

Changing composition of volatile organic compounds in Manhattan during the Covid-19 shutdown implies changing sources

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Abstract

As emissions of volatile organic compounds (VOCs) from motor vehicles continue to decline, chemical products and processes like glues, paints, and cleaning products have become significant, non-traditional VOC sources in American cities. Air samples taken in Upper Manhattan from January to May 2020 contain a broad range of compounds with diverse functional groups and origins. After the Covid-19 shutdown in March, the abundances of most compounds stayed the same or increased compared to benzene, a proxy for motor vehicle use. These results provide evidence that the importance of non-combustion sources to urban air composition and quality increased amid changes in behavior during the pandemic.

1 Introduction

Air pollution is a major driver of deaths and morbidity worldwide. Globally, the Institute for Health Metrics and Evaluation estimates that outdoor air pollution from particulate matter (PM) and ozone contributed to 4.1 million deaths in 2019, or 7 percent of all deaths. Exposure to these pollutants affects human health by increasing the likelihood of lower-respiratory infections, chronic obstructive pulmonary disease, heart disease, and similar disorders. High ambient PM concentrations are also associated with decreases in cognitive ability and newborn birth weight.¹ The Organisation for Economic Co-operation and Development forecasts that air pollution will reduce global gross domestic product by 1 percent by 2060 because of lowered labor productivity and agricultural crop yields.²

Many processes generate particulate matter and ozone. In the United States, volatile organic compounds (VOCs) and their downstream oxidative products have predominated as PM sources since the 1970s. VOCs make up a class of compounds diverse in their structures and origins — some natural, some anthropogenic — but unified by their tendency to enter the gas phase at ambient temperatures.

For decades, the primary source of VOCs in American cities has been combustion-related petroleum derivatives, particularly gasoline and diesel in cars, trucks, and other motor vehicles. Compounds like benzene and toluene leak out of storage, evaporate from fuel tanks, or fail to combust during vehicle operation and enter the atmosphere. Once vaporized, VOCs are free to react with oxygen and nitrogen oxides to produce ozone and secondary organic aerosols, a form of PM.³

Sustained technological improvements and policy changes have brought motor vehicle VOC

emissions down significantly. For instance, catalytic converters allow cars to oxidize gasoline completely, rather than release byproducts of incomplete combustion. New regulations require fuels to contain compounds that are less volatile and have lower potentials to produce aerosols. In Los Angeles, VOC emissions decreased 80 percent from 1990 to 2020 despite constant or increasing vehicle population and fuel use.⁴

However, Los Angeles and similar cities are still failing to hit their air quality targets. As motor vehicle emissions have declined in urban VOC inventories, further efforts to drive them down are yielding diminishing returns. As a result, other, non-combustion sources have risen in priority as targets for pollution control.

Prime among these other sources are volatile chemical products and processes. This broad label encompasses consumer products like furniture and perfumes; commercial products like paints, cleaning products, and construction materials; and industrial chemicals like solvents and glues. These products release VOCs throughout their entire lifetime, from manufacture to use to breakdown. Indeed, unlike fuels, which are meant to be combusted to carbon dioxide and water, chemical products are often intended to evaporate as part of their use. Thus, they release many times more VOCs per kilogram of product than gasoline and diesel do. As a group, chemical products' contribution to VOC emissions is now about equal in magnitude to that of motor vehicles.⁵

Motor vehicle VOC emissions have distinctive compound profiles compared to emissions from other sources. Gasoline comprises a variety of aliphatic and aromatic compounds, along with additives like ethanol. In particular, benzene is extremely characteristic of combustion-related emissions, and atmospheric benzene largely comes from motor vehicles and associated sources.⁶

In contrast, chemical products and processes contain compounds that have more heteroelements, especially oxygen. This difference is more than incidental: the increased polarity and altered activity induced by oxygen atoms is frequently essential to product function. Therefore, the presence or absence of certain compound classes in the atmosphere can demonstrate the contribution of various VOC sources to total emissions.

The Covid-19 pandemic began in December 2019 in Wuhan, China and rapidly spread around the world over the following months. New York City experienced an explosion of cases in early March 2020, leading Governor Andrew Cuomo to call for a shutdown of non-essential activity on March 20.⁷ Changes in traffic and mobility from before to after the shutdown are well-documented. The Metropolitan Transit Authority released figures showing an approximate 70 percent decrease in bridge and tunnel crossings within NYC from the start of March to the end. By May, crossings had recovered to about half of their pre-pandemic value.⁸

This study investigates the composition of atmospheric VOCs above Manhattan in the first half of 2020. By analyzing air samples taken from January to May, it also explores how the relative abundances of specific compounds changed across the surge in Covid cases and ensuing shutdown. Theoretically, the drastic decrease in motor vehicle use should have led to a decrease in concentrations of combustion-related VOCs, while the pandemic's effect on chemical product and process use is more uncertain. This study finds that the abundances

of the majority of analyzed compounds relative to benzene increased, implying that changes in behavior occurred during the shutdown that altered the importance of combustion-related and non-combustion-related VOC sources.

2 Methods

Air was sampled in Upper Manhattan in two nearby locations in early 2020. From January to March 2020, samples were taken at the rooftop observatory of the Advanced Science Research Center of the City University of New York (hereafter the "pre-shutdown" samples, 85 St. Nicholas Terrace, New York, NY 10031). The rooftop is 86 m above sea level in a well-ventilated area. In May 2020, due to limitations caused by the shutdown, samples were taken at a personal residence in East Harlem (the "post-shutdown" samples).

Samples were collected as described by Sheu et al. (2018).⁹ Adsorbents quartz wool, glass beads, Tenax TA, and Carbopack X were cleaned by passing through nitrogen at maximum temperatures for several hours. Borosilicate glass tubes were packed with the adsorbents in the aforementioned order to capture VOCs with varying affinities and volatilities. The tubes were conditioned to further remove contamination using nitrogen for at least 6 hours at maximum temperatures, then topped with brass caps.

Air was pumped through filters doped with sodium thiosulfate to remove reactive ozone, polytetrafluoroethylene filters to remove particulate matter, then the adsorbent tubes at rates between 0.1 and 0.2 standard liters per minute for 1 to 5 hours. When sample collection ended, tubes were capped and placed in a cooler filled with ice.

Samples were analyzed with gas chromatography-electron ionization-mass spectrometry. Helium gas was run through the tubes at 300 °C to desorb attached analytes and deposit them onto a trap packed with quartz wool, Tenax TA, and Carbopack X chilled to -10 °C. The analytes were thermally desorbed (Gerstel TD3.5+/CIS) from the trap into the gas chromatograph (Agilent 7890B) with helium ramped from 30 °C to 310 °C at 400 °C/min, then held for 6 minutes.

Analytes were separated on a HP-5-MS-UI column (Agilent, 30 m × 0.25 mm × 1 µm) held at 30 °C for 5 minutes, ramped to 325 °C at 10 °C/min, then held for 3 minutes. Effluent was directed to a vacuum electron-impact quadrupole mass spectrometer (Agilent 5977A).

Output files were converted using OpenChrom (1.5, Lablicate) and analyzed with TERN (2.2.18, Aerodyne Research) in Igor Pro 8 (WaveMetrics). Resulting data were analyzed and visualized with the `tidyverse` (1.3.1) in R (4.2.0).¹⁰⁻¹⁴

3 Results

45 compounds were identified from the air samples, comprising a diverse group of chemicals with many different functional groups. Table 1 shows a selection of identified VOCs, split by compound class.

Aliphatic	Aromatic	Oxygenated	Other
isooctane	benzene	furfural	<i>para</i> -chlorobenzotrifluoride
methylcyclohexane	toluene	butyl acetate	tetrachloroethylene
limonene	naphthalene	methyl benzoate	1,2-dichloroethane
menthol	1,3-xylene	benzophenone	decamethylcyclopentasiloxane
α -pinene	styrene	propylene glycol	

Table 1: A selection of VOCs identified in Upper Manhattan from January to May 2020.

As mentioned above, the presence of aromatic compounds like benzene and toluene implies the use of gasoline and diesel. Aromatics are also of interest because they have greater potential to form secondary organic aerosols, a form of particulate matter.³

Esters, ketones, and other oxygenated compounds are often present in volatile chemical products as flavoring, solvents, or decomposition byproducts. Aliphatic compounds can fit into either category: isooctane and methylcyclohexane are present in gasoline, while limonene, menthol, and α -pinene are natural products often used as fragrances in personal care and cleaning products.¹⁵

Benzene concentrations at the CUNY site pre-shutdown averaged 0.70 ppb, while concentrations post-shutdown averaged 0.39 ppb, an overall decrease of 44 percent (Figure 1). However, four samples in late January had abnormally high amounts of benzene compared to toluene, as A.1 shows. These imbalances are typical of periods with strong VOC contributions from non-traffic sources, such as wildfires.¹⁶

Though wildfires can significantly impact air quality, they remain intermittent in the New York City area. On the other hand, motor vehicles and volatile chemical products contribute consistently to VOC and particulate matter levels. To focus on comparing these sources and to avoid misattributing high benzene levels due to biomass burning, the four outlier samples were removed from further analysis.

With these samples removed, benzene mixing ratios averaged 0.53 ppb before the shutdown and declined 26 percent afterward. Similarly, toluene concentrations decreased 22 percent from 0.59 ppb in early 2020 to 0.46 ppb in May. These drops align with expectations that lowered traffic during the shutdown would lead to lowered VOC emissions from motor vehicles.

Randomization inference can be used to estimate the likelihood that, if there were no true differences between the pre- and post-shutdown periods, the observed data could have arisen by chance. In contrast to traditional, asymptotic methods, randomization inference can give p -values that do not rely on large sample sizes to be valid. In addition, the procedure can generate p -values for arbitrary test statistics.¹⁷ All p -values that follow were obtained by randomization inference.

In this case, the null hypothesis that no difference in a compound’s mixing ratio exists between the pre- and post-shutdown periods can be tested by assuming each sample could have been taken in either period. By randomly assigning measurements to either period,

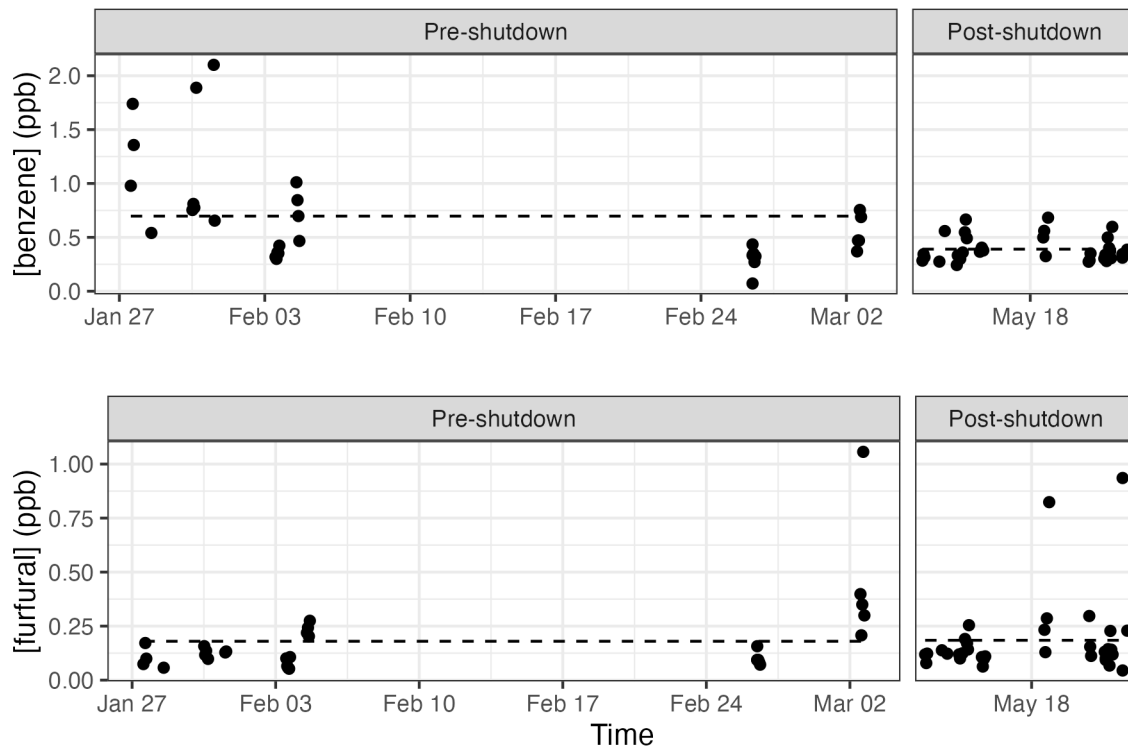


Figure 1: Atmospheric concentrations of benzene and furfural, in parts per billion (ppb). Dotted lines indicate average concentrations in each period.

calculating the change in mean simulated concentrations, and repeating many times, an approximate distribution of possible differences under the null is generated. p -values are obtained by finding the number of times where the simulated change is at least as large as the observed change.

Under the one-sided alternative hypothesis that post-shutdown motor-vehicle VOC concentrations were lower than pre-shutdown concentrations, $p = 0.002$ for benzene, allowing the null of no difference to be rejected at the $\alpha = 0.05$ level. The difference in toluene mixing ratios is marginally significant at $p = 0.062$.

Furfural is an oxygenated compound released by wood furniture and other agricultural products as they decompose. Its concentration remained nearly constant across the shutdown from 0.19 ppb before to 0.18 ppb after (Figure 1; two-sided, $p = 0.940$), suggesting its sources did not change in magnitude. This also matches expectations, as it seems unlikely that the pandemic affected existing furniture stock.

Gas standards for the majority of identified VOCs were unavailable, so their concentrations in each period could not be directly calculated. However, the ratios of their observed, chromatographic peak areas to benzene’s peak area in each sample are available. Normalizing peak areas in this way corrects instrument drift that can occur when analyzing samples over the span of weeks (Figure A.2). Therefore, ratios in samples taken before and after the shutdown are directly comparable. Benzene was chosen as a reference compound

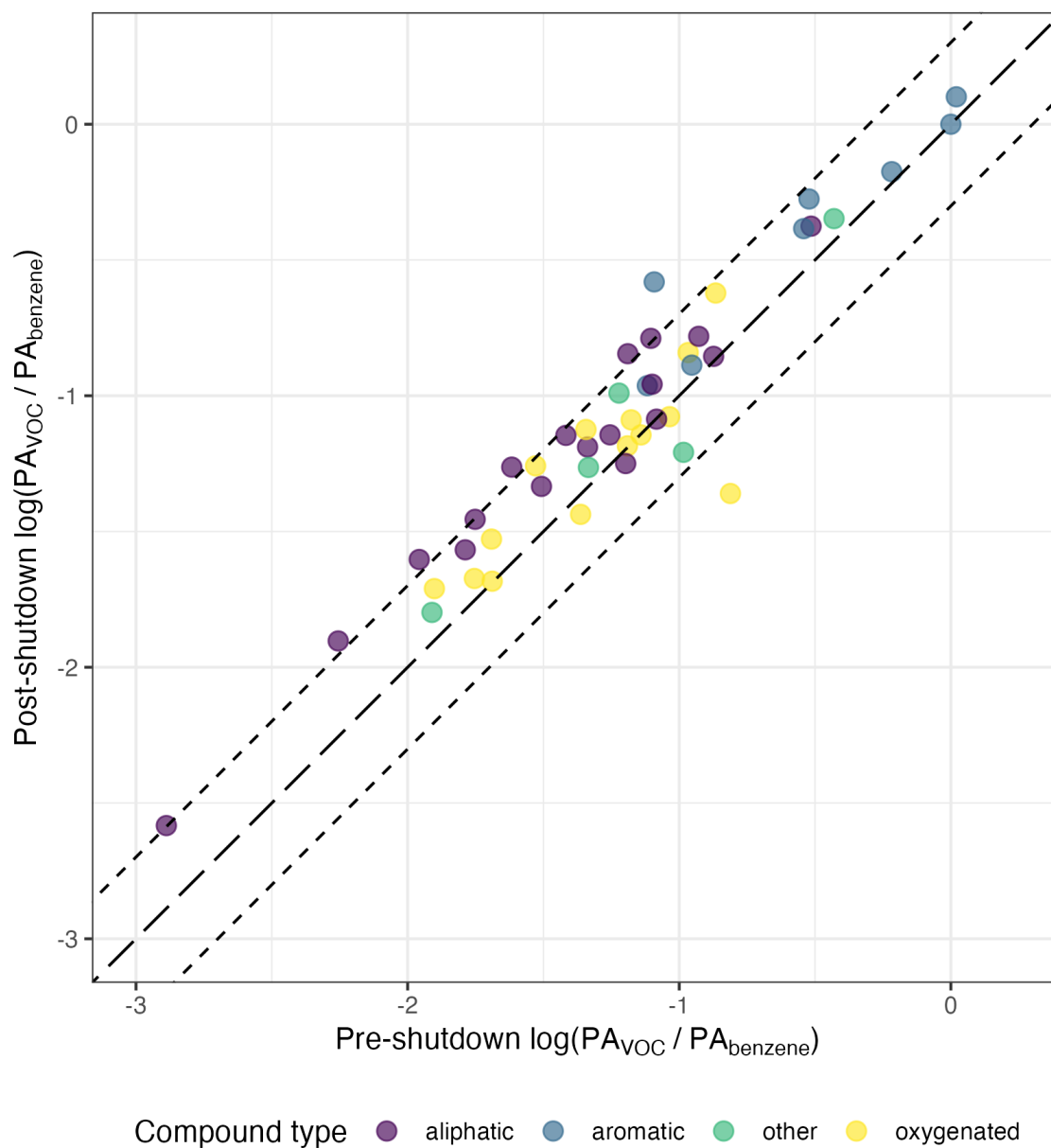


Figure 2: Average VOC/benzene peak area ratios for each compound, before and after the shutdown. A compound on the central dotted line has equal ratios in both periods. The higher and lower dotted lines bound compounds with post-shutdown ratios between twice and half as large as their pre-shutdown ratios, respectively.

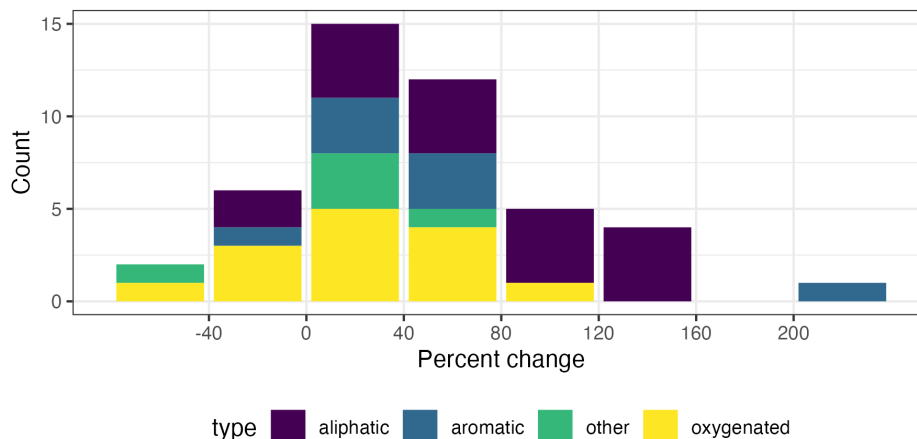


Figure 3: The distribution of percent changes of average VOC/benzene peak area ratios for each compound across the shutdown.

because it serves as a proxy for motor vehicle use.

Figure 2 shows average VOC/benzene peak area ratios in each period. As expected, ratios for 37 out of 44 compounds increased after March 2020, indicating their sources’ emissions grew in importance relative to gasoline and diesel. The average increase in peak area ratios was 46.1 percent (one-sided, $p = 0.0002$).

The distribution of changes in average ratios, split by compound type, is pictured in Figure 3. On average, aliphatic compounds had the largest increases (66 percent), followed by aromatic (54 percent) and oxygenated compounds (22 percent). Styrene had the largest ratio increase (225 percent), while methyl methacrylate had the greatest decrease (-72 percent). Figure A.4 shows the sample-level distribution of peak area ratios for these and other compounds of interest.

4 Discussion

These results show that benzene decreased in both its absolute concentration and its relative abundance compared to other VOCs from January to May 2020.

There are two primary caveats in interpreting these results.

First, the analytical methods used in this study are generally reliable, but may have some limitations.⁹ Figure A.3 compares calculated concentrations for benzene and toluene with simultaneous measurements by proton-transfer-reaction mass spectrometry (PTR-MS; unpublished data). PTR-MS is another technique that can provide real-time concentrations for a limited range of compounds. Results from both methods align for benzene, but PTR-MS shows higher mixing ratios for toluene for a large proportion of pre-shutdown samples.

This study’s methods may also underestimate concentrations of low-molecular weight

oxygenates. Several esters found in urban settings in Sheu et al. (2021) either were not identified or had lower abundances than expected in these samples.¹⁸

These compounds could have been lost at multiple points during the process, including initial sampling and adsorption, transport, storage, and incomplete desorption. As a consequence, since esters are commonly used in volatile chemical products, this lapse in measurement may have led calculations to underrate their emissions contributions.

Refinements of the sampling process are needed to accurately analyze simple esters. However, note that this study compares samples all taken with the same methods. As a result, any biases should affect measurements across the shutdown similarly, somewhat mitigating their effects.

Second, because these data are observational without a source of random variation, statements that the pandemic or shutdown directly caused changes in VOC mixing ratios cannot be made. Though Covid-19's rapid spread was a semi-unexpected shock, restrictions on research prevented post-shutdown air samples from being taken until May 2020 — almost two months after the start of the pandemic, and too late for a regression discontinuity-esque design to be convincing.

Beyond pandemic-related disruptions, other, confounding factors may have contributed to the observed differences:

Seasonal changes in emissions behavior. VOC emissions can change in type and magnitude over the course of a year, even in usual years. For instance, warmer spring weather might encourage people to walk more and drive less in May compared to January, causing a drop in benzene concentrations. Or, construction projects tend to ramp up in the spring and summer, leading to greater use of paints, wood, and other volatile chemical products. Since data on individual VOCs was only collected in 2020, these speculated trends cannot be definitively confirmed or denied.

Still, the shutdown's limits themselves bound the effect of typical seasonal changes. Congestion, as measured by the additional time required to get to a destination due to traffic, was still only 15 percent of 2019 levels in May 2020, and non-essential construction was banned in New York until June 8. The pandemic induced such drastic changes in daily life that they may overwhelm ordinary shifts.

Seasonal changes in atmospheric dynamics. Atmospheric chemistry and transport vary between seasons. In the spring and summer, VOCs are rapidly oxidized by photochemistry with ozone and hydroxyl radicals. These reactions occur an order of magnitude more slowly in the winter because of decreased sunlight and humidity.¹⁹ Additionally, temperature inversions in the winter can impede vertical mixing, preventing VOC emissions from exiting cities.²⁰ Since compounds have different physical and chemical properties, changing seasons can change the ratios of compound concentrations, even if emissions are constant.

Difference in sampling sites. Shutdown restrictions prevented the original CUNY site from being used to take samples in May. Each site might have had different hyperlocal sources with their own characteristic VOCs, affecting the observed

compound abundances. However, this effect is mitigated because the locations were nearby and well-ventilated.

From a causal inference perspective, the treatment effect of interest is the difference between the peak area ratios that were actually observed in May 2020 and the ratios that, had the pandemic never happened, would have been observed in May. The reasons above suggest that pre-shutdown measurements from January to March fail to serve as proper counterfactuals for post-shutdown data, so the treatment effect cannot be identified.

Zangari et al. (2020) found that the drops in $\text{PM}_{2.5}$ and NO_2 concentrations in New York City from January to May 2020 were not significantly different from the parallel decreases each year in 2015-2019.²¹ These results need not apply to individual VOC concentrations, especially if changes in pollutant mixing ratios are largely controlled by transport dynamics. Still, they emphasize the need for longitudinal data on VOC concentrations, not just relative abundances.

5 Conclusion

Long dominated by trends in motor vehicle use, urban air quality in the United States has begun to depend on emissions from chemical products and processes. The Covid-19 shutdown provided a miniature acceleration of these trends by massively lowering personal mobility and traffic volumes. In this study, analysis of air samples taken in New York City demonstrated that non-combustion sources rose in prominence as VOC sources in May 2020 as compared to January through March.

Further research should investigate whether this phenomenon occurs seasonally, or if shutdown conditions created a unique, unprecedented event. Additional improvements to sampling techniques could also discover a wider range of compounds, giving further insight into which volatile chemical products most influence air quality.

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A Appendix

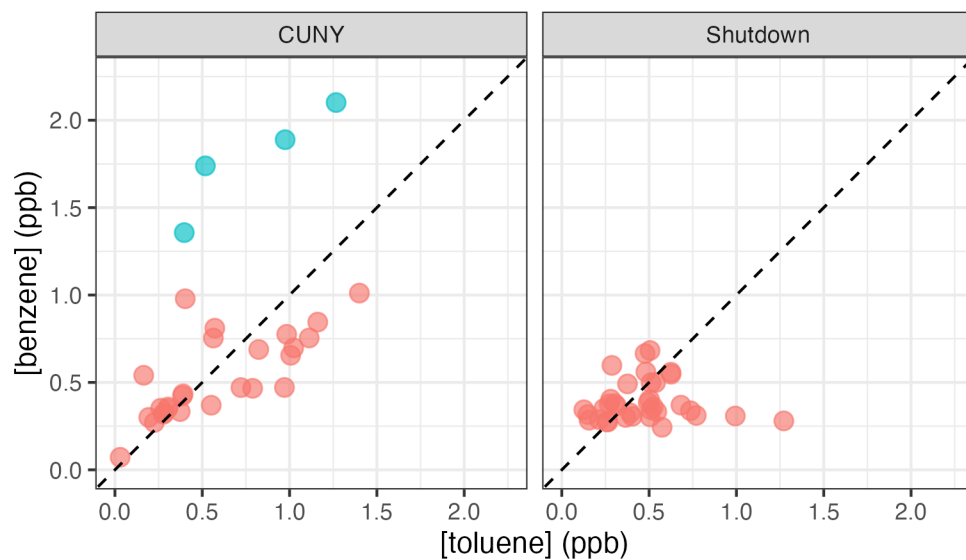


Figure A.1: Benzene and toluene concentrations in each sample. Dotted lines indicate a one-to-one ratio. Samples in blue were removed from further analysis because their high benzene:toluene ratios reflect biomass burning.

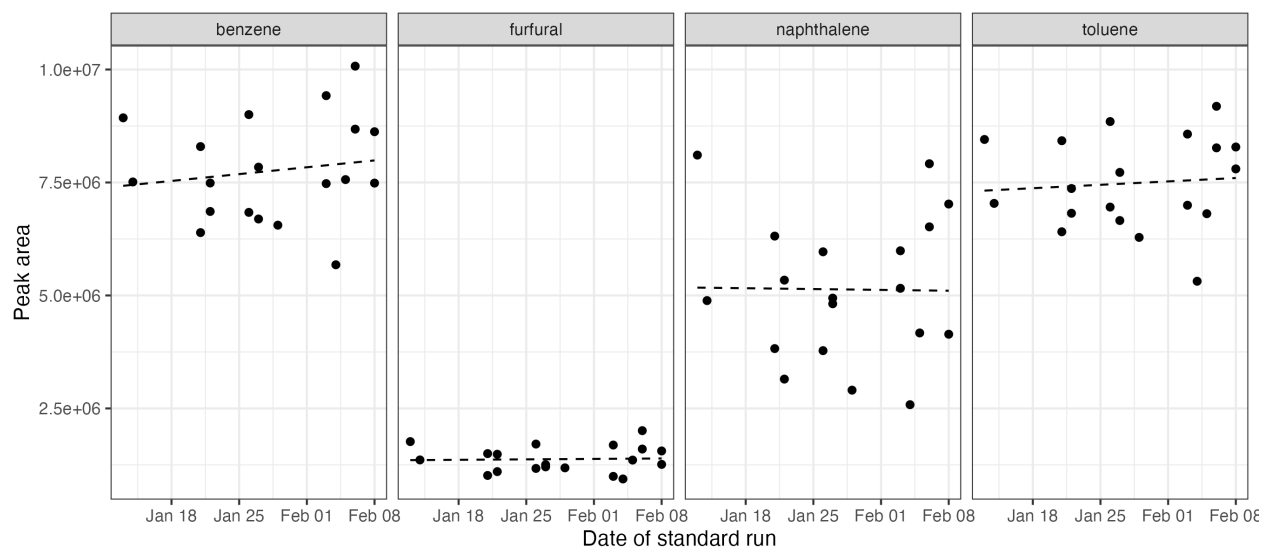


Figure A.2: Signal areas for selected compounds in gas standards run during sample analysis in early 2021.

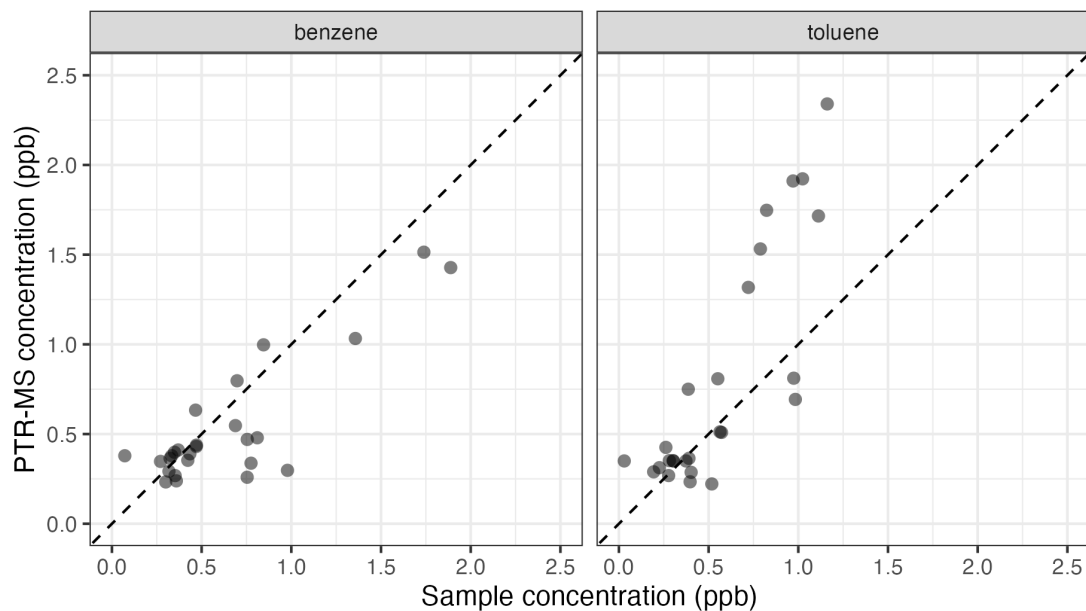


Figure A.3: Compound concentrations derived from air samples used in this study versus live concentrations measured with proton-transfer-reaction mass spectrometry (PTR-MS). The dotted lines indicate identical measurements from both methods. All measurements were taken before the shutdown.

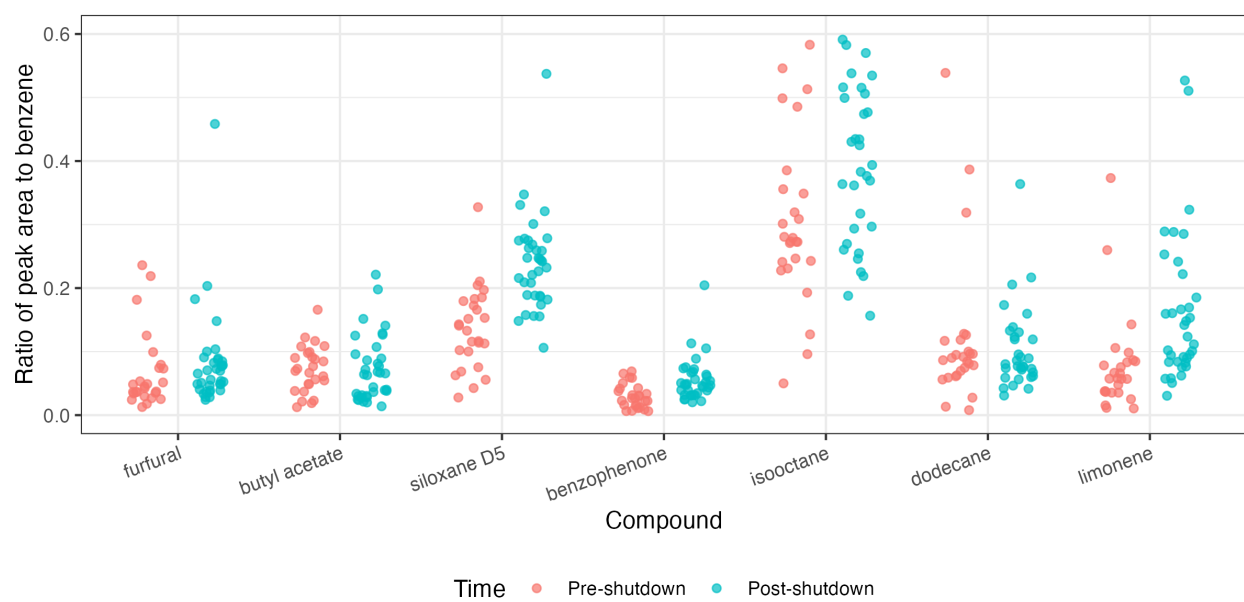


Figure A.4: Distributions of VOC/benzene peak area ratios for each sample for selected compounds.