveridge 2007). Environmental justice as defined by the State of California includes “deterrence, reduction, and elimination of pollution burdens for populations and communities experiencing the adverse effects of that pollution, so that the effects of the pollution are not disproportionately borne by those populations and communities” (California Legislature 2020). According to CalEnviroscreen, an environmental justice tool created by the State of California, West Oakland residents experience this disproportionate burden, ranking in the 90th percentile for pollution levels as compared to the entire state (OEHHA 2021). Much of the pollution burden in West Oakland originates from the industrial and transportation activities servicing the nearby Port of Oakland (Fisher et al. 2006, MacIver et al. 2022). Due in part to the social impacts of decades of discriminatory redlining practices, regulators have been slow to recognize and address the pollution burden in West Oakland. This study will contribute to environmental justice efforts in West Oakland by characterizing the potential hazards of a specific pollution event.

Data Collection

We measured concentrations of VOCs from the roof of a nine-story building (BWW) in downtown Berkeley, CA, using a Vocus proton transfer reaction time-of-flight mass spectrometer (PTR-ToF-MS) which drew air from an inlet located on a tower an additional ten meters above the roof surface (a total of 40 meters above ground). At this location, as is common in the San Francisco Bay region, the wind primarily comes from the west. We collected wind speed and direction data on the roof via a LI-Cor sonic anemometer which confirmed the predominant wind direction. The sonic anemometer allowed us to determine the wind direction during the period following the fire when VOC concentrations peaked at BWW. The measurement site is surrounded by mixed high and low density residential along with low density commercial areas. Starting at approximately 9 PM on August 9, and continuing until around 9 AM the following morning, higher than average concentrations of certain VOCs were detected by the Vocus. We also observed a similar pattern in $PM_{2.5}$ concentrations over the same time period, which corroborates the theory of the pollutants originating from the recycling fire.

To measure VOC concentrations in ambient air at BWW, we used a highly sensitive mass-spectrometer capable of detecting hundreds of VOCs simultaneously below the parts-per-trillion level. The Vocus is described in detail elsewhere (Krechmer et al. 2018), and summarized briefly here. First, a proton-transfer reaction with H_3O^+ ionizes the VOCs collected from ambient air. Only VOCs with a proton affinity greater than water can be ionized, so alkanes are not detected by the PTR-ToF-MS, but most functionalized VOCs (e.g., ketones, aldehydes, alcohols, siloxanes, thiols, etc.) and unsaturated hydrocarbons are able to be measured. Ionized VOCs are pulsed into a time-of-flight mass spectrometer and detected by a multi channel plate detector. The exact mass to charge ratio (m/z) of a VOC is determined by the ion's time of flight through the mass spectrometer. The time-of-flight mass analyzer allows for the detection of hundreds of VOCs simultaneously; in this case, we monitored the m/z of 480 molecular formulae. The Vocus relies on a focusing ion-molecule reactor to concentrate the ion signal, allowing for higher sensitivity than previous PTR-ToF-MS instruments (Krechmer et al. 2018). The ratio of electric field strength to ion number concentration (E/N) is useful for determining the level of fragmentation and ion clustering expected in the ion molecular reactor. We operated the Vocus with E/N = 121 townsend to minimize fragmentation (Td, 1 Td = 10^{-21} Vm^2). The high sensitivity of the Vocus allows us to detect pollutants that may have been diluted in concentration significantly over the course of transport from West Oakland to downtown Berkeley.

We calibrated VOC concentrations using two standard gas mixtures (a total of 26 individual compounds) and a platinum catalyst to generate "zero air" (air without organic gasses). We automated the calibrations and instrument background measurements to be performed twice daily, and calibration parameters were interpolated across the dataset. VOCs not included in the calibration gas mixture were calibrated according to the linear relationship between the calibrant VOC sensitivity and proton transfer reaction rate constant. We used a default reaction rate ($2.25*10^{-9}$ cm^3/molecule/s) to calculate concentrations for non-calibrant VOCs. The uncertainty is 20% for VOCs directly calibrated for, and 50% for VOCs calculated using the default rate constant.

We collected $PM_{2.5}$ measurements from two secondary sources, lower-cost PurpleAir sensors and the BErkeley Atmospheric CO_2 Observation Network ($BEACO_2N$). PurpleAir manufactures sensors for use by the general public, and the combined network exhibits high spatial resolution over many urban areas, especially where the cost of the sensors does not prevent their widespread deployment. PurpleAir measures $PM_{2.5}$ concentrations using a laser device which detects interferences in the passage of light. An algorithm then determines the number of particles of a certain size that interrupted the laser, and this data is added to an online database (Wallace et al. 2021). PurpleAir sensors are not reliably maintained except potentially by customers, and therefore the $PM_{2.5}$ data collected from these sensors can be unreliable. In contrast, $BEACO_2N$ sensors are maintained by researchers at the University of California. $BEACO_2N$ sensors are primarily a CO_2 monitoring strategy, but they also contain a nephelometric particulate matter sensor, similar to the ones used by PurpleAir (Shusterman et al. 2016). A $BEACO_2N$ sensor was collocated with the Vocus on the roof of the site in downtown Berkeley, along with a nearby sensor at ground level. The PM sensors used in PurpleAir and $BEACO_2N$ require proprietary calibration equations to interpret. There are multiple different calibration methods as well as a correction equation published by the EPA (Jaffe et al. 2023, U. S. Government Accountability Office 2024). For the purpose of this study, we are most concerned with the relative magnitude of $PM_{2.5}$ concentrations across space and time, so we relied on the default calibrations of each sensor with no corrections.

Given that the main purpose of this study is to estimate VOC concentrations, we are less concerned about the accuracy of the $PM_{2.5}$ measurements than their comparability between locations for the purposes of calculating plume dilution. However, we still confirm the quality of data collected from PurpleAir through multiple methods. First, we only collect data from outdoor-specific sensor models that were confirmed to be located outdoors, to prevent any indoor concentrations from biasing our data low. Second, each PurpleAir sensor operates two simultaneous detector channels. We removed sensors from the analysis if at least one of the two channels was malfunctioning, or if the channels showed significant disagreement with each other throughout the fire period (greater than 2x difference for concentrations above 10 $\mu g/m^3$). Third, we compared the time-series of collocated PurpleAir and $BEACO_2N$ devices to confirm the accuracy of the PurpleAir sensors which have a higher spatial density. Through comparison with $BEACO_2N$ sensors that are maintained and calibrated more regularly, we were able to confirm the reliability of PurpleAir measurements for use later in the analysis (Appendix A).

Analysis

Analysis of BWW data

To determine the compounds measured that were associated with the smoke emitted from the fire, we computed the correlation between $PM_{2.5}$ concentrations and the VOC concentrations measured using the Vocus. First, we compared the higher time resolution PurpleAir data to the lower resolution $BEACO_2N$ data to ensure that the PurpleAir data was reliable. The PurpleAir sensor closest to the Berkeley site records concentrations three times every ten minutes. Data analysis was performed in Spyder, a scientific Python environment (Rossum and Drake 2010). We aggregated the Vocus data into average concentrations for all VOCs for every minute. For every point of $PM_{2.5}$ concentration, we selected the same minute of Vocus concentrations. We then constructed a correlation matrix and calculated the R^2 value (using the NumPy programming library) for each Vocus compound and the $PM_{2.5}$ measurements (Harris et al. 2020). We conducted the same procedure with the $BEACO_2N$ $PM_{2.5}$ data as well, which was averaged for every minute of measurement. Following this, we identified the top correlated VOCs with each $PM_{2.5}$ sensor, and then identified additional VOCs that were highly correlated with these 'top' compounds. We combined these highly correlated ($R^2 > 0.75$) species into a list of compounds that we suspected originated from the recycling facility fire. We then cleaned the list of any compounds where the formula was unknown and identified potential water clusters (compounds formed through reactions with water vapor inside the Vocus). Following data cleaning, we identified 111 different compounds associated with the smoke from the fire.

After establishing the list of potential compounds originating from the fire, we identified compounds designated as HAPs by the EPA. Certain compounds, such as styrene, were clearly sourced from the fire. Other compounds, such as benzene, were partially attributable to the fire, but also to regular diurnal emission patterns in downtown Berkeley from traffic. We then calculated the average enhancement in certain compounds that could be attributed to the fire by subtracting the average concentrations for the compounds of interest from the two days preceding August 9th, and dividing this number by the concentrations from the preceding two days. Additionally, we calculated enhancements similarly for $PM_{2.5}$ concentrations at the locations of multiple PurpleAir sensors.

Analysis of plume dynamics

We then attempted to determine the dynamics of the smoke plume that originated from the fire at the facility. We relied on a chemical transport model from the National Oceanic and Atmospheric Administration (NOAA) known as HYSPLIT. This model draws on local meteorological conditions to predict the dynamics of a pollution plume from a point source; it has been used to model the dispersion of smoke from industrial fires in urban areas in the past (Stein et al. 2015). HYSPLIT uses a hybrid lagrangian and eulerian method of predicting atmospheric transport based on meteorological data and source location inputs (Stein et al. 2015, Rolph et al. 2017). The HYSPLIT model is capable of generating both predicted trajectories and dispersion of pollutants from a point source, as well as source attribution of air parcels. To characterize the dynamics of pollutant transport and dispersion, we modeled the concentration gradients of a potential pollutant emitted over space and time from the facility at the time of the fire. We also modeled the overall trajectory of the plume to determine which communities may have been exposed to smoke from the fire.

The HYSPLIT model also allows for the calculation of backwards trajectories, which essentially runs the same model as the forward trajectory from a pollution point source, but backwards in time from a location where measurements were taken. Back-trajectory model results can therefore be a very effective tool for pollution source attribution. However, the model results are not reliable at the neighborhood level, but are more effective at lower spatial resolutions. To improve this, we ran the back-trajectory model using meteorological inputs from the High Resolution Rapid Refresh (HRRR) model, which has a spatial resolution of 3 km (roughly ⅓ of the distance between BWW and the facility), supplied by NOAA. We ran HYSPLIT through the online browser tool offered by NOAA, the Real-time Environmental Applications and Display sYstem (READY). READY automatically imports the meteorological input data and can generate geographic information system (GIS) outputs of the model results (Rolph et al. 2017). We generated back-trajectory results using the HRRR meteorological inputs, the starting point at BWW where the VOCs were detected, and settings that modeled the origin of the air parcel at each hour. HYSPLIT then generated GIS outputs showing the trajectory and origin of each air parcel that was detected at each hour during the period following the fire. We specifically focussed on the trajectories between 4 and 7 AM on August 10th, as this is the period during which some of the highest peaks in VOC concentrations were detected at BWW.

Analysis of pollutant concentrations

We then estimated the ambient concentrations and average enhancement of the HAPs originating from the fire in West Oakland. We attempted multiple methods in order to ensure our results were as realistic and accurate as possible. First, given the placement of PurpleAir and BEACO$_2$N sensors, we estimated the dilution of the smoke from the fire by approximating the dilution of PM$_{2.5}$ between West Oakland and downtown Berkeley. We again relied on the results of the HYSPLIT model to determine the relationship between the air we measured at BWW and the air in close proximity to the facility. Our main goal was to determine the numerical relationship between ambient air concentrations of hazardous pollutants at the two sites. After estimating the possible concentrations of hazardous VOCs the West Oakland community was exposed to, we investigated whether the exposure reflected any known disparities in pollution, and whether it was part of a broader pattern of environmental justice issues in the area.

We identified multiple transport events between West Oakland and Berkeley via HYSPLIT, PurpleAir, and wind direction from the sonic anemometer. We chose to focus on one specific transport event nicknamed ‘Plume B’. For Plume B, we calculated the average PM$_{2.5}$ concentration from a West Oakland PurpleAir sensor closest to the fire between 4 and 5 AM and calculated a similar average from BWW between 5 and 6 AM, following the transport of the plume. HYSPLIT results confirmed that the transport of the air parcel took roughly an hour between the two locations. We applied the ratio between average concentrations of PM$_{2.5}$ near the fire and BWW to the average concentrations of VOCs of interest measured between 5 and 6 AM using the Vocus. By multiplying the concentrations of VOCs by the inverse dilution ratio of the PM$_{2.5}$ in Plume B, we were able to estimate the average concentrations of VOCs in West Oakland and compare these to the exposure limits for individual HAPs.

We determined that Plume B had the highest dilution ratio according to data collected from the PurpleAir network. To assess the overall impact of all transport, rather than focussing on the other transport events (Plumes A and C), we chose to calculate the 12-hour averages of PM$_{2.5}$ at sites in West Oakland and Berkeley. We calculated the dilution ratio following the method described above, except both locations were averaged over the same time period (9 PM to 9 AM). We then multiplied the inverse of the dilution ratio by the average concentrations of HAPs detected with the Vocus to estimate the 12-hour average concentrations of these compounds in West Oakland. We also calculated the 24-hour average concentration of $PM_{2.5}$ from the sensor closest to the fire in order to determine if any exposure limits or regulatory standards for $PM_{2.5}$ were exceeded following the fire. Additionally, we calculated the inverse dilution ratio between PurpleAir sensors collected from multiple locations in the Oakland area and used these ratios to estimate 12-hour concentrations of certain HAPs across space. The HAPs selected were the four compounds with the highest average concentrations detected by the Vocus over the fire period. We then mapped these concentrations across the Oakland area as a medium for visually assessing potential spatial disparities associated with race.

RESULTS

Downtown Berkeley

We collected measurements of concentrations of $PM_{2.5}$ and VOCs in the ambient air in the vicinity of BWW during the period following the fire. The $PM_{2.5}$ measurements from the BEACO$_2$N and PurpleAir sensors were generally in agreement regarding the concentrations over time (Appendix A). Therefore, we used $PM_{2.5}$ concentrations from both sensors as a proxy to determine association with the fire. The time-series of VOC concentrations for certain compounds were strongly correlated ($R^2 > 0.75$) with the time-series of $PM_{2.5}$ data; we consider these compounds to be strongly associated with the fire (Appendix B). A breakdown of the identities of major VOC compounds that were detected following the fire is presented in Figure 1. Slightly over ⅛ of the total mixing ratio of VOCs sensed by the Vocus during the period in which the smoke plume settled in Berkeley were associated with the fire. Ethanol emissions made up an even greater share of the total mixing ratio, but the time-series of ethanol concentrations was not correlated with the concentrations of $PM_{2.5}$, thus we determined that the measured ethanol did not originate from the fire.

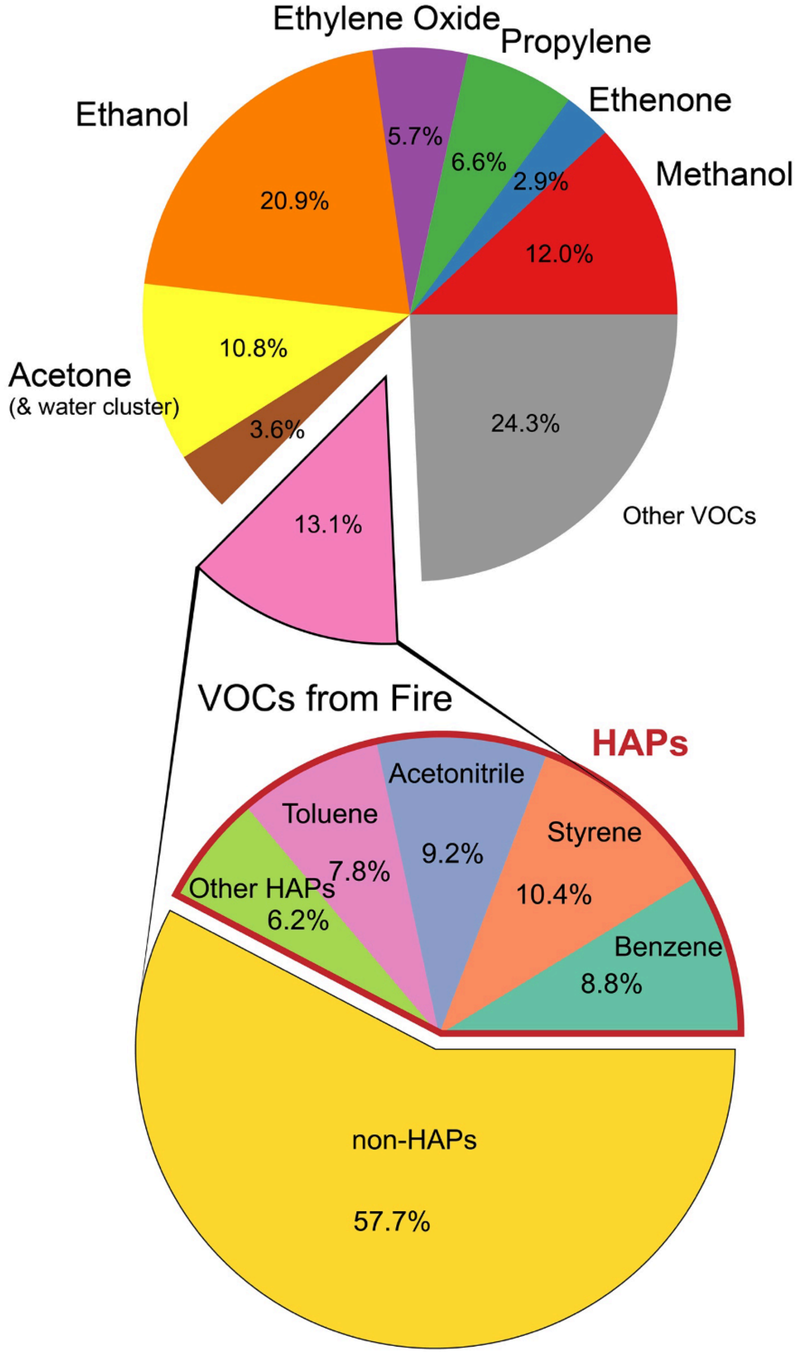

Figure 1. Median concentration (ppb) of each VOC out of total median VOC signal during fire event. Pie charts illustrating the portions of total median VOC signal detected by the Vocus from 9 PM August 9th to 9AM August 10th, 2023. The ~13% of VOC concentration that originated from the fire is expanded in the bottom chart to show the large portion of HAPs (outlined in red) detected in the total signal attributable to the fire.

Within the 13% of the concentration that we associated with the fire, we identified slightly under half of this concentration to be due to HAPs (Figure 1). Toluene, acetonitrile, styrene, and benzene were the HAPs observed at the highest concentrations. Styrene and acrylonitrile were measured at extremely low concentrations (< 0.1 ppb) prior to the start of fire, indicating that the concentrations measured at BWW likely almost entirely originated from the recycling fire. In contrast, other compounds, such as benzene and toluene, likely came from a mix of conventional sources, such as traffic, in addition to being carried to BWW in the smoke plume. We compared the median and peak concentrations of all HAPs detected in BWW to the most applicable exposure limits available from the EPA and found that all of the compounds were at least one order of magnitude from exceeding exposure limits (U.S. EPA OAR 2015). This analysis was performed in Spyder using HAPs exceedance levels compiled by the EPA which were converted to ppb level to ensure comparability with concentrations measured using the Vocus (Rossum and Drake 2010, Harris et al. 2020).

In order to compare the concentrations of VOCs measured in the period following the fire with the typical background concentrations measured at BWW, we calculated average enhancement for all compounds detected during the period of the fire (Table 1). Most of the HAPs that we found to be associated with the fire reflected increased enhancement during the fire period when compared to the previous days' concentrations. In particular, styrene concentrations reached nearly 23 times the typical concentrations detected at BWW, while acrylonitrile concentrations were more than 47 times the levels seen in the previous two days (Table 1). We observed especially large enhancement ratios for nitrogen-containing compounds and styrene. We also observed certain compounds, such as toluene and acetonitrile, at lower concentrations following the fire than the previous days. We confirmed that these compounds showed a clear diurnal pattern relating to traffic and solvent emissions that may have obscured the enhancement which came from the fire. Despite the influence of the diurnal cycles, these compounds were highly correlated with the $PM_{2.5}$ concentrations from the fire, and so we still included these compounds in our analysis.

Table 1. Average enhancement ratios for HAPs. Average enhancement at BWW was calculated by dividing the average concentrations following the fire by the average concentrations during the two days prior to the fire, during the same time period that the fire impacted air quality. *Note that benzene was detected using the charge transfer product and not the proton transfer product. Therefore, the benzene formula is not the protonated formula, but the molecular formula.

Name	**Protonated Formula**	**Average Enhancement**
Acrylonitrile	$C_3H_4N^+$	48
Pyrrole	$C_4H_6N^+$	8.6
Acrylamide	$C_3H_6NO^+$	12
Benzene	*$C_6H_6^+$	3.4
Phenol	$C_6H_7O^+$	3.3
Styrene	$C_8H_9^+$	23
Styrene Oxide	$C_8H_9O^+$	2.5
Naphthalene	$C_{10}H_9^+$	4.0
Quinoline	$C_9H_8N^+$	5.8
Dibenzofuran	$C_{12}H_9O^+$	2.1
Acetonitrile	$C_2H_4N^+$	0.62
Toluene	$C_7H_9^+$	0.69

Plume Dynamics

The Vocus at BWW is collocated with a sonic anemometer that is capable of measuring wind speed and direction. During the period in which we detected VOCs associated with the fire, the predominant wind direction was from the southwest direction (Figure 2). The facility where the fire occurred is roughly southwest of BWW. It is possible that the smoke plume traveled from the southwest before reaching downtown Berkeley, potentially impacting communities along the path. We attempted to confirm the path the plume traveled from its origin at the facility in West Oakland to the Vocus location in Berkeley via multiple methods. The first was via the measurements recorded by the sonic anemometer on the roof of BWW, which showed that wind was coming from the direction of the facility during the periods when elevated VOC concentrations were detected by the Vocus (Figure 2). The data from the sonic anemometer were supported by $PM_{2.5}$ concentrations and model run results as well (Figures 3, 4, 5).

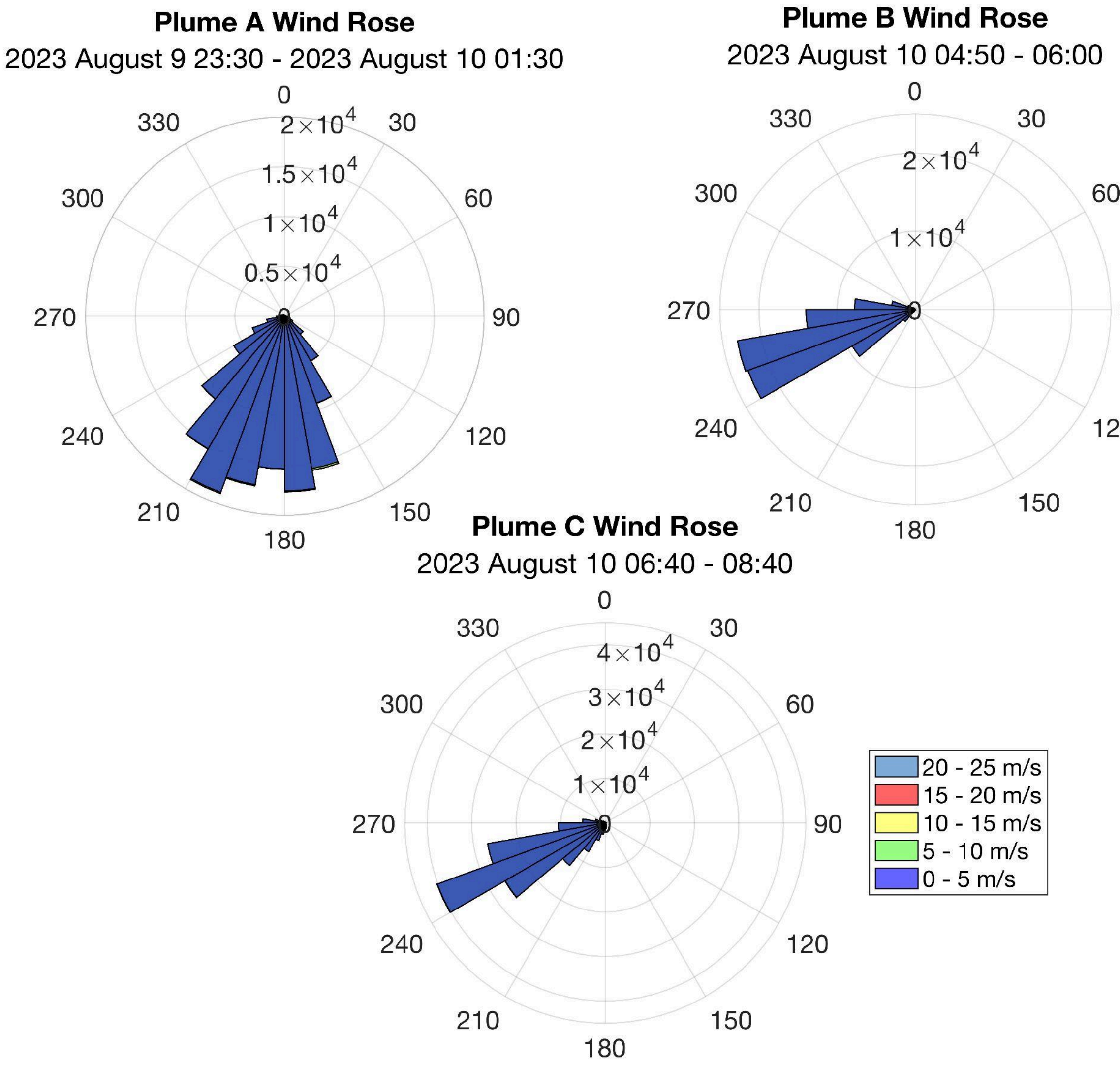

Figure 2. Wind roses for each plume at BWW. Wind speed and direction data was collected by the sonic anemometer. Plumes were identified as distinct transport events via the PurpleAir data and are shown in Figure 3.

We used $PM_{2.5}$ data collected from PurpleAir sensors near the facility to determine when exactly emissions of $PM_{2.5}$ began to become significant when compared to the typical diurnal cycle of $PM_{2.5}$ emissions from traffic and industry. We found that the $PM_{2.5}$ concentrations spiked in West Oakland around 11:30 PM PST on August 9th, nearly six hours following the start of the fire (Figure 3). We believe the smoke could have possibly moved in another direction prior to the spikes of $PM_{2.5}$, and therefore these emissions from the start of the fire until 11:30 PM may not have been detected near BWW.

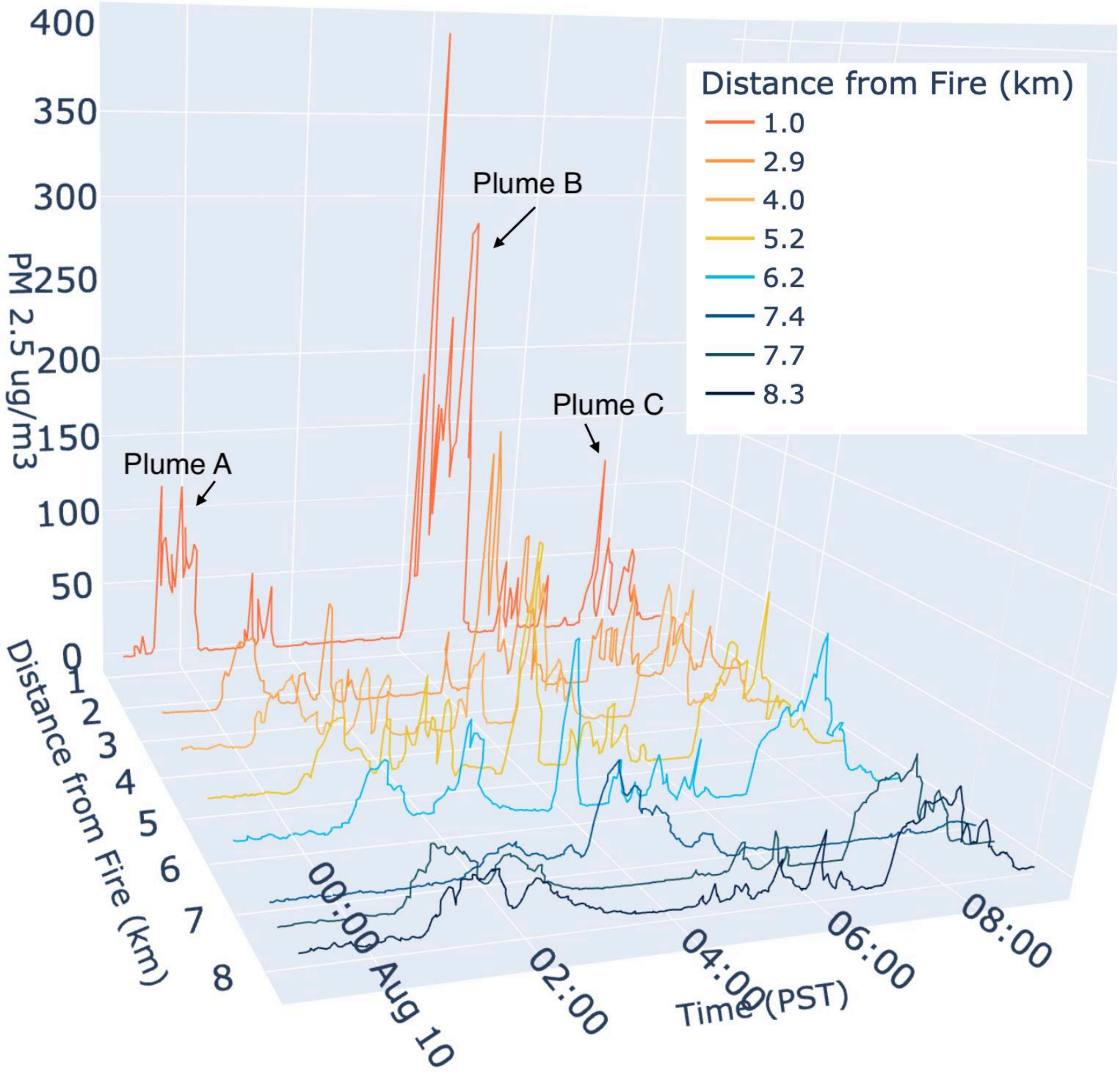

Figure 3. 3D line-plot of $PM_{2.5}$ concentrations over time and space. Each line corresponds to a single PurpleAir sensor located between the facility and BWW, and are ordered on the figure by their distance from the fire. Sensors are shown on a map in Figure 4.

The $PM_{2.5}$ concentrations and distance from the fire of each sensor demonstrated an inverse relationship, indicating dilution as the transport occurred. Figure 4 highlights the locations of the PurpleAir sensors that roughly follow the path of transport for plume B. The path of transport was confirmed by the results from the HYSPLIT model. We ran forward trajectory and dispersion models to attempt to characterize the movement of the plume away from the facility fire. These preliminary HYSPLIT results did not agree very well with the $PM_{2.5}$ concentration time series acquired from Purple Air sensors. The forward trajectory results indicated the smoke plume only traveled east. However, the backwards trajectory results from HYSPLIT were in agreement with both $PM_{2.5}$ concentrations and the wind speed and direction measured at BWW, indicating the smoke plume traveled north, as well. HYSPLIT predicted transport roughly coinciding with the three major plumes (A, B and C) which were confirmed to have occurred in the early morning of August 9th (Figure 5). Both HYSPLIT results and $PM_{2.5}$ concentrations estimated transport to have taken roughly an hour each time.

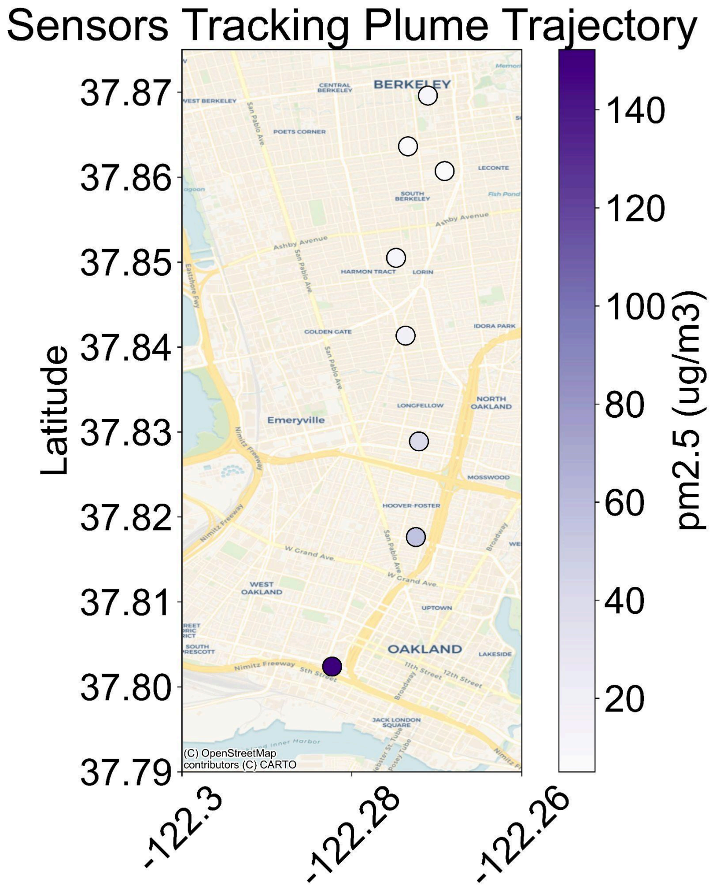

Figure 4. PurpleAir sensors tracking plume B. Geographic locations of the purple air sensors used to track plume trajectory that are identified in Figure 3.

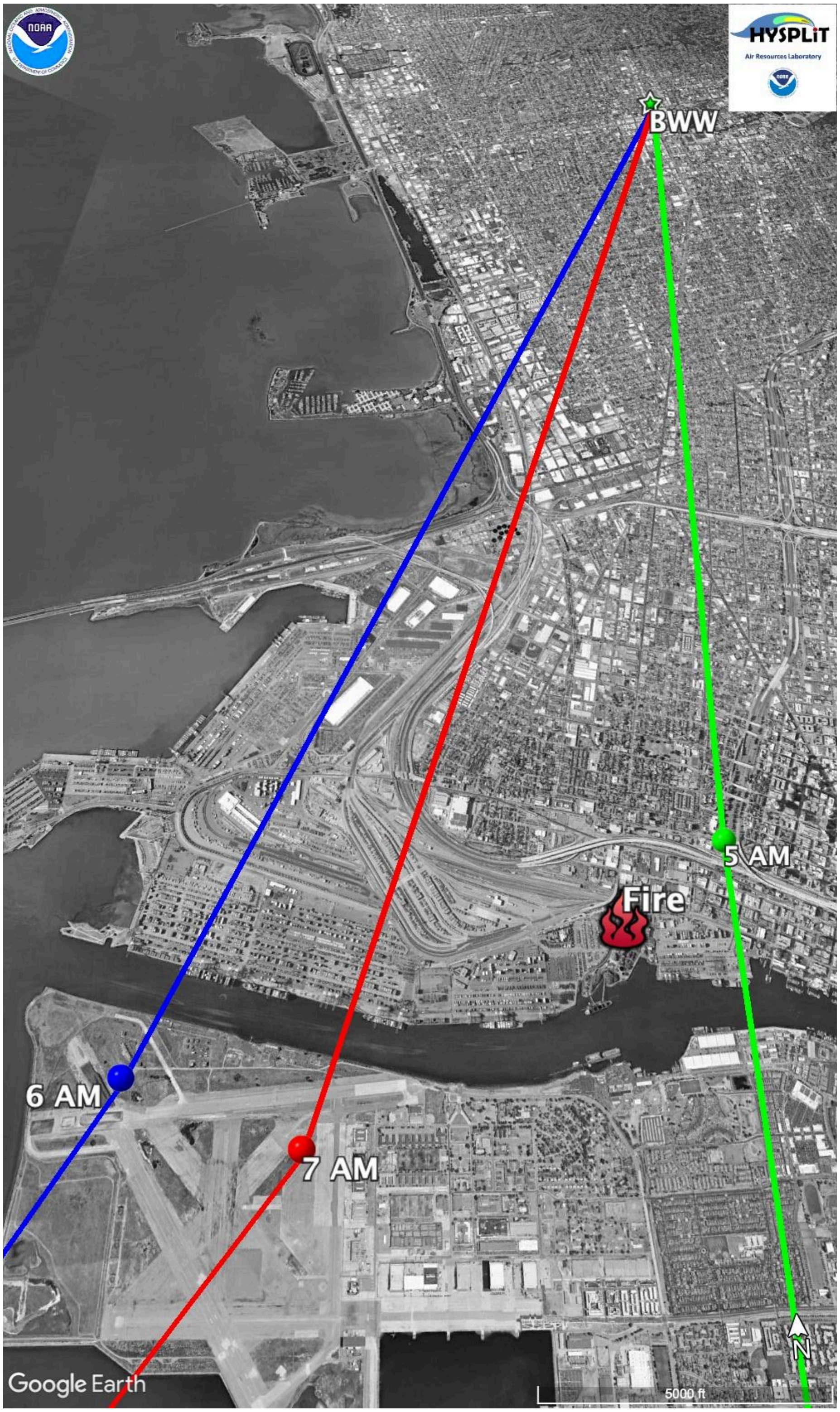

Figure 5. Map of HYSPLIT back-trajectory output for 5-8 AM PST. HYSPLIT back-trajectory was run using the source at BWW and HRRR 3-km meteorological data.

West Oakland

To determine the concentrations of VOCs that originated from the fire, especially HAPs, in areas such as West Oakland that were near the facility, we again relied on $PM_{2.5}$ concentration data collected by PurpleAir sensors, as well as results from the HYSPLIT model. When applying the dilution factor we determined by dividing the $PM_{2.5}$ concentrations at BWW by those at the facility, we estimate that the 12-hour average concentration of styrene near the facility following the fire was 0.43 ppb (Table 2). $PM_{2.5}$ concentrations following the fire period were elevated to over 25 times the baseline measurements taken from previous dates, indicating serious enhancement of PM concentrations in an area where PM is already a major health concern.

Table 2. Estimated 12-hour average concentrations for select VOCs in West Oakland and Emeryville. HAPs concentrations in West Oakland were calculated by applying the inverse dilution factor to VOC concentrations from BWW. Enhancement ratio was calculated by dividing the concentrations from the period following the fire from the average of the same period from the previous two days. *Berkeley concentrations are not estimated, but instead measured.

Location	Estimated Styrene (ppb)	Estimated Benzene (ppb)	Estimated Acetonitrile (ppb)	Estimated Toluene (ppb)	Mean PM 2.5 (ug/m3)	PM 2.5 Enhancement Ratio
W. Oakland	0.43	0.39	0.20	0.23	23	26
Berkeley*	0.22	0.20	0.10	0.12	12	7.3
Emeryville	0.27	0.25	0.13	0.15	15	13

In order to examine the spatial distribution of the smoke from the fire, we plotted the estimated 12-hour average concentrations of the four major HAPs detected (Figure 1) on a map of the Oakland-Berkeley area (Figure 6). These maps allow us to examine the disparities in concentration that may reflect underlying environmental justice issues. As expected, the concentrations closest to the source of the smoke were the highest in the Oakland area, but the concentrations across the water in Alameda were the lowest on the map, indicating the transport of smoke was primarily towards the north-east (Figure 6). In addition to the total 12-hour average concentration during the fire period, we also calculated the dilution factor for plume B, which was used to estimate 1-hour averages of VOC concentrations near the fire.

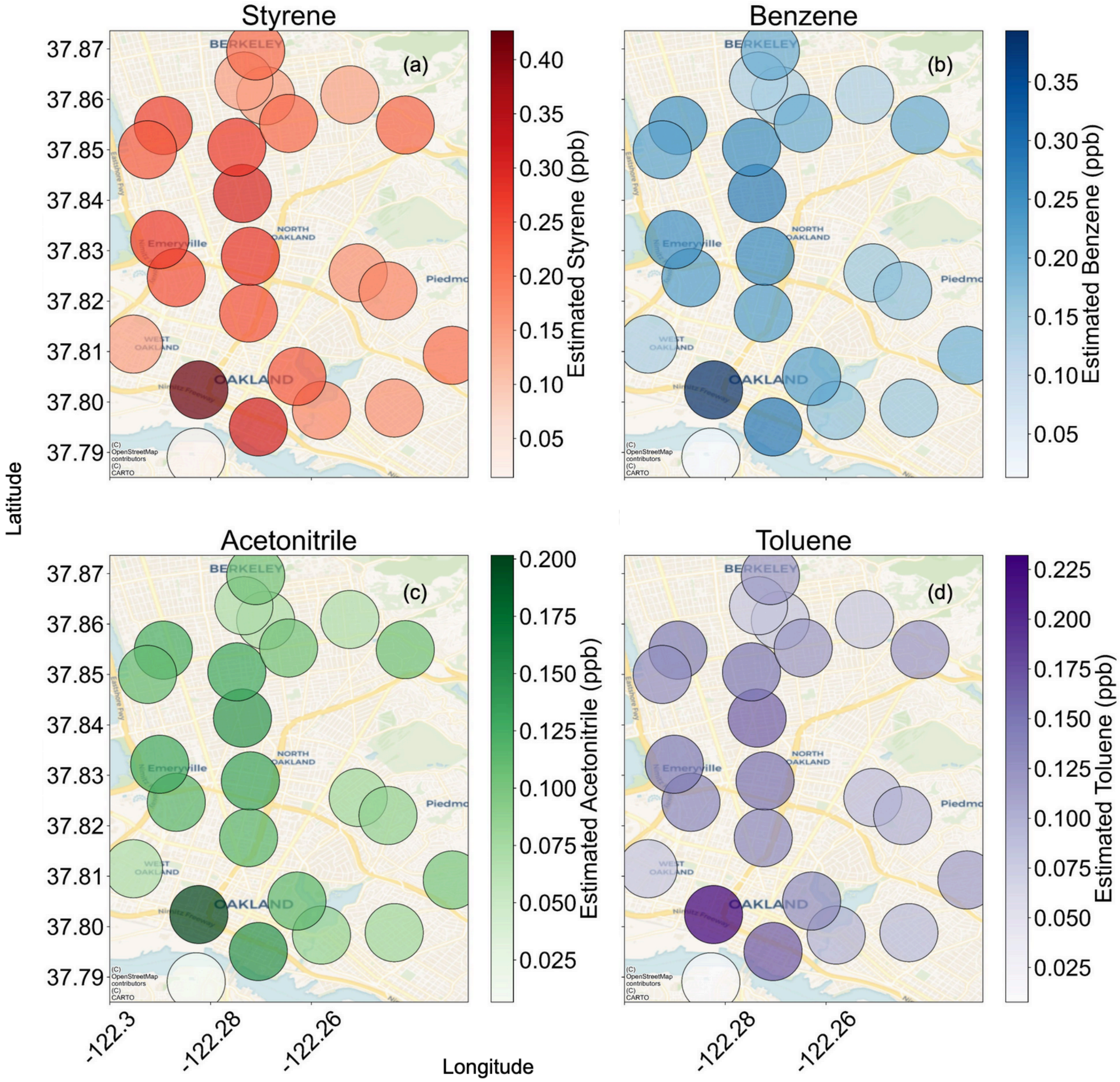

Figure 6. Maps of estimated concentration of major HAPs. These four HAPs were chosen because they were the HAPS with the highest concentrations detected at BWW (Figure 1).

DISCUSSION

In this project, we determined the impact of an industrial fire event on VOC concentrations in the area in proximity to the facility. Many studies have attempted to analyze VOC emissions from biomass burning, but few have quantified VOC emissions from industrial combustion like the Radius Recycling fire (Brilli et al. 2014, Koss et al. 2018, Holder et al.

2023). Measurements of VOC concentrations were conducted in Berkeley via costly methodologies that require regular maintenance by highly educated personnel. In contrast, our $PM_{2.5}$ measurements came from a lower-cost air pollution sensor network that often requires little-to-no maintenance, but cannot quantify individual VOCs (U. S. Government Accountability Office 2024). These two different data categories were combined in this analysis to estimate concentrations of VOCs in a location where there was no ability to directly measure these compounds. We found that the estimated average concentrations of certain VOCs in West Oakland were an order of magnitude above those comparable in Berkeley.

Downtown Berkeley Ambient Air

In downtown Berkeley at the VOC measurement site, the smoke plume from the facility impacted the ambient air quality significantly through the transport of pollutants from West Oakland. Measurements of VOC and $PM_{2.5}$ concentrations were elevated during the night following the fire, which coincided with wind conditions indicating air transport from the direction of the facility. Ambient $PM_{2.5}$ concentrations in urban areas generally peak following rush hour traffic, and generally decrease after midnight as traffic density decreases significantly (Zhao et al. 2009). The diurnal pattern of $PM_{2.5}$ concentration measured in Berkeley deviated significantly from the pattern generally noted in literature and observed in the $PM_{2.5}$ dataset the previous week, with multiple peaks detected beginning around midnight. The pattern indicates that the enhancement in $PM_{2.5}$ did not originate from ambient traffic pollution, but was the result of a specific point source, the facility fire. Comparison of concentrations of VOC and $PM_{2.5}$ measurements indicated that many VOCs followed a similar pattern to $PM_{2.5}$. A correlation analysis helped us identify which VOCs had the highest correlation with $PM_{2.5}$, and therefore, originated from the same source (Rossum and Drake 2010, Harris et al. 2020). We found one specific compound, styrene, to have an average enhancement of nearly 23 times pre-fire levels during the period following the fire (Table 2). Styrene can enter the air through the burning of plastics, rubbers and other poly-styrene-containing materials (Westblad et al. 2002, Arora and Manila 2021). Given that typical ambient concentrations of styrene were insignificant compared to the concentrations measured following the fire, we conclude that the most likely source of elevated concentrations of styrene (and other VOCs highly correlated with $PM_{2.5}$) is the fire at the facility.

After identifying a list of VOCs detected in Berkeley that potentially originated from the fire, we found that none of the HAPs on the list exceeded concentration limits for human health and safety (U.S. EPA OAR 2015). All the highest average concentrations over a one-hour period in Berkeley were at least an order of magnitude below the exposure limits, indicating that the health risk from elevated VOC concentrations in Berkeley was relatively minor compared to the risk closer to the facility. Even though concentrations of hazardous VOCs in Berkeley were not considered dangerous alone, they were indicative of dilution from the source, potentially indicating dangerous exposure levels elsewhere. Our source attribution of VOCs to the facility fire due to the correlation with $PM_{2.5}$ is accurate and reliable enough to estimate VOC concentrations closer to West Oakland, where exposure may have been more severe.

Characterizing Plume Dynamics

We attempted to address the lack of measurements of hazardous VOCs in West Oakland during the fire period using measurements made in Berkeley, which required us to characterize the transport of the smoke plume between the two locations. As stated in the previous section, wind direction measured in Berkeley during the times of peak VOC enhancement aligned with the direction of the facility fire. These results were confirmed via HYSPLIT modeling of air parcel trajectory and dispersion, as well as direct measurements from the PurpleAir and $BEACO_2N$ sensor networks across the region between BWW and the facility. During the initial period of the fire from ignition (5:30 PM) to control (9:00 PM), concentration of $PM_{2.5}$ in West Oakland stayed close to typical baseline levels. The HYSPLIT model outputs corroborate this, showing transport away from the West Oakland-Berkeley direction during this period. Following control of the fire in which the blaze was restricted to the internal section of a pile of steel scrap, concentrations of $PM_{2.5}$ began to rise in West Oakland, peaking at 150 $\mu g/m^3$ when averaged over one-hour. There is no 1-hour exposure limit or regulatory standard for $PM_{2.5}$, but the 24-hour average federal standard is 35 $\mu g/m^3$ (U.S. EPA OAR 2024). There are multiple potential explanations for the trend of pollutants increasing in concentration following control of the fire. One is that the smoldering of the waste following control was limiting complete combustion of the fuel and thus leading to higher emissions of $PM_{2.5}$ and VOCs compared to the earlier flaming combustion. Lower temperatures and decreased access to oxygen during smoldering have been shown to lead to higher emissions factors of organic particulates as compared to emissions burning from an open flame (Jen et al. 2019, Liang et al. 2022a). Another possible explanation is that the nighttime planetary boundary layer height was significantly lower than the daytime height, which could cause increased concentrations due to accumulation of emissions within a smaller volume (Soleimanpour et al. 2023). Wind speed within the boundary layer also decreases on average at night, which could explain how higher concentrations were able to accumulate without being dispersed quickly, as they were during the afternoon.

Our estimation of dilution was somewhat simplified and thus may have potentially biased our estimates of HAPs in West Oakland. As organic particles suspended in air increase in concentration, higher proportions of the material transition from the gas phase (in the form of or similar to VOCs) to the solid phase (in the form of PM). As dilution of the organic particles decreases overall concentrations, lower saturation of the gaseous organics forces more solids back into the gas phase (Liang et al. 2022b). Closest to the source where concentrations are high, more of the emissions are in the form of PM. As the smoke ages and dilutes, more of the emissions transition to the gaseous form (Liang et al. 2022b). This means that our dilution ratio of $PM_{2.5}$ between West Oakland and Berkeley may have been impacted by these transitions, and thus we may have estimated a higher ratio of VOC/$PM_{2.5}$ in Berkeley than the likely ratio in West Oakland. This might lead to our estimates of some VOCs in West Oakland to be biased high. However, this bias is most applicable to the least volatile compounds detected by the Vocus, as thus may not have biased our measurements of highly volatile compounds such as HAPs.

Results of HYSPLIT backward-trajectories from the location of VOC measurements at BWW estimated transport of air parcels between West Oakland and Berkeley between 4:00 and 8:00 AM on August 10th (Figure 5). However, the HYSPLIT model is predominately used for tracking large-scale pollutant transport rather than transport within a specific urban area, and thus might be too coarse in spatial resolution to offer useful results alone (Su et al. 2015, Stein et al. 2015, Rolph et al. 2017). We confirmed HYSPLIT results through examination of $PM_{2.5}$ concentrations measured by PurpleAir sensors across time and space. Through comparison of HYSPLIT and PurpleAir results, we were able to identify three distinct smoke transport events from the facility to Berkeley between 11:00 PM on August 9th and 9:00 AM on August 10th

(Figure 3). In each transport event, $PM_{2.5}$ concentrations were diluted to a unique extent, with the most significant dilution occurring in the transport roughly between 4:00 and 6:00 AM on August 10th (plume B). Characterizing plume dynamics, transport, and dilution allows us to estimate the concentration of VOCs in West Oakland in the absence of direct VOC measurements in this location.

West Oakland Ambient Air

The proximity of the facility to West Oakland exposes a community that is already subjected to a high pollution burden to significant concentrations of hazardous VOCs in the smoke from the fire. We applied the calculated dilution factor for $PM_{2.5}$ transport to the HAPs detected at BWW to estimate the mean concentrations of VOCs in West Oakland during the period prior to plume transport. The plume present in West Oakland from 4:00 to 5:00 AM had the highest dilution factor for $PM_{2.5}$. Therefore, we calculated the HAPs concentrations for this period to test if any exposure levels were exceeded. While we did not estimate any exceedances in HAP concentration during this period, we did find that the peak 1-hour average concentration of benzene (a HAP) was estimated to be 4.2 ppb. The lowest 1-hour average exposure limit For benzene is 8.4 ppb (U.S. EPA OAR 2015). Our estimates show that the 1-hour exposure limit was not exceeded during this period. The dilution of plumes A and C was not as significant as the dilution of plume B, so we chose to focus on the average over the entire 12-hour period following the fire.

Even if exposure limits for individual VOCs were not exceeded during a single timeframe, it is possible that West Oakland residents experienced negative health effects from cumulative exposure to combined pollutants emitted from the fire. Given the severity of $PM_{2.5}$ concentrations measured via lower-cost sensor networks, we can assume that particulates impacted human health in addition to VOCs that are identified as HAPs by the EPA. However, 24-hour averages of $PM_{2.5}$ concentrations near the facility did not show exceedance of the federal regulatory standard (U.S. EPA OAR 2024). West Oakland's proximity to the Port of Oakland has led to a serious pollution burden from the impacts of industry related to the Port (Fisher et al. 2006, Grow and Beveridge 2007, MacIver et al. 2022). Communities of color are more likely to be located near heavily polluting industry than white communities, and are also more likely to be exposed to higher concentrations of air pollutants, especially in areas like West Oakland that were formerly subject to redlining practices (Perlin et al. 2001, Mohai et al. 2009, Jia and Foran 2013, Lane et al. 2022). Figure 6 illustrates how areas closest to the fire in West Oakland experienced the highest concentrations of HAPs, indicating the disparities in pollution burden. Regulatory action against the facility has not managed to limit the release of pollutants into West Oakland, especially through accidents such as fires (DTSC 2023, Madyun 2023). Further monitoring of the releases of air toxics from the facility could improve the ability of the community to hold the facility responsible for negligent releases of hazardous substances.

Monitoring air quality via lower-cost sensors is likely to remain important in the areas around the facility. One potential strategy to improve monitoring is to install other types of lower-cost sensors nearby. Certain sensors, such as the EPA's SPod, are capable of detecting large emissions events like the fire and capturing air for later analysis (MacDonald et al. 2022, U. S. Government Accountability Office 2024). These sensors are a combination of a device that can measure overall VOC concentrations and a canister that can sample ambient air for laboratory analysis. When VOCs are detected above a certain threshold, the canister is activated and an air sample is collected (MacDonald et al. 2022). The device then notifies the owner that the canister is ready for collection. This type of sensor would enable direct quantification of hazardous VOCs that are released from the facility, greatly improving the West Oakland community's knowledge of exposure.

ACKNOWLEDGEMENTS

This project was a collaborative effort. I would like to thank Dr. Allen Goldstein and all the members of his lab, especially Erin Katz for collecting the Vocus data and helping design the project, Michael Milazzo for advice throughout the process, and Robin Weber for making everything work properly. Professors Dennis Baldocchi, Ronald Cohen, Joshua Apte and their groups were instrumental in providing additional data. Special thanks to Naomi Asimow for providing BEACO$_2$N measurements and Professor Tina Chow for advice on transport modeling. This thesis would not have been possible without Patina Mendez, Annie Miller, and the rest of the ESPM 175 and 100 teaching teams. Finally, the support of my peers Jiawen Tang, Mara St. Amant, Tia Pappas, and Patrick Jacobson was invaluable in helping me complete my thesis.

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APPENDIX A: BEACO$_2$N vs. PurpleAir

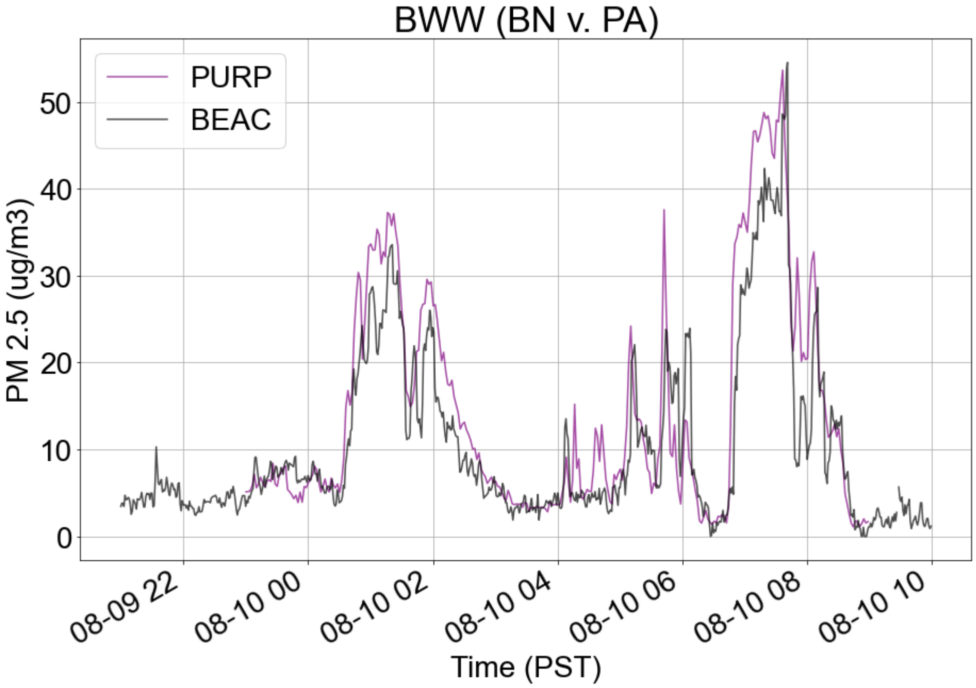

Figure A1. BEACO$_2$N vs. PurpleAir time series. Time series of sensors located near BWW.

APPENDIX B: $PM_{2.5}$ vs. VOCs

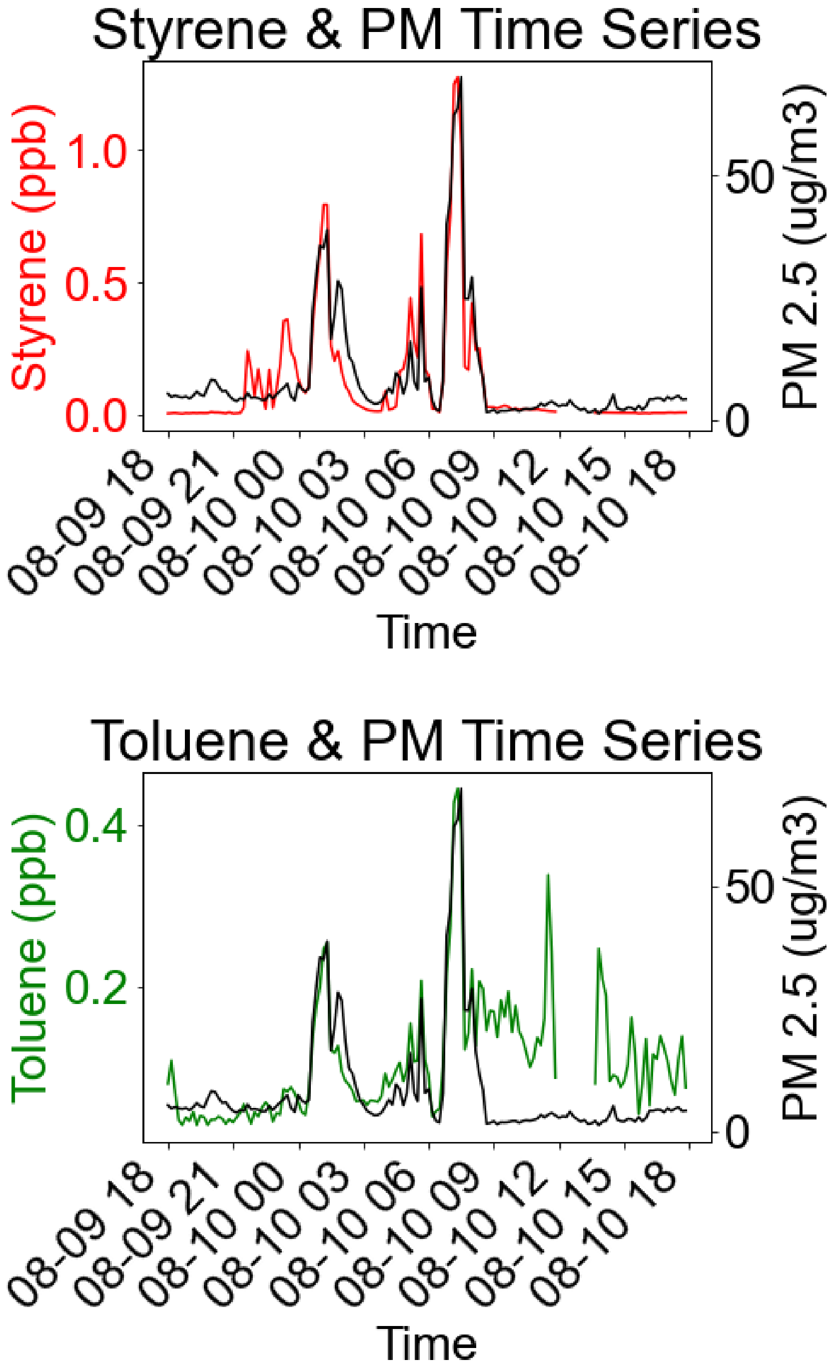

Figure B1: Styrene and Toluene vs. $PM_{2.5}$ time series. Toluene time series shows the diurnal cycle from 12 PM to 6 PM PST.