



DELAWARE DEPARTMENT OF
NATURAL RESOURCES AND
ENVIRONMENTAL CONTROL

June 2021

Claymont Community Volatile Organic Compound Study

Claymont, Delaware: Final Report



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Executive Summary

In April of 2019 the Division of Air Quality (DAQ) initiated the six-month Claymont Volatile Organic Compound Study to address air quality concerns for the community of Claymont, Delaware. Concerns focused on air pollution that may originate from the nearby Claymont/Marcus Hook, Pennsylvania border where several industrial facilities are located. The pollutants of greatest concern were volatile organic compounds (VOCs), particularly benzene.

Monitoring for VOCs was performed following the U.S. Environmental Protection Agency Toxic Organic Compendium Method TO-15, using evacuated canisters supplied by a contract lab. Samples were collected for 24 hours beginning at midnight, every three days, and were sent off to the contract laboratory for analysis. A site was selected within the community at the New Castle County Woodshaven Kruse Park in Claymont. Monitoring for VOCs with the TO-15 method has been conducted long-term

at DAQ's permanent MLK NCore monitoring site in Wilmington, Delaware using a different laboratory. To better compare sites, samples were collected at MLK every sixth day and were analyzed using the same laboratory as the Claymont site.

The study began in April of 2019 and concluded at the end of September of 2019. The goals of this study were to: characterize VOCs found in Claymont, compare those concentrations to the MLK site in Wilmington, and to determine if VOC concentrations varied by wind direction. The laboratory analyzed for 58 compounds. Of the 58 compounds, only 15 were detected with enough data of sufficient quality for study. Overall VOC concentrations were found to be very low at both sites. No statistically significant differences were detected between concentrations at Claymont and MLK. Finally, no statistically significant differences were detected in concentration by wind direction or day of week.

Plain Language Summary

In April of 2019, Delaware's Division of Air Quality (DAQ) initiated the six-month Claymont Volatile Organic Compound (VOC) Study to address air quality concerns for the community of Claymont, Delaware. Concerns focused on air pollution that could originate from the nearby Claymont/Marcus Hook, Pennsylvania border where several industrial facilities are located. The pollutants of greatest concern were what are referred to as volatile organic compounds (VOCs). There are many different VOC chemicals and DAQ chose a laboratory study method that could tease out a larger number of different VOCs from a single sample.

The study began in April of 2019 and concluded at the end of September of 2019. The first goal was to determine the different VOCs and amounts found in Claymont. The next goal was to compare the observed VOCs and amounts in Claymont to those observed in Wilmington where there is a long history

of VOC monitoring. The last goal was to determine if VOCs and amounts in Claymont varied by wind direction or day of the week.

The laboratory study looked for 58 different VOCs. When the study was complete only 15 VOCs were observed often enough to compare at both Claymont and Wilmington. Overall VOC amounts were found to be very low in both communities. The amount of each VOC in both communities was relatively the same and each VOC was found in both communities. The amount of any VOC did not vary in any meaningful way by the direction of the wind or by the day of the week in Claymont.

The study shows that VOCs observed in Wilmington are very similar in both specific VOCs and amount as those seen in Claymont. DAQ continues to monitor VOCs in Wilmington.

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Glossary of Terms & Acronyms

Air Toxics: Toxic air pollutants, also called air toxics or hazardous air pollutants, are pollutants that are known or suspected to cause cancer or other serious health effects, such as reproductive effects or birth defects, or adverse environmental effects

Ambient Air: Generally, the atmosphere; usually refers to the troposphere.

BTEX: Acronym for Benzene, Toluene, Ethylbenzene, and Xylene volatile organic compounds typically associated with petroleum refining and burning of fuels in transportation.

DAQ: Delaware Division of Air Quality

DNREC: Delaware Department of Natural Resources and Environmental Control

EPA: United States Environmental Protection Agency

Exceedance: An incident occurring when the concentration of a pollutant in ambient air is higher than the NAAQS

FEM: Federal Equivalent Method for monitoring air pollution

Flag: A data qualifier that can indicate more information about the quality of a data point

GC/MS: Gas Chromatography and Mass Spectrometry

HAPS: Hazardous Air Pollutants

MDL: Minimum detection limit

NAAQS: National Ambient Air Quality Standard set by EPA to protect human health and welfare.

NCore: National Core monitoring station, part of an enhanced national EPA monitoring program, successor to the NAMS program

ppb: Parts per billion by volume.

ppm: Parts per million by volume.

RL: Reporting Limit, may also be referred to as Quantitation Limit

SLAMS: State and/or Local Air Monitoring Stations

TO-15: Toxic Organic Compendium Method 15, EPA method for Determination of Volatile Organic Compounds (VOCs) in air collected in specially-prepared canisters and analyzed by Gas Chromatography/Mass Spectrometry (GC/MS)

µg/m³: Micrograms per cubic meter

VOC: Volatile Organic Compounds

24-hour Average: The average concentration for a 24-hour period

Introduction

This study was conducted to address the concerns raised by the community of Claymont, Del., regarding air quality in the community. Located in the northeast corner of New Castle County, Claymont is bounded north by the state line bordered by the

City of Marcus Hook, Pa. (Figure 1). On the eastern boundary is the Delaware River. Historically this community has been impacted by local industrial activities such as steel milling, oil refining and chemical manufacturing.

Figure 1
Claymont location within Delaware and boundary map.

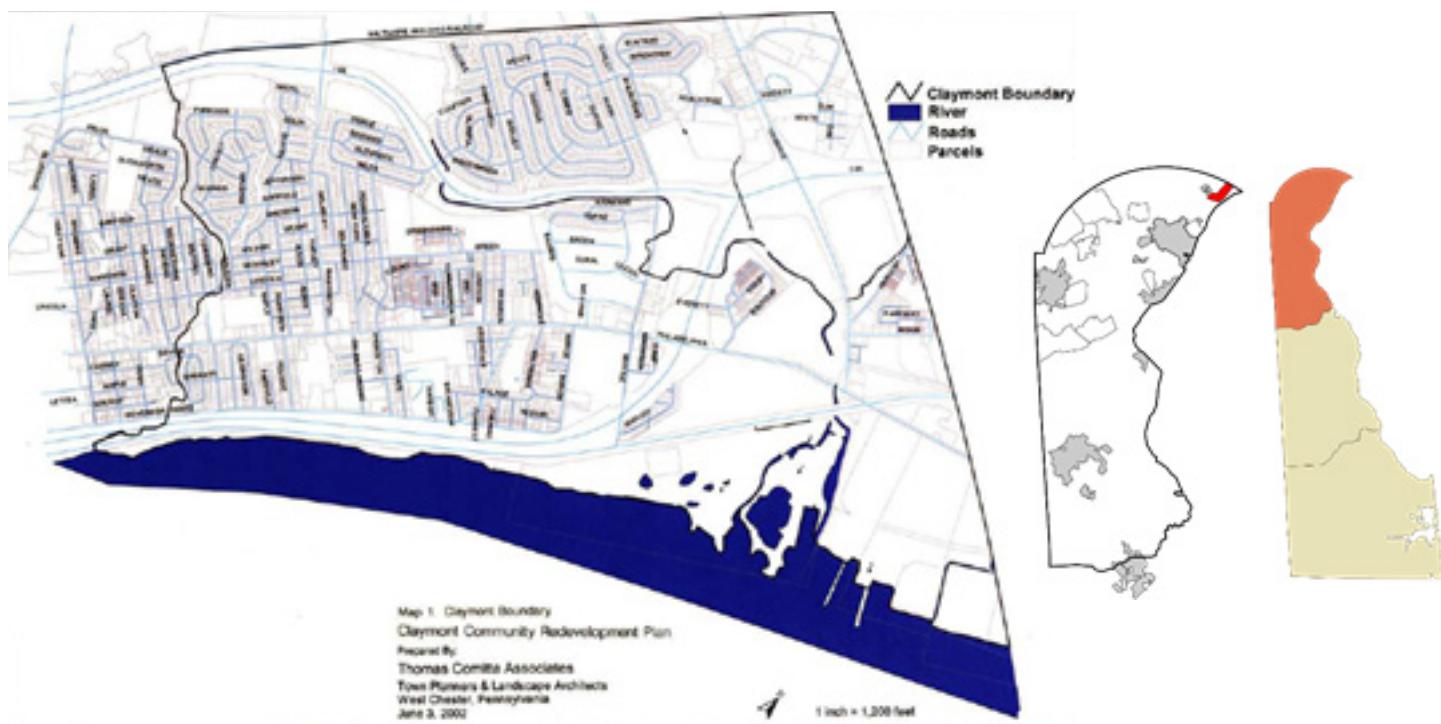


Figure 1: Claymont location within Delaware and boundary map.

Source: Boundary Map, <https://www.nccde.org/DocumentCenter/View/947/ClaymontBoundaries---Map-1-PDF>
State/County Map, Rcsprinter123 - Own work, CC BY-SA 3.0, <https://commons.wikimedia.org/w/index.php?curid=33922162>

Over the years, several monitoring efforts have been conducted in the community as well as private citizen monitoring. As industrial activities have changed or ceased, the air quality has improved over the last few decades. The community still has concerns, specifically with pollution that may be coming from the Claymont/Marcus Hook border where several industrial facilities in Delaware and the Marcus Hook Industrial Complex are located. The

Industrial Complex includes 45 acres in Delaware and 80 acres in Pennsylvania with both states permitting operations on their respective portions. Historically a refinery was operated at this location but following company acquisitions and mergers it is currently being transformed from a refinery to a hub for a natural gas pipeline. The majority of the permitted activities are governed by the State of Pennsylvania Department of Environmental Protection (PADEP).

In April of 2019 the DNREC Division of Air Quality (DAQ) initiated the six month Claymont VOC Study to address community concerns by evaluating local air quality for concentrations of

certain pollutants. The pollutants of greatest concern were volatile organic compounds (VOCs), which may originate from the nearby Claymont/Marcus Hook border.

Figure 2

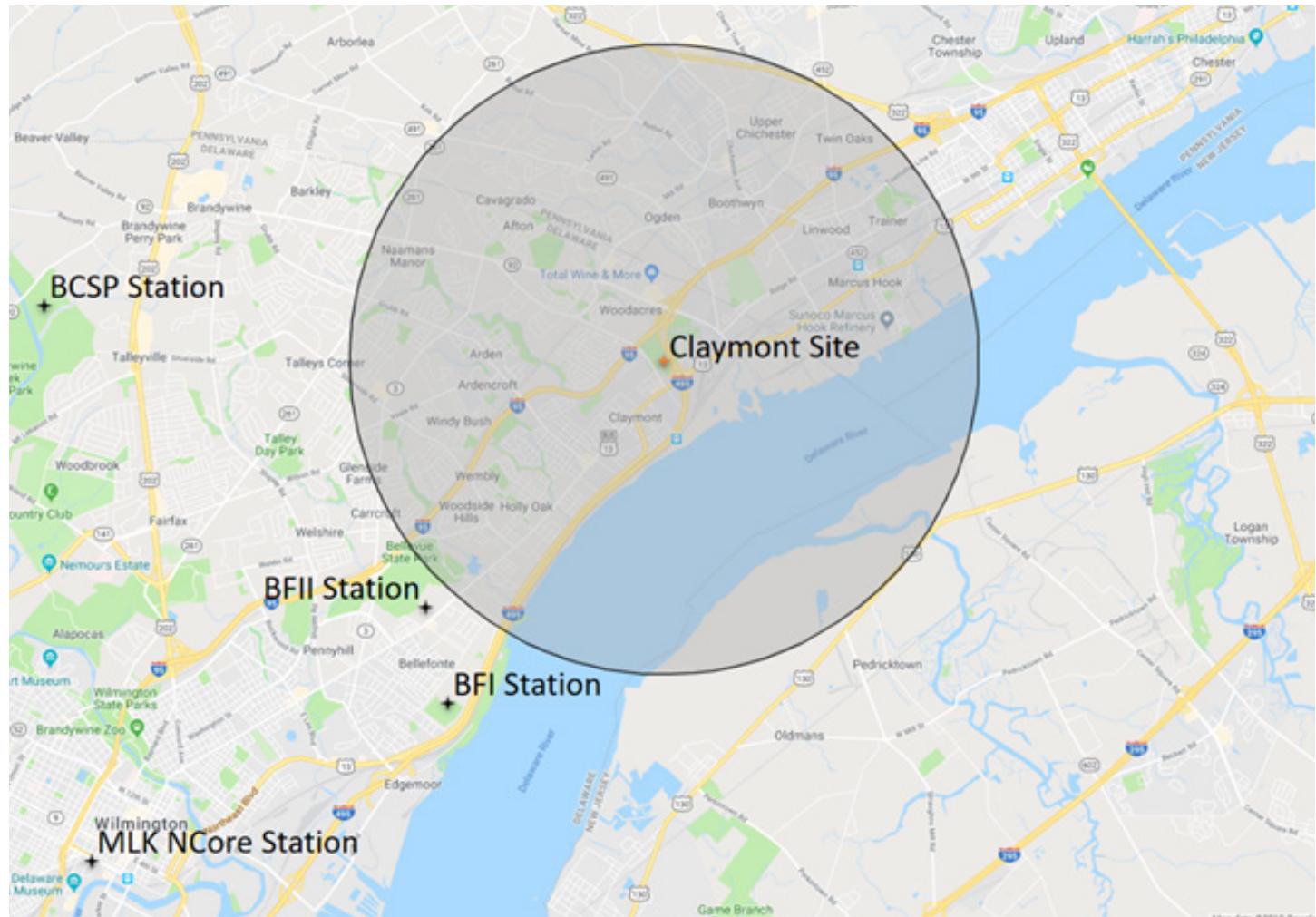


Figure 2: Claymont Site in the New Castle County Woodshaven Kruse Park with 3 mile radius and the locations of DAQs local monitoring sites

Sampling was conducted at Woodshaven Kruse Park in Claymont. For comparison, samples were collected during the same period using the same sampling method and lab at DAQ's central long-term

Martin Luther King (MLK) National Core (NCore) / Photochemical Assessment Monitoring Station (PAMS) site in Wilmington (Figure 2). Sampling concluded at the end of September 2019.

Objectives

The ambient air monitoring efforts were intended to characterize ambient concentrations of VOCs. The ambient air monitoring efforts were intended to characterize ambient concentrations of VOCs in the community of Claymont, and provide information on the following issues:

1. Characterize concentrations of VOCs in the community
2. Determine if VOCs measured when wind is from the direction of the Claymont/Marcus Hook border are similar or different from VOCs measured when the wind is from other directions as a way to estimate the impacts on the community.
3. Compare concentrations at Claymont to nearby monitoring sites, primarily DAQ's NCore/PAMS site at MLK in Wilmington, DE.

This project followed EPA Compendium Method TO-15, "Determination of Volatile Organic Compounds (VOCs) in Air Collected in Specially Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry (GC/MS) for both sampling and analysis methodology." (Reference 1). One fixed sampling location at the New Castle County Woodshaven Kruse Park was selected based on accessibility, position relative to the community and downwind relative to the Claymont/Marcus Hook border.

Implementation

Site Selection

A single site was selected based on requirements for access, budget, relation to the community and central to possible sources of pollution. The site selected was located at the New Castle County Woodshaven Kruse Park, $\frac{3}{4}$ of a mile from the Delaware Pennsylvania border. To the extent possible and practical, consideration of the monitor siting criteria detailed in the Code of Federal Regulations (CFR) Chapter 40 Section 58, Appendix E (Reference 2) was followed. This site was formerly used for Evraz Steel downwind particulate monitoring for the Claymont community. The former site infrastructure was used to support monitoring equipment for this study, which helped significantly with budgeting.

Figure 3



Figure 3: Chain-link fence site in NCC Woodshaven Kruse Park selected for this project

Monitoring Parameters

The monitoring project focused on the following parameters:

- 24-hour sample for volatile organic compounds (VOCs)
- Wind speed / wind direction (Delaware Environmental Observation System)

Methods

DAQ conducted ambient air sampling for VOCs on a 1-in-3 day schedule (once every third day), based on the national sampling calendar. Sampling began on Wednesday, April 3, 2019 and ended following the last sampling event on September 30, 2019. Deviations to the schedule due to staff availability, extreme weather events, and state holidays were noted on the monthly field sheets.

Monitoring was conducted with evacuated canister sampling as specified in EPA Method TO-15. Unless otherwise noted, each sampling event began approximately at 23:59 Eastern Standard Time (EST) and ended at 23:59 EST the next day for a 24-hour duration.

The sampling apparatus consisted of SUMMA® 6-liter canisters provided by Test America Labs (TAL). Over the course of the study TAL underwent a corporate change and is now identified as Eurofins. Canisters were fitted with an inlet assembly that had a critical orifice calibrated for 24-hour sampling without power requirement, a particulate filter and a digital timer valve system used to program sampling start and end times. The canister and inlet assembly were mounted on a tripod at the monitoring site for sampling. For quality assurance purposes, each sampling event was collocated. These paired samples were set up sequentially so that one pair sampled on day one and a second pair sampled on day three. This schedule allowed time to service samplers between sample collections and allowed for flexibility in sample setup scheduling by the operators.

Additionally, paired canisters using the same canister and inlet assembly setup were placed on the roof of the MLK NCore/PAMS monitoring station in Wilmington, Del. Sampling occurred on an every 6-day schedule followed by analysis by TAL. Every six days these canisters would sample during the same period as a pair at the Woodshaven Kruse Site. This allowed for DAQ to compare collected data from both sites using the same laboratory for analysis.

Figure 4



Figure 4: Canister inlet assembly, canisters setup on holder, and holder/sampler assembly placed on a tripod configured to hold 2 sets.

Data Collection

Each sampling event was logged and recorded on monthly field sheets. After 24 hours of sampling, the canisters remained under vacuum (negative pressure), and once the batch was finished sampling the batch was shipped to the analytical laboratory (Eurofins) for analysis. Contract laboratory analysis and reporting took approximately two to three weeks once DAQ shipped the sampled canisters. Eurofins issued a laboratory analytical final report after each laboratory analysis. Data from these laboratory reports was compiled by DAQ for analysis.

Quality Assurance

All monitors were operated per approved SOPs and manufacturer specifications. Quality control and assessment procedures followed the project Quality Assurance Project Plan for this Claymont VOC Study (Reference 3). The EPA conventional method quality objectives (MQOs) for all monitors were followed unless otherwise indicated.

Data Analysis

Data Summary

Samples were collected from April through September of 2019, with the sampling schedule set to follow the EPA National Sampling Schedule. In Claymont samples were collected every three days and at the MLK NCORE site samples were collected every six days. At both sites a collocated sample was collected on each scheduled sample day.

Data capture, measured as at least one valid sample collection per sample day, exceeded 80% at both sites. Due to issues with the timer mechanisms, successful collocated sampling fell below 75% at both sites (Table 1).

Table 1

Individual Samplers

	Claymont A	Claymont B	MLK A	MLK B
% Data Capture	87%	61%	80%	57%

Table 1: Percent data capture for each paired sample at Claymont and MLK

Samples were analyzed in batches by Eurofins following EPA method TO-15. After analysis Eurofins submitted a report to DAQ with the concentrations and relevant laboratory quality assurance records for each analysis. Two limits are calculated and reported by the lab. The lower limit or method detection limit (MDL) refers to the lowest concentration detectable by the analytical instrument. The high limit or reporting limit (RL) is defined as the lowest concentration a compound can be reliably measured, as opposed to detected. Concentrations below the MDL were reported as non-detects. Concentrations below the RL were reported and flagged as below the RL but above the MDL. Additional issues were indicated in a narrative and flagged as appropriate.

A total of 58 VOC compounds were analyzed for in each sample (Appendix A). Of those compounds only 21 had concentrations detected above the MDL in over 50% of the samples. Furthermore, of those 21 compounds, three were found to co-elute or were considered contamination and three compounds did not have enough concentrations above zero to be analyzed with confidence. Table 2 indicates the remaining 15 compounds that were above the MDL, did not co-elute, and had sufficient number of samples above zero to be characterized in this study.

Table 2

Grouping	Compound	% Non-detect	% > RL	% Data Flagged
BTEX	Benzene	0	34	62
Compounds	Toluene	2	98	2
(HAPs)	Ethylbenzene	31	19	79
	m-Xylene & p-Xylene	29	0	100
Hazardous	Chloromethane (Methyl Chloride)	0	100	4
Air	2-Butanone (Methyl Ethyl Ketone)	0	44	52
Pollutants	Carbon disulfide	0	44	54
(HAPs)	Trichloroethene	32	29	71
	Tetrachloroethene	9	23	75
	Hexane	0	16	84
	Chloroform	17	1	99
	Carbon tetrachloride	0	0	100
Non-HAP	Trichlorofluoromethane	0	92	5
VOCs	Dichlorodifluoromethane	0	32	67
	1,1,2-Trichloro-1,2,2-trifluoroethane	0	0	100

Table 2: Claymont Study sample summary table for compounds with sufficient data for evaluation

Quality Assurance

There are several different methods to handle results below the MDL. The results in this study below the MDL, reported as non-detects, were recorded as a zero. Several samples were flagged as below the RL. Sample concentrations that are below the RL are considered to be approximate and are flagged by the laboratory. Only Toluene, Chloromethane, and Trichlorofluoromethane had over 50% of their concentrations above the RL.

Variability for some compounds is greater between collocated samples than between the two sites, indicating significant uncertainty regarding the concentration detected. This is not unusual in collocated VOC samples at extremely low concentrations, as observed in the long-term monitoring at MLK. Percent differences were calculated as $200 * |(A-B)| / (A+B)$, where A denotes the "A" or primary samples and B denotes the collocated "B" samples. Only six of the 15 compounds had average percent differences under 30%. Some variability is due to extreme outliers which were not invalidated in this analysis.

To compare both sites, the collocated data at each site was averaged together. Since concentrations are so low, often below the RL, and variability is high, averaging the concentrations reduces some of the variability for comparison. If a collocated sample was not collected due to a timer malfunction or other field issue, the one collected sample value is used for the concentration.

VOC Comparison between MLK and Claymont

Overall concentrations were found to be very low at both sites. Additionally, most data were flagged as below the RL indicating that the concentrations are approximate. No significant differences could be detected between sites for any of the 15 compounds studied (Table 3).

Table 3

	Compound	Average Claymont (ppb)	Average MLK (ppb)	Difference (ppb)
BTEX Compounds (HAPs)	Benzene	0.2	0.2	0
	Toluene	1.2	0.97	0.23
	Ethylbenzene	0.1	0.1	0
	m-Xylene & p-Xylene	0.12	0.17	-0.05
HAPs	Chloromethane (Methyl Chloride)	0.87	0.85	0.02
	2-Butanone (Methyl Ethyl Ketone)	1.48	0.97	0.51
	Carbon disulfide	0.83	0.81	0.02
	Trichloroethene	0.16	0.15	0.01
	Tetrachloroethene	0.16	0.13	0.03
	Hexane	0.52	0.58	-0.06
	Chloroform	0.03	0.04	-0.01
	Carbon tetrachloride	0.07	0.07	0
Non-HAP VOCs	Trichlorofluoromethane	0.25	0.25	0
	Dichlorodifluoromethane	0.46	0.46	0
	1,1,2-Trichloro-1,2,2-trifluoroethane	0.07	0.07	0

Table 3: Average VOC concentrations (ppb) and differences between sites for the 15 evaluated compounds

The compounds referred to as BTEX Compounds were studied because they are often associated with petroleum product combustion and refining. BTEX compounds can be indicators of both mobile sources and refineries. The BTEX Compounds are Benzene, Toluene, Ethylbenzene, and m&p Xylenes. When results were compared between Claymont and MLK, no significant differences could be detected. When visualized as boxplots in Figure 5, all the distributions (boxes) overlap significantly despite some outliers in each compound.

Figure 5

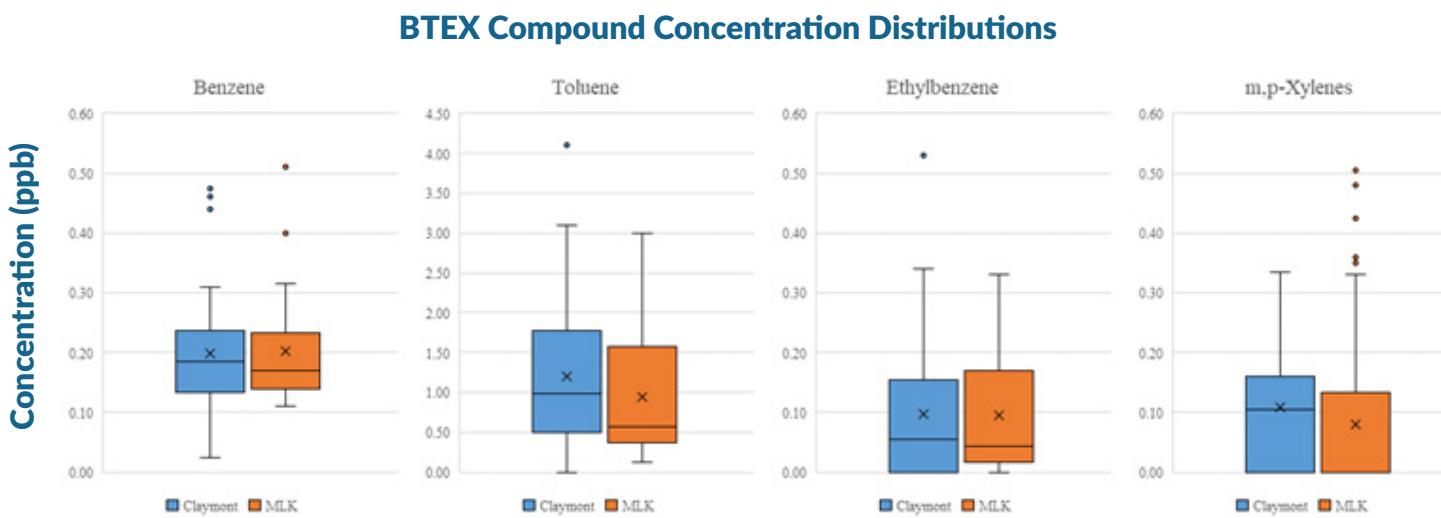


Figure 5: Distribution plots for BTEX compounds *note scale differs by pollution

VOC Characterization at Claymont

Meteorological data was obtained from the Delaware Environmental Observation System Claymont site which was adjacent to the sampling location for each sample day. A wind rose, Figure 6, shows that the wind blew most frequently from the Northwest.

The degree of variability in wind speed and direction over a 24-hour sample period allows only for an estimate of the directionality of compounds. Directionality was studied several different ways for each compound and no significant differences could be detected. Specifically, the BTEX Compounds which could be indicative of petroleum combustion or production, did not show any significant differences in concentrations based on wind direction.

Figure 6

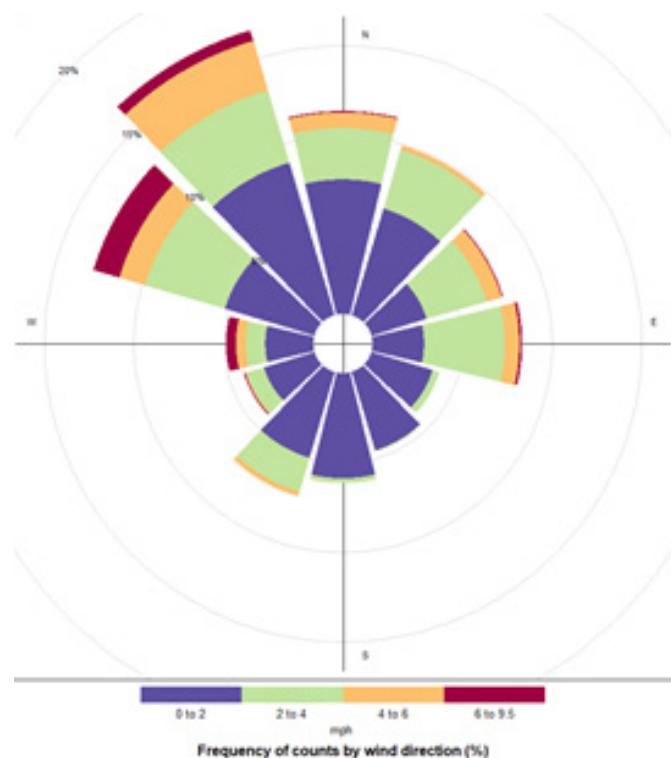


Figure 6: Claymont wind rose, indicating the frequency wind blew from each indicated direction and average range of wind speed by direction

Studying the average concentrations of VOCs by day of the week can sometimes serve as an indicator of sources. A higher weekday versus weekend pattern can help distinguish a source that operates during the work week versus weekends. Evaluation of concentrations by day of week showed no significant associations with weekday versus weekend, partially as a result of consistently low concentrations.

Conclusions

Utilizing the standard method for VOC detection, EPA TO-15, the goals of this study were to; characterize VOCs found in Claymont, compare those concentrations to the MLK site in Wilmington, and to determine if VOC concentrations varied by wind direction. Overall VOC concentrations were found to

be very low at both sites. No statistically significant differences were detected between concentrations at Claymont and MLK. Finally, no statistically significant differences were detected in concentration by wind direction or day of week.

References

1. EPA Compendium Method TO-15, Determination of Volatile Organic Compounds (VOCs) in Air Collected in Specially Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry (GC/MS) for both sampling and analysis methodology, 1999.
2. Code of Federal Regulations: CFR Chapter 40 Section 58, Appendix E "Probe and Monitoring Path Siting Criteria for Ambient Air Quality Monitoring"
3. DAQ: Quality Assurance Project Plan for the Field Sampling Plan for Ambient Air Volatile Organic Compound Monitoring in Claymont, DE

Appendix A

List of 58 Volatile Organic Compounds analyzed for by Eurofins

- | | | | |
|-----|--|-----|---------------------------------------|
| 1. | 1,1,1-Trichloroethane | 30. | Ethylbenzene |
| 2. | 1,1,2,2-Tetrachloroethane | 31. | Hexachlorobutadiene |
| 3. | 1,1,2-Trichloroethane | 32. | Isopropylbenzene |
| 4. | 1,1-Dichloroethane | 33. | Methyl tert-butyl ether |
| 5. | 1,1-Dichloroethene | 34. | m-Xylene & p-Xylene |
| 6. | 1,2,4-Trichlorobenzene | 35. | Naphthalene |
| 7. | 1,2,4-Trimethylbenzene | 36. | o-Xylene |
| 8. | 1,2-Dibromoethane (EDB) | 37. | Styrene |
| 9. | 1,2-Dichloro-1,1,2,2-tetrafluoroethane | 38. | trans-1,2-Dichloroethene |
| 10. | 1,2-Dichlorobenzene | 39. | trans-1,3-Dichloropropene |
| 11. | 1,2-Dichloroethane | 40. | Vinyl acetate |
| 12. | 1,2-Dichloropropane | 41. | Vinyl bromide |
| 13. | 1,3,5-Trimethylbenzene | 42. | Vinyl chloride |
| 14. | 1,3-Butadiene | 43. | Isopropyl alcohol |
| 15. | 1,3-Dichlorobenzene | 44. | Acetone |
| 16. | 1,4-Dichlorobenzene | 45. | Chloromethane |
| 17. | 1,4-Dioxane | 46. | Tetrahydrofuran |
| 18. | 4-Methyl-2-pentanone (MIBK) | 47. | Methylene Chloride |
| 19. | Benzyl chloride | 48. | 2-Butanone (Methyl Ethyl Ketone) |
| 20. | Bromodichloromethane | 49. | Trichlorofluoromethane |
| 21. | Bromoform | 50. | Carbon disulfide |
| 22. | Bromomethane | 51. | Dichlorodifluoromethane |
| 23. | Chlorobenzene | 52. | Hexane |
| 24. | Chloroethane (Methyl Chloride) | 53. | Toluene |
| 25. | Chloroform | 54. | Benzene |
| 26. | cis-1,2-Dichloroethene | 55. | Tetrachloroethene |
| 27. | cis-1,3-Dichloropropene | 56. | Carbon tetrachloride |
| 28. | Cyclohexane | 57. | Trichloroethene |
| 29. | Dibromochloromethane | 58. | 1,1,2-Trichloro-1,2,2-trifluoroethane |