AIR POLLUTION
CONTROL DISTRICT

AIR TOXICS MONITORING REPORT

JULY 2020 - JUNE 2021

From the Director

Our air monitoring section is a nationwide leader, not only because they work with diligence and precision, but because they are willing to utilize new equipment, methods, and practices to collect more data on Louisville's air than ever before.

Data is powerful. In the early 2000s monitoring data showed that Louisville's air quality was unacceptable. Residents and community groups used this data to support their calls for change and in response the APCD used it as the basis for the Strategic Toxic Air Reduction (STAR) Program, one of the nation's most stringent local regulatory programs for air toxics, and regulated sources took steps to reduce their emissions. The new data shared in this report allows us all to understand Louisville's progress since, and informs our work as we continue to implement the laws and programs that improve Louisville's air quality.

Our work is a team effort, and I would like to recognize the work of Air Monitoring Program Manager Billy Dewitt, Data Analyst & QA/Air Toxics Supervisor Bryan Paris, and Air Monitoring Chemist Andrea Cooley along with all of the other supervisors, scientists, analysts, and technicians that keep our air monitoring network running: Brian Ahlers, Jesse Carpentier, Tom Lobb, Natalie Nuss, Starlet Raj, Shane Stiles, Laura Wilson, and Dongmei Zhang.

With my thanks to all,

Rachael Hamilton, Director

Contents

Background

History

Residents have long been impacted by odors and other air pollution issues attributed to emissions from Rubbertown, an industrial complex in west Louisville which received its nickname from tire and synthetic rubber plants that were built there during World War II, but now has plants that produce a wide variety of chemicals and materials (See Appendix page 22, Map of Rubbertown).

Between April 2000 and April 2001, the Louisville Metro Air Pollution Control District (APCD), the US Environmental Protection Agency (EPA), the Kentucky Division for Air Quality, and the University of Louisville worked with the West Jefferson County Community Task Force (WJCCTF) to conduct an air monitoring study of toxic air pollution at twelve sites in western Louisville and Jefferson County. The purpose of the study was to determine if residents were being exposed to airborne concentrations of toxic air pollutants that posed unacceptable risks to human health.

In April 2003, the *West Louisville Air Toxics Study Risk Management Plan, Part 1: Process and Framework* was issued. The Risk Management Plan established the process to identify the sources of the pollutants measured above target risk levels, the options available to lower the ambient concentrations for these pollutants, and the elements of a risk communication plan and process to inform the community on relevant issues and activities.

The final *West Louisville Air Toxics Risk Assessment Report* was completed in October 2003. The report details the methods and findings of a risk assessment conducted by Sciences International, Inc. on the data collected in the study.

This process, referred to as the West Louisville Air Toxics Study (WLATS), found that Louisville's air had unacceptably high levels of toxic air pollutants. Following the release of the report along with studies done by EPA and others, the APCD began the process of developing a comprehensive regulatory package to address Louisville's toxic air pollution.

On June 21, 2005, the Strategic Toxic Air Reduction (STAR) Program was officially implemented by a set of regulations adopted by the Louisville Metro Air Pollution Control Board. The STAR Program provides a framework for assessing and addressing toxic air pollution in Louisville Metro, referred to in the regulations as toxic air contaminants (TACs). Since the program's inception, emissions of Category 1 TACs (monitored during WLATS at a concentration representative of a cancer risk greater than 1 in one million or a non-cancer Hazard Quotient (HQ) greater than 1.0.) have decreased by about 96%. Emissions of all categories of TACS have dropped almost 80%.

After the completion of WLATS, the University of Louisville and the WJCCTF continued

sampling with canisters at select sites from 2005-2013.

Air Monitoring

The APCD's air monitoring network measures air quality at five sites throughout the city. The monitoring data collected include pollution concentrations, radioactivity, and general meteorological information.

The primary pollution levels measured are for **"criteria" pollutants**, six commonly occurring pollutants that have been deemed harmful to public health and the environment through the Clean Air Act. The monitored levels of these pollutants are used to determine the Air Quality Index (AQI) as well as our area's attainment with National Ambient Air Quality Standards (NAAQS). The pollutants are: ground-level ozone (O_3), Particle Pollution (PM_{10} and $PM_{2.5}$), carbon monoxide (CO), sulfur dioxide (SO_2), nitrogen dioxide (NO_2), and lead[1] (Pb). The monitoring methods used for criteria pollutants are strictly regulated by EPA and standardized across the country.

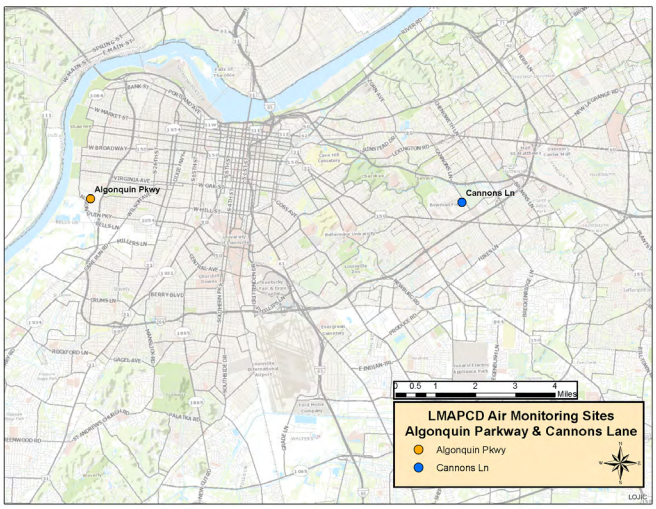
An **air toxic,** also referred to as a hazardous air pollutant (HAP) by EPA or toxic air contaminant (TAC) by the APCD's STAR Program, is any air pollutant that is not a "criteria" pollutant but may reasonably be anticipated to cause serious chronic or acute health effects in humans at certain levels. Air toxics have traditionally been much more difficult and expensive to monitor for than the criteria pollutants. Monitoring for air toxics in Louisville is not required by EPA, and monitoring methods across the country are less standardized than criteria pollutant monitoring.

[1] In 2016, the EPA authorized the APCD to discontinue active monitoring of airborne lead (Pb) because levels are far below the NAAQS and are not expected to increase at the present time.

Project Overview

The data featured in this report are produced through a project by the APCD to utilize a field-deployable automated Gas Chromatograph (auto-GC) and provide concentrations of a specific set of air toxics, referred to here as "target compounds" (see Appendix page 24, Information on Target Compounds). This new technology, developed through EPA research, can collect data in near real-time on concentrations of volatile organic compounds (VOCs), which are a large class of compounds that have varied impacts on human health and the environment. Monitoring for air toxics is a new application of auto-GC technology, and APCD staff have played a national role in the use and development of the equipment.

Auto-GCs have now been added to two APCD air monitoring sites. The first was installed at the APCD's Algonquin Parkway site with the sole purpose of monitoring for the APCD's target air toxics VOCs. The other was later installed at the APCD's Cannons Lane site as part of EPA's Photochemical Assessment Monitoring Station (PAMS) network, which measures ozone pollution precursors, including photochemically reactive VOCs, and meteorological measurements. As of February 2023, APCD staff added the ability to report matching target compounds from the Algonquin and Cannons Lane sites. A map and more information on the timeline of the work at each site are included below.



Algonquin Parkway

The APCD's Algonquin Parkway site is located in western Louisville. Used as a "maximum impact site" during the West Louisville Air Toxics Study, the site is located directly downwind of the predominant wind direction passing over the Rubbertown industrial complex (see Appendix page 22, Map of Rubbertown).

The auto-GC was installed at the APCD's Algonquin Parkway site in September 2017. In January 2018, an Air Monitoring Chemist was hired to operate the equipment and evaluate the

data. From February to August 2018 the APCD completed field evaluation of the equipment to determine how well the system worked. Based on field testing and feedback from the APCD, the vendor removed the equipment in two phases to make modifications and upgrades. From July to December 2019 staff completed more testing of the auto-GC and refinement of its data management system.

In January of 2020, staff implemented a full set of QC (Quality Control) and QA (Quality Assurance) procedures. These were created through discussions with a national work group and based on the APCD's own experience with the equipment.

In fall of 2020, staff completed full standard operating procedures and a quality assurance project plan, which were submitted to EPA. The first Air Toxics Data Summary Report was provided to the Air Pollution Control Board in January of 2021, using data collected in September 2020.

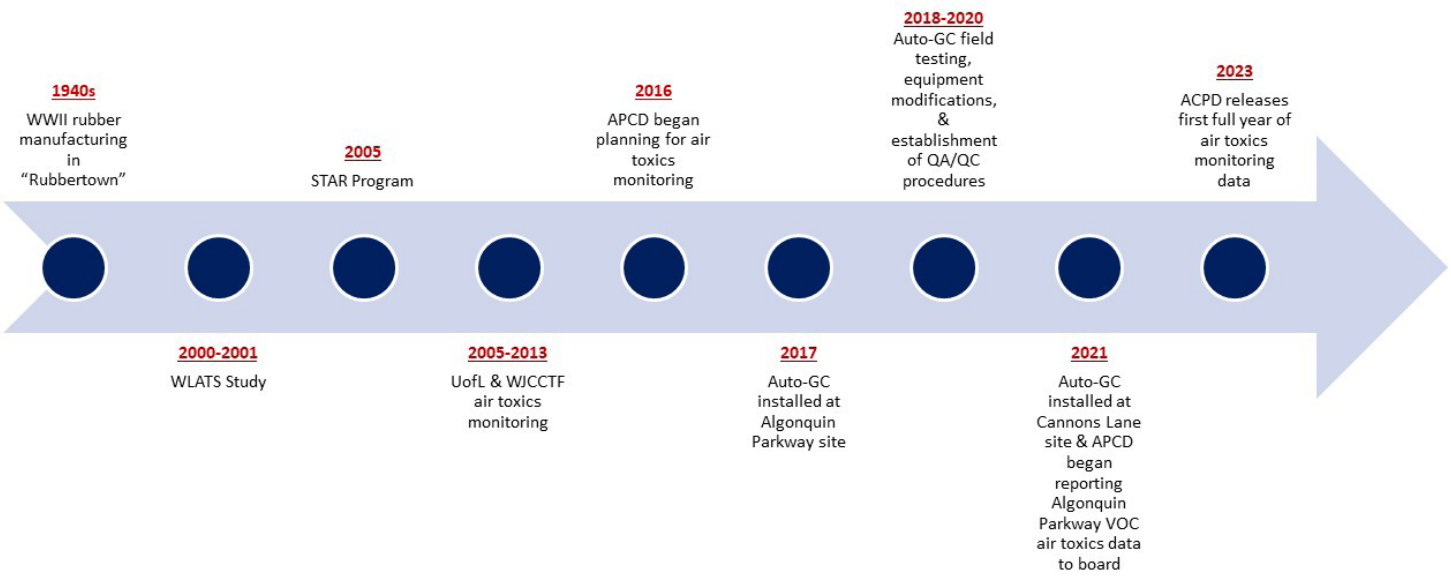
The data used in this report was collected from the Algonquin Parkway site's auto-GC from July 2020 to June 2021.

Cannons Lane

The auto-GC was installed at the APCD's Cannons Lane site in January 2021. From May to June 2021, quality control equipment was acquired and the auto-GC equipment was prepared for routine analysis. From July to August 2021, the auto-GC collected data for EPA's Photochemical Assessment Monitoring Station (PAMS) season.

Following the 2021 PAMS season the auto-GC system was inspected on a biweekly basis to maintain readiness for 2022 PAMS season, which occurred from July to August 2022. Annual maintenance occurred in May and June 2022.

Since September 2022 the auto-GC has continued routine data collection and validation. In February 2023, the APCD added quality control procedures to allow reporting of all APCD target compounds from both the Algonquin and Cannons Lane sites.



Data Collection & Reporting

Previous air toxics monitoring projects in Louisville, such as the West Louisville Air Toxics Study (WLATS) have used sampling methods that capture a "snapshot" of what is in the air. This involves physically setting out and collecting canisters, which are then shipped to a lab for analysis. The canisters fill with ambient air over a period of time, often 24 hours, which doesn't allow for recording of short term spikes.

The APCD field-deployable auto-GC measures gases by separating them out, or "speciating" them, in the field. The equipment can be configured to analyze a specific set of Volatile Organic Compounds (VOCs) and automatically sample the air at set intervals. The equipment is networked to provide continuous near-real time data.

	West Louisville Air Toxics Study (2001-2002)	Auto-GC (2017-Present)
Sampling Period	Sample for 24 hour period	40 minute sample each hour
Sampling Frequency	One sample per 12 day period	20-21 Ambient Samples per day

A 40-minute sampling period begins near the top of each hour. Simultaneously, the auto-GC separates and measures the compounds in the sample from the previous hour. The system collects 20-21 ambient samples of each target pollutant each day.

Three to four hours of each day are taken to perform quality control checks to assess the equipment's accuracy and that it is working properly. This includes using "zero air system blanks" to assess the cleanliness of the system as well as toxics and PAMS standards to check the retention times and quality control of the system. These standards work by putting known quantities of the pollutants of interest in the system to double check that the system is identifying them at proper quantities. This is followed by another "zero air system blank" to clean out the system.

On a daily basis, the auto-GC system is remotely checked to ensure it is in good working order and no spikes have been detected. Any valid spikes from compounds of concern are evaluated and reported to APCD management for follow up by other APCD staff as appropriate. On a weekly basis, the previous week's quality control checks are reviewed to make sure the equipment is identifying and measuring each compound correctly. On an ongoing basis, these quality control checks are used to assist in ambient data review.

While the auto-GC systems are automated, manual post processing of data is also required on a routine basis. This is due to constantly changing atmospheric conditions, such as humidity,

which can interfere with the automated analytical methods that the instrument relies upon. The large number of compounds analyzed allow for some instances of interferences between compounds (co-elution). As such, a trained chemist constantly monitors the system and post processes a significant portion of the thousands of data points generated every week.

On a weekly basis, staff:

- Run a series of checks to ensure ambient and quality control data are complete, accurate, and representative of the conditions when measurements were made.
- Review systematic and data errors from the auto-GC.
- Review quality control check results.

On a monthly basis, staff:

- Compare monthly averages of the data to assess the bigger picture and spot outliers.
- Calculate the percent of data completeness.
- Place Air Quality System (AQS) qualifier and null codes on data to provide data quality information to end user (see Appendix page 28, APCD Technical Note on Auto-GC VOC Data Validation & Data Availability).
- Make sure post-processed files are documented appropriately.
- Evaluate trends.

Data Quality Scores

Data Quality Score (DQS) is an APCD-derived scoring system that is used to help communicate the confidence and quality of the VOC data to the public and data users.

Data Quality Score Guide	
Green	High confidence in peak identification. No significant coelution[1] or carryover[2] concerns.
Yellow	Less confidence in peak identification or quantification due to coelution[1], carryover[2] or other data quality concerns.
Red	Peak cannot be confidently identified in ambient chromatograms.

A DQS provides a general indication of confidence and data quality after all quality control and assurance processes have been implemented. More detailed data quality issues are documented as part of routine data review and the data validation process. While a single sample from the auto-GC produces data for multiple compounds, the DQS can vary significantly for each compound.

While some compounds can be accurately measured and reliably quantified by the system with little human intervention, other compounds require significant analysis and post processing by a trained chemist. Even with additional effort from a trained chemist, some compounds are more reliable than others due to unavoidable interferences. **Raw DQS** is the quality of the near real time raw data from the instrument. **Post Processed DQS** is the quality of the data after manual processing by APCD staff. The table below shows the Raw and Post Processed DQS for the target compounds during the 12 month period of July 2020-June 2021.

DQS for auto-GC Long-Term Averages July 2020 - June 2021				
APCD Target Compound	**Raw DQS**	**Post DQS**	**Why isn't Raw DQS green?**	**Why isn't Post DQS green?**
1,3-Butadiene	yellow	green	retention time shifting[3]	
1,4-Dichlorobenzene	red	red	carryover[2]	carryover[2]
Acrylonitrile	red	red	coelution[1]	coelution[1]
Benzene	green	green		
Bromoform	yellow	yellow	coelution[1]	coelution[1]
Carbon Tetrachloride	red	red	coelution[1]	coelution[1]
Chloroform	yellow	yellow	coelution[1]	coelution[1]
Ethyl Acrylate	yellow	yellow	coelution[1] & carryover[2]	coelution[1] & carryover[2]
Ethylbenzene	green	green		
Methyl Methacrylate	yellow	yellow	carryover[2]	carryover[2]
Styrene	green	green		
Tetrachloroethylene	yellow	yellow	carryover[2]	carryover[2]
Toluene	green	green		
Trichloroethylene	yellow	yellow	coelution[1]	coelution[1]
Vinyl chloride	yellow	yellow	retention time shifting[3] and coelution[1]	coelution[1]

[1] - **Coelution** happens when more than one pollutant is measured at the same time and mistakenly identified as a single pollutant.

[2] - **Carryover** is when pollutants are not properly removed after previous samples.

[3] - **Retention time** is the amount of time it takes a compound to be separated from the other compounds and then detected. A retention time window is the time range in which a compound is expected to be detected by the auto-GC. If the auto-GC detects a peak in that window, then the system will identify the peak and calculate the concentration based on the peak area. **Retention time shifting** is when a peak moves out of its assigned retention time window and is no longer properly identified. When this happens, the chemist must post-process those data to ensure peaks are properly identified and calculated results are correct.

The DQS for a compound can change over time as the APCD and the manufacturer make modifications to the auto-GC system to improve performance and reliability.

Confident identification of **Carbon Tetrachloride** and **Acrylonitrile** was a challenge due to coelution with unidentified compounds. Due to these significant data quality concerns, quality controlled data will no longer be produced for these compounds. Raw data will continue to be checked for any spikes.

1,4-Dichlorobenzene has been a challenge due to data quality issues related to interference/ carryover from the routine standards. The data validation approach has changed over time in an attempt to address this challenge and **1,4-Dichlorobenzene** is now listed with a yellow DQS.

Since the 2020-2021 data were collected, **Methyl Methacrylate** and **Tetrachloroethylene** have seen an improvement in their DQS and other compounds like **Ethyl Acrylate** and **Vinyl Chloride** have seen some data quality concerns improve. The table below shows the Raw and Post Processed DQS for the target compounds as of February 2023.

New DQS February 2023				
APCD Target Compound	**Raw DQS**	**Post DQS**	**Why isn't Raw DQS green?**	**Why isn't Post DQS green?**
1,3-Butadiene	yellow	green	retention time shifting	
1,4-Dichlorobenzene	yellow	yellow	carryover	carryover
Acrylonitrile[1]	N/A	N/A	N/A	N/A
Benzene	green	green		
Bromoform	yellow	yellow	coelution	coelution
Carbon Tetrachloride[1]	N/A	N/A	N/A	N/A
Chloroform	yellow	yellow	coelution	coelution
Ethyl Acrylate	yellow	yellow	coelution	coelution
Ethylbenzene	green	green		
Methyl Methacrylate	green	green		
Styrene	green	green		
Tetrachloroethylene	green	green		
Toluene	green	green		
Trichloroethylene	yellow	yellow	coelution	coelution
Vinyl chloride	yellow	yellow	retention time shifting	coelution

[1] No longer producing quality assured data.

For more on project changes and adjustments, see Appendix page 28, APCD Technical Note on Auto-GC VOC Data Validation & Data Availability.

Board Reports

As data collection and quality assurance procedures are completed for calendar months of air toxics data, concentrations and other relevant information are provided to the Air Pollution Control Board in a report at their monthly meeting and posted to the APCD website.

Compound[T]	Ambient Data Summary				STAR BACs	
	Monthly Summary[D]			Long Term Average[L]	STAR Cancer BAC_C*	STAR Chronic NonCancer BAC_{NC}*
	Monthly Average	Max 24hr Avg	% Data Recovery			
1,3 Butadiene	0.13	0.30	76.8	0.13	0.02	0.90
1,4-Dichlorobenzene	0.24	0.31	2.2	0.14	0.02	133.10
Acrylonitrile	0.00	0.07	82.6	0.02	0.01	0.92
Benzene	0.23	0.69	82.6	0.22	0.14	9.40
Bromoform	0.00	0.00	82.5	0.00	0.09	6.77
Carbon_Tetrachloride	0.28	1.11	81.5	0.36	0.03	0.02
Chloroform	0.01	0.09	82.4	0.02	0.01	61.48
Ethyl_Acrylate	0.02	0.14	76.8	0.03	N/A	7.33
Ethylbenzene	0.10	0.32	82.5	0.08	0.09	230.00
Methyl_Methacrylate	0.04	0.21	79.0	0.08	N/A	171.00
Styrene	0.03	0.09	81.7	0.04	0.40	234.75
Tetracholoroethylene	0.02	0.10	74.7	0.03	0.57	5.90
Toluene	0.93	2.71	82.6	0.75	N/A	1327.60
Trichloroethylene	0.00	0.00	82.2	0.00	0.04	0.37
Vinyl_Chloride	0.00	0.03	75.1	0.02	0.09	39.14

Monthly average is the average concentration over the month of validated data. **Max 24-hour average** is the highest concentration over the course of a 24-hour period in the month of validated data. **Long-term average** represents the average for the most recent 12 month period of validated data.

% Data Recovery represents the percentage of time that valid ambient data are available compared to the maximum amount of time in a given time period (*e.g.,* day, week, month, year). Due to required quality control checks for the auto-GC system, the maximum possible data recovery in a given day, week, or month is typically 87.5% (at a minimum, 3 hours each day are not available to represent ambient conditions due to quality control checks that the system is undergoing).

STAR BAC (benchmark ambient concentration) refers to the concentration of a toxic air contaminant (TAC) that is determined pursuant to APCD Regulation 5.20 to meet the environmental acceptability goals of APCD Regulation 5.21.

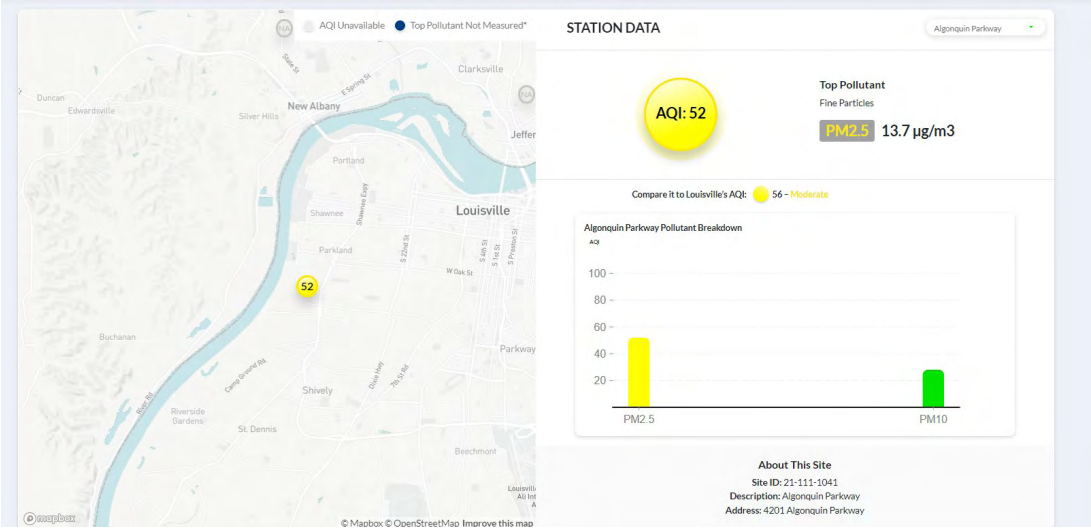
STAR Cancer BAC_c is the concentration of a TAC that represents an additional lifetime cancer risk of one in a million.

STAR Chronic Cancer BAC$_{NC}$ is the concentration of a TAC at or below which no adverse effects are expected. The BAC$_{NC}$ represents a Hazard Quotient of 1.0. With the exception of ethyl acrylate, the BAC$_{NC}$ is averaged on an annual basis; ethyl acrylate is averaged on a 24-hour basis.

A table of BACs used in the STAR program is available here.

Near Real-Time Data

While the data collected are not fully quality assured in real-time, they can help the APCD analyze short-term pollution events and share concentrations of select target compounds (those with highest confidence in raw data) through Louisville Air Watch, the APCD's real-time air monitoring website.



A Detailed Breakdown of Data

For more information on Toxics Air Monitoring, please visit APCD's Air Quality Monitoring page

	Hourly Value	Unit
1,2,3-Trimethylbenzene:	0	Parts per billion
1,2,4-Trimethylbenzene:	0.01	Parts per billion
2,2,4-Trimethylpentane:	0.03	Parts per billion
3-Methylpentane:	0.03	Parts per billion
Benzene:	0.12	Parts per billion
Cyclohexane:	0	Parts per billion
Ethylbenzene:	0.01	Parts per billion
Isobutane:	0.18	Parts per billion
M-Xylene + P-Xylene:	0.03	Parts per billion
Methyl_Methacrylate:	0.18	Parts per billion
N-Butane:	0.54	Parts per billion
O-Ethyltoluene:	0	Parts per billion
O-Xylene:	0.01	Parts per billion
P-Ethyltoluene:	0	Parts per billion
Propane:	3.09	Parts per billion
Styrene:	0	Parts per billion
Tetrachloroethylene:	0.17	Parts per billion
Toluene:	0.08	Parts per billion

Data, Reports, & Analysis

Volatile Organic Compound Data Summary for July 2020 - June 2021

The data below are part of a project by the Louisville Metro Air Pollution Control District to provide air toxics concentrations using a field-deployable auto-GC. The concentrations are produced by new applications of technology that continue to be evaluated. This report summarizes monitored data from select compounds collected by the APCD's auto-GC instrument located at the Algonquin Parkway site. Hourly measurements are summarized as period averages and maximum 24-hour concentrations in parts per billion by volume (ppbV) for the period of interest. Longer term averages[L] may also be provided for comparison.

The APCD uses its air toxics monitoring data in routine monthly screenings for potential impacts from air toxics. On daily basis, any valid spikes from compounds of concern are evaluated and reported to APCD management for follow up by other APCD staff as appropriate. Concentrations will be compared to Benchmark Ambient Concentrations (BACs) under the Strategic Toxic Air Reduction (STAR) program and may be used to investigate emission sources and in future risk assessments, like the West Louisville Air Toxics Study (WLATS). A risk assessment may help determine how residents living, working, and going to school in the area may be exposed to harmful levels of ambient air toxics concentrations; identify what, if any, increased health risks they may face; and identify if additional emission reductions may be necessary. In some cases, the APCD may conduct additional air toxics monitoring as part of a special study.

This data summary is based on preliminary data. The data are subject to change based on findings in subsequent data validation evaluation. Compounds shown in green reflect higher confidence in data quality while those shown in yellow and red[T] have lower confidence. All values are reported to two decimal places using standard rounding conventions; the % data recovered is provided as an initial indicator of representativeness for the intended time period.

Compound[T]	Ambient Data Summary				STAR BACs	
	Period Summary[D]			Long Term Average[L]	STAR Cancer BAC_C	STAR Chronic NonCancer BAC_{NC}
	Period Average	Max 24hr Average	% Data Recovery			
1,3 Butadiene	0.13	1.42	69.6	0.13	0.02	0.90
1,4-Dichlorobenzene	0.14	0.64	40.3	0.14	0.02	133.10
Acrylonitrile	0.02	0.45	67.8	0.02	0.01	0.92
Benzene	0.22	1.4	75.9	0.22	0.14	9.40
Bromoform	0.00	0.02	75.7	0.00	0.09	6.77
Carbon Tetrachloride	0.35	1.35	60.8	0.35	0.03	0.02
Chloroform	0.02	0.59	75.4	0.02	0.01	61.48

Ethyl Acrylate	0.03	0.81	73.1	0.03	N/A	7.33
Ethylbenzene	0.09	0.36	75.9	0.09	0.09	230.00
Methyl Methacrylate	0.08	0.73	72.7	0.08	N/A	171.00
Styrene	0.04	0.21	75.2	0.04	0.40	234.75
Tetracholoroethylene	0.04	0.29	71.8	0.04	0.57	5.90
Toluene	0.81	3.13	75.9	0.81	N/A	1327.60
Trichloroethylene	0.00	0.01	75.5	0.00	0.04	0.37
Vinyl Chloride	0.01	0.69	69.2	0.01	0.09	39.14

Data Quality Score Guide		
Red	Yellow	Green

[T] Compounds in yellow have moderate confidence in data quality while compounds in red have low confidence in data quality due to interference or contamination concerns. More on Data Quality Scores is available in the **Data Collection Procedures** section of this report.

[L] Long Term Average represents the average for a 12 month period of validated data. In this case, the long term average represents the same time frame as the target period (July 2020 - June 2021), therefore the concentrations are the same.

[D] Notes:

*As used in the Strategic Toxic Air Reduction (STAR) Program, "benchmark ambient concentration" (BAC) means the concentration of a toxic air contaminant (TAC) that is determined pursuant to Regulation 5.20 to meet the environmental acceptability goals of Regulation 5.21. BACs are reported in micrograms per cubic meter ($\mu g/m^3$). The BACs above have been converted from micrograms per cubic meter ($\mu g/m^3$) to parts per billion by volume (ppbV) at 25 degrees Celsius and 1 atmosphere.

The BAC for a carcinogen (BAC_C) is the concentration of a TAC that represents an additional lifetime cancer risk of one in one million (1x10-6). The BAC_C is averaged on an annual basis.

The BAC for the non-carcinogenic effects of a TAC (BAC_{NC}) is the concentration of a TAC at or below which no adverse effects are expected. The BAC_{NC} represents a Hazard Quotient of 1.0. With the exception of ethyl acrylate, the BAC_{NC} is averaged on an annual basis; ethyl acrylate is averaged on a 24-hour basis.

Table of BACs used in the STAR program.

Compounds are “Category 1” TAC under the STAR Program except Ethylbenzene, which is a Category 2 TAC, and Styrene, Methyl Methacrylate, and Ethyl Acrylate, which are Category 4 TACs. The non-category 1 TACs were selected because they are highly photochemically reactive in the formation of ozone pollution or because of their potential to create objectionable odors (See Appendix page 24 for more on TAC categories).

Additional Explanation and Details for Data Summary

1,4-Dichlorobenzene has been a challenge due to data quality issues related to interference/ carryover from the routine standards. This often results in the inability to accurately measure ambient concentrations and the data validation approach has changed over time in an attempt to address this challenge. The data for this compound should be interpreted with caution.

Confident identification of Carbon Tetrachloride and Acrylonitrile have been a challenge due to coelution with unidentified compounds. This often results in the inability to accurately measure ambient concentrations. The data for these compounds should be interpreted with caution. As a result, quality-assured data will no longer be produced for these compounds and their concentrations will not be included in the comparisons below. Raw data will continue to be checked for any spikes on a daily basis.

Comparison to West Louisville Air Toxics Study (2000-2001)

The last significant air toxics study completed in Louisville was the West Louisville Air Toxics Study (WLATS), completed between April 2000 and April 2001 (see Background pages 4-5). For more on the difference in data collection procedures between the current auto-GC and the WLATS, consult the Data Collection Procedures section of this report on pages 8-13.

The values in the table below represent the additional estimated lifetime cancer risk per one million people created by the ambient concentrations measured of each compound. All target compounds (see Appendix page 24, Information on Target Compounds) with estimated additional lifetime cancer risk values from WLATS and a sufficient data quality score from the current monitoring program are included in the table below. All other target compounds and Category 1 TACS are covered in the following "Other Notable Compounds" section.

The WLATS estimated cancer and non-cancer risk using a 95% UCL, a conservative statistical method, and the median. APCD has provided the annual average consistent with the averaging period used for the BAC_C in the STAR Program. The values below are provided for informational reference only

WLATS Measured Cancer Risk vs. auto-GC Cancer Risk

Compounds	WLATS 95% Cancer Risk 2000-2001[1]	WLATS Median Cancer Risk 2000-2001[2]	auto-GC Monitoring Cancer Risk 2020-2021[3]
1,3-Butadiene	500	57	7.0
Benzene	32	14	1.6
Bromoform	13	-	0.0
Chloroform	77	5.6	2.0
Tetrachloroethylene	12	4.9	0.1
Trichloroethylene	16	-	0.0
Vinyl Chloride	4.6	1.1	0.1

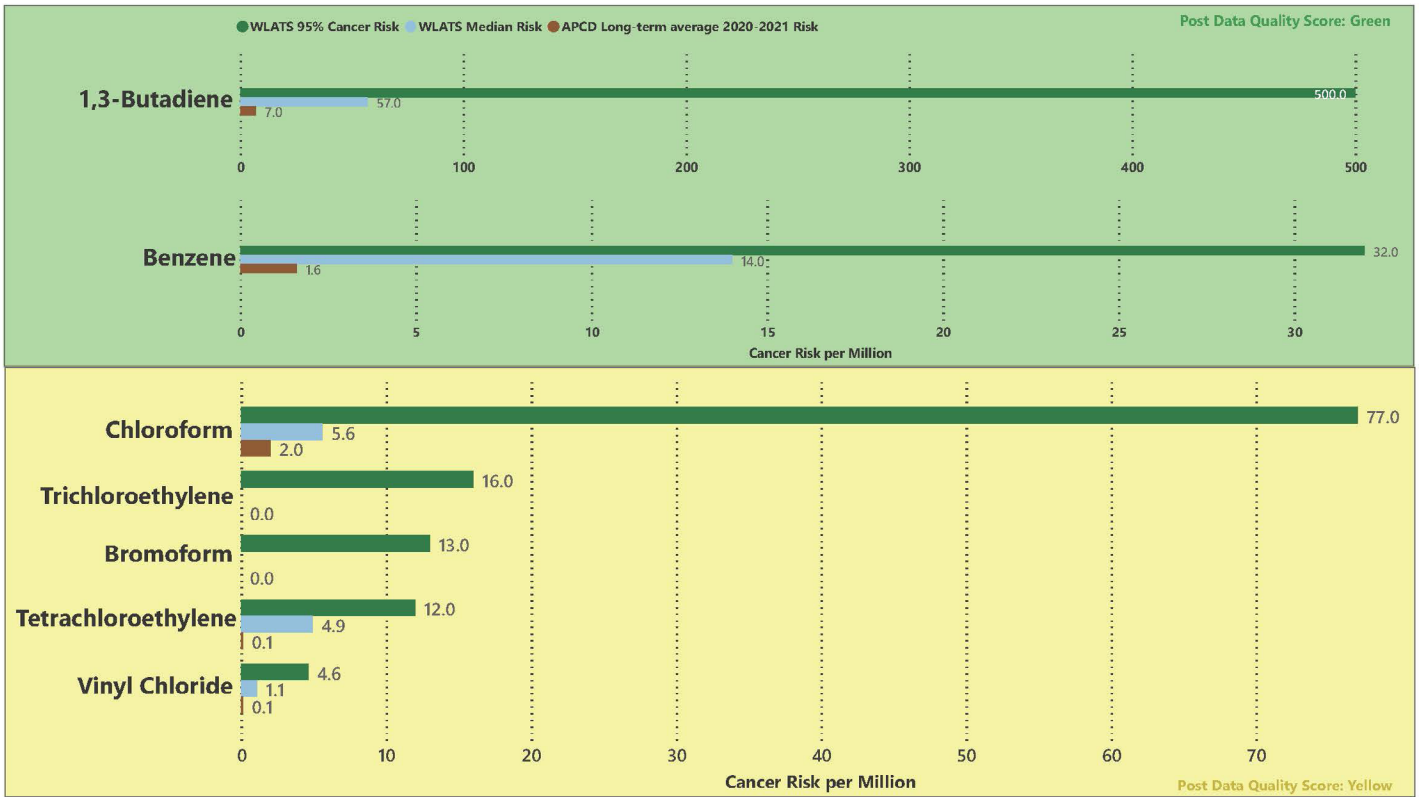
[1]Calculated using the 95% upper confidence limit (UCL) from the highest monitoring site during the West Louisville Air Toxics Study (2000-2001). This is meant to be conservatively high, and there is a 95% chance the actual risk is at or below this value.

[2]Calculated using the median air concentration at the highest site during the West Louisville Air Toxics Study (2000-2001).

[3]Calculated using the long-term average monitored at the APCD's auto-GC at the Algonquin Parkway Monitoring Site (2020-2021).

In the years since WLATS, there have been significant reductions in ambient concentrations of, and health-based risk produced by, many of the compounds listed in the table above. These improvements can broadly be attributed to the APCD's Strategic Toxic Air Reduction (STAR) program as well technological improvements for stationary and mobile sources of air pollution. Many process changes and control devices mentioned were the result of regulatory programs such as STAR. Below are some significant factors and considerations for each compound, followed by other notable compounds from WLATS not included in this table.

Risk Value from APCD auto-GC (2020-2021) and Values from WLATS (2000-2001)



- The addition of a control device at American Synthetic Rubber Company (ASRC) resulted in emissions reductions of **1,3 Butadiene.**
- In 2011, new EPA controls on gasoline significantly cut emissions of **Benzene** and **1,3 Butadiene**, as well as other air toxics like formaldehyde, acetaldehyde, acrolein, and naphthalene.
- Industrial use of compounds like **Bromoform** and **Tetrachloroethylene** has decreased.
- Controls were used to reduce emissions of **Chloroform** at Citgo, which released 3.04 tons in 2000 and .08 tons in 2021.
- **Trichloroethylene** emissions at Reynolds decreased from 1.85 tons in 2000 to 0 tons in 2021.
- Lubrizol emissions of **Vinyl Chloride** decreased from 2.29 tons in 2000 to 0.57 tons in 2021, Outer Loop Recycling and Disposal Facility decreased from 0.70 tons in 2000 to 0.036 tons in 2021; Oxy Vinyls emitted 1.94 tons in 2000 and has since closed.

Other Notable Compounds

- **Chloroprene** was a significant driver of estimated lifetime cancer and acute non-cancer risk during the WLATS and is currently regulated as a Category 1 TAC. Louisville's lone source of **Chloroprene** emitted 290 tons in 2000 and has since closed.
- Due to data-quality concerns **1,4-Dichlorobenzene** is not in the comparison table. Updated processes have improved the data quality for the compound, and newer data will allow for more confident comparison.
- Due to data quality concerns, quality assured data will no longer be produced for **Acrylonitrile**. There have been emissions reductions. Zeon Chemicals emitted 40.15 tons of **Acrylonitrile** in 2001 and .57 tons in 2021.
- Due to data quality concerns, quality assured data will no longer be produced for **Carbon Tetrachloride.** There is now little to no current use of **Carbon Tetrachloride**, but it has an 85-year atmospheric lifespan and remains in the air.
- Since the WLATS, **Ethyl Acrylate** was de-listed and is no longer evaluated as a cancer risk. Rohm & Haas emitted 4.63 tons in 2000 and .5 tons in 2021 and Altuglas emitted 5.32 tons in 2000 and .21 tons in 2016. Zeon emitted 3.94 tons in 2000 and 9.17 in 2021.
- There are 6 remaining Category 1 TACs that are not being monitored by the auto-GC. **Arsenic**, **Cadmium**, **Chromium**, and **Nickel** are metals (not VOCs) and therefore cannot be monitored by an auto-GC. **Formaldehyde** also cannot be detected by the auto-GC equipment. **Methylene Chloride** can be detected by the auto-GC but is difficult to confidently identify in ambient data due to VOC interferents and humidity impacts on the raw data.

Comparisons to Other Monitoring Sites Throughout the US

The charts below show the ambient concentration of each target compound measured in parts per billion by volume (ppbV) at other air monitoring sites throughout the country. The STAR Cancer BAC_c provided at the bottom of each table is the concentration of a compound that represents an additional lifetime cancer risk of one in one million ($1x10^{-6}$). To get the total cancer risk, divide the ambient concentration by the BAC_c.

The comparable sites were chosen to offer a range of populations, industry, etc. Details about site location, nearby sources, and sampling frequency are offered below. All data below was collected during calendar year 2021 unless otherwise noted.

Site	Compound (ppbV)				
	1,3 Butadiene	Benzene	Bromoform	Chloroform	Ethyl Acrylate
APCD Site	0.13	0.22	0.00	0.02	0.03
Site 1	0.133	0.223	-	-	-
Site 2	0.012	0.142	0.001	0.009	0.001
Site 3	0.041	0.232	0.030	-	-
Site 4	0.407	0.211	-	-	-
Site 5	0.032	0.229	-	0.002	-
Site 6	0.215	0.447	-	-	-
STAR BAC_c	0.02	0.14	0.09	0.01	N/A

Site	Compound (ppbV)			
	Ethylbenzene	Methyl Methacrylate	Styrene	Tetracholoroethylene
APCD Site	0.09	0.08	0.04	0.04
Site 1	0.056	-	0.158	0.004
Site 2	0.022	0.001	0.013	-
Site 3	0.051	0.000	0.041	0.044
Site 4	0.056	-	0.016	0.003
Site 5	0.052	0.007	0.015	0.005
Site 6	0.102	-	0.092	-
STAR BAC_C	0.09	N/A	0.40	0.04

Site	Compound (ppbV)		
	Toluene	Trichloroethylene	Vinyl Chloride
APCD Site	0.81	0.0	0.01
Site 1	0.345	0.004	0.0001
Site 2	0.151	-	0.684
Site 3	0.263	0.039	0.041
Site 4	0.412	-	0.123
Site 5	0.433	0.014	-
Site 6	0.514	-	-
STAR BAC_C	N/A	0.04	0.09

The APCD's Algonquin Parkway Air Monitoring Site is located in west Louisville. The site is located directly downwind of the predominant wind direction passing over the Rubbertown industrial complex and as such, is designed to measure the maximum impact from Rubbertown's industrial sources of pollution (see Appendix, page 22, Map of Rubbertown).

Site 1 is in a field on a middle school property in the middle of a residential neighborhood. Two miles west is an industrial area that has shipping depots. There is an industry area about three miles southwest. It has some freight depots, a landfill. About two miles southeast is another landfill. The international airport is about eight miles southwest. The property is southeast of downtown Atlanta by about seven miles. Samples at this site are taken one of every six days.

Site 2 is located south of an industrial complex in Calvert, KY made up of Ashland Chemical, Carbide Industries, Wacker Chemical Corporation, Arkema Inc, CC Metals and Alloys, Airgas, Cymetech, Lubrizol Corporation, and Westlake PVC Corporation. The nearest residential area is half a mile to the south. This station is sited to capture maximum vinyl chloride emissions and samples the air for 24-hours every twelfth day.

Site 3 is in a semi-industrial area near rail yards and a Marathon terminal. Several neighborhoods are nearby. Many schools are within a 1-2 mile radius. The station is around 7 miles southwest of downtown Detroit. This station, operated by Marathon, samples for VOCs one of every six days.

Site 4 is in Philadephia, PA and was sited to help assess the impact of the petroleum refinery on the local community. The area was identified by air quality modeling. Samples at this site are taken one of every six days.

Site 5 is at 16th St Health Center in Milwaukee, WI. This is a mostly residential area in a similarly sized city as Louisville, KY. Samples at this site are taken one of every six days.

Site 6 is located in a field next to a church and down the road from a school. It is about a mile from significant residential area. The monitor is about a mile and a half southeast of a large chemical manufacturer and a few miles north of a significant shipping and industrial corridor in Houston, Texas. This station operates an auto-GC with similar sampling times to APCD's.

Summary

The APCD's air monitoring section is a leader in utilizing advancing technologies to monitor the ambient air, and has successfully implemented air toxics monitoring via an auto-GC at two of its air monitoring sites, Algonquin Parkway and Cannons Lane. Since installation in 2017, APCD staff have made significant strides in understanding the use of this equipment and improving reliability of the data collected (see pages 11-14 and Appendix page 28, APCD Technical Note on auto-GC VOC Data Validation & Data Availability).

As an early adopter of the equipment, APCD staff has offered their knowledge of the auto-GC system to air monitoring agencies in the EPA's National PAMS Network that have installed similar equipment. During the initial year of field evaluation several issues were discovered that resulted in upgrades by the vendor to PAMS auto-GCs nationwide. The EPA Office of Research and Development (ORD) has also collocated several VOC monitoring and sampling technologies at the APCD's Algonquin Parkway site in order to improve understanding of new VOC monitoring technologies and compare results to the APCD's auto-GC data.

The auto-GC at the Algonquin Parkway air monitoring site, which is sited to measure the maximum cumulative impact from Rubbertown sources (see Appendix page 22, Map of Rubbertown), was installed in 2017. After significant testing and quality assurance work, its first year of quality-assured air toxics data was collected July 2020-June 2021 (see pages 14-15).

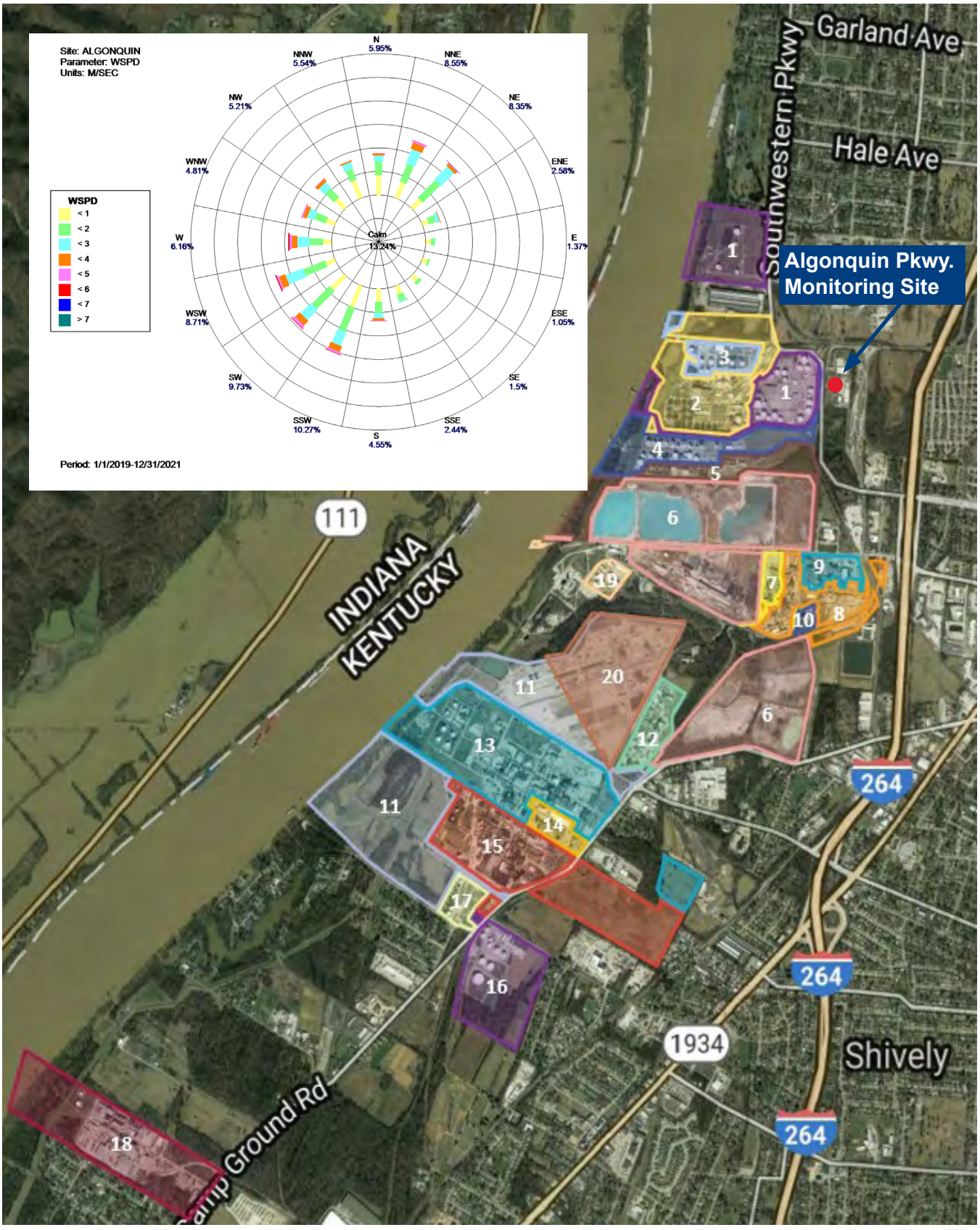
In the years since the West Louisville Air Toxics Study (2000-2001), there have been significant reductions in ambient concentrations of, and health-based risk produced by, many of the target compounds. These improvements can broadly be attributed to the APCD's STAR program as well technological improvements for stationary and mobile sources of air pollution (see pages 16-18).

The auto-GC at the Cannons Lane air monitoring site was installed in January 2021 and initially used for EPA PAMS monitoring. As of February 2023 this auto-GC will now collect air toxics data that can be used for comparison to the auto-GC at the Algonquin Parkway site. This will allow the APCD to greater understand the disparate impacts of air toxics pollution throughout Louisville, a known environmental justice issue. To provide some context on how different areas might be impacted by air toxics, a comparison to other monitoring sites has been made available in this report (see pages 18-20).

AIR POLLUTION
CONTROL DISTRICT

APPENDIX

Map of Rubbertown



Facility List

1 – MPLX Terminals - Algonquin (Gas Terminal)
2 – Morris Forman Water Quality Treatment Center
3 – Buckeye Terminals, LLC (Gas Terminal)
4 – Valero (Gas Terminal)
5 – Chevron (Gas Terminal)[1]
6 – Carbide Industries (Chemical Manufacturing)
7 – Polyone[2]
8 – Lubrizol Advanced Materials (Plastic and Resin Manufacturing)
9 – Zeon Chemicals Synthetic (Rubber Manufacturing)
10 – Recast Energy Industrial (Energy Service Provider)
11 – The Chemours Company (Chemical Manufacturing)
12 – Eckart America Corporation (Aluminum Smelting and Alloying)
13 – Rohm and Haas Kentucky (Plastics and Resin Manufacturing)
14 – Altuglas International (Acrylic Manufacturing)
15 – American Synthetic Rubber Co. (Synthetic Rubber Manufacturing)
16 – MPLX Terminals - Kramers Ln. (Gas Terminal)
17 – Citgo (Gas Terminal)
18 – Bakelite Synthetics (Formerly Hexion) (Plastics and Resin Manufacturing)
19 – TransMontaigne (Gas Terminal)
20 – DuPont Specialty Products USA (Chemical Manufacturing)

[1] Minor Source
[2]Closed

Description of Map

The above map shows the facilities located in the Rubbertown industrial area. The area gets its name from tire and synthetic rubber plants that were built there during World War II near existing refineries, but many of the facilities have changed over time and the area now produces a variety of chemicals and materials. The Algonquin Parkway Air Monitoring site is located to measure the maximum cumulative impact from Rubbertown's industrial sources of pollution.

The wind rose located in the top left corner of the map above shows where the wind at the Algonquin site came from over the course of 2019-2021 (Note: this graphic shows where the wind is coming from, not where the wind heads after it passes the site). The wind at Algonquin Parkway most often came from southwest, south-southwest, and west-southwest, all the general direction of Rubbertown in relation to the monitoring site.

Information on Target Compounds

All compounds below are regulated as Hazardous Air Pollutants by EPA and Toxic Air Contaminants regulated by the local Strategic Toxic Air Reduction (STAR) Program. The STAR Program regulates four categories of TACs (for comprehensive list see APCD Regulation 5.23).

Category 1 TACs includes the 17 compounds monitored in the 2000 to 2001 West Louisville Air Toxics Study at a concentration representative of a cancer risk greater than 1 in one million or a non-cancer Hazard Quotient (HQ) greater than 1.0.

Category 2 TACs are 19 compounds not included as Category 1 TACs that have an EPA Risk-Screening Environmental Indicators (RSEI) Full Model Relative Risk Score equal to or greater than 500 based on the 2002 Toxics Release Inventory (TRI) reported air emissions for Jefferson County.

Category 3 TACs include the compounds identified by the EPA pursuant to Section 112(k) of the Clean Air Act as presenting significant risks to public health in urban areas that are not included in Category 1 Toxic Air Contaminants or Category 2 Toxic Air Contaminants.

Category 4 TACs include the Hazardous Air Pollutants (HAPs) listed by the EPA pursuant to Section 112(b) of the Clean Air Act that are not included in Category 1 Toxic Air Contaminants, Category 2 Toxic Air Contaminants, or Category 3 Toxic Air Contaminants.

A group of these compounds are also monitored for through EPA's **Photochemical Assessment Monitoring Station (PAMS)** network. The main objective of the required PAMS sites is to develop a database of ground-level ozone pollution precursors and meteorological measurements to support ozone model development and track the trends of important ozone precursor concentrations.

1,3 Butadiene

STAR Category	Reason for Monitoring	PAMS Compound
Category 1 TAC	Identified in WLATS	Yes

Description: Used in plastic, chemical, and synthetic rubber manufacturing. Also comes from automobile exhaust, forest fires, wood combustion, cigarette smoke, and oil refining. (EPA Hazard Summary | NIH Compound Summary)

1,4-Dichlorobenzene

STAR Category	Reason for Monitoring	PAMS Compound
Category 1 TAC	Identified in WLATS	No

Description: Used to control moths, molds, mildews, as a deodorizer/disinfectant, as a

chemical intermediate, and to control tree-boring insects. (EPA Hazard Summary | NIH Compound Summary)

Acrylonitrile

STAR Category	Reason for Monitoring	PAMS Compound
Category 1 TAC	Identified in WLATS	No

Description: Used in acrylic and modacrylic fiber, plastic, synthetic rubber, and acrylic acid manufacturing. Also found in automobile exhaust and in cigarette smoke. (EPA Hazard Summary | NIH Compound Summary)

Benzene

STAR Category	Reason for Monitoring	PAMS Compound
Category 1 TAC	Identified in WLATS	Yes

Description: Used as a solvent for a variety of industries. Also found in gasoline, crude oils, automobile exhaust, jet fuel, cigarette smoke, and wood, coal, & oil combustion emissions. (EPA Hazard Summary | NIH Compound Summary)

Bromoform

STAR Category	Reason for Monitoring	PAMS Compound
Category 1 TAC	Identified in WLATS	No

Description: Used in mineral ore separation, as a laboratory reagent, and in the electronics industry. Also comes from water treatment and is naturally produced by phytoplankton & seaweeds. (EPA Hazard Summary | NIH Compound Summary)

Carbon Tetrachloride

STAR Category	Reason for Monitoring	PAMS Compound
Category 1 TAC	Identified in WLATS	Yes

Description: Historically used in refrigerant, propellant manufacturing, and as an industrial oil, lacquer, varnish, wax, and resin solvent. Can also come from landfills. Does not occur naturally. No longer used in area but has a long atmospheric lifespan. (EPA Hazard Summary | NIH Compound Summary)

Chloroform

STAR Category	Reason for Monitoring	PAMS Compound
Category 1 TAC	Identified in WLATS	No

Description: Used in the production of the refrigerant freon HCFC-22. Also comes from chlorination treatment of water, paper mills, hazardous waste sites, and landfills. In the past was used as an extraction solvent. (EPA Hazard Summary | NIH Compound Summary)

Ethyl Acrylate

STAR Category	Reason for Monitoring	PAMS Compound
Category 4 TAC	Local Emissions	No

Description: Used in paint, adhesive, textile, paper coatings, leather resins, & acrylic fiber manufacturing. No longer evaluated as a cancer risk. (EPA Hazard Summary | NIH Compound Summary)

Ethylbenzene

STAR Category	Reason for Monitoring	PAMS Compound
Category 4 TAC	Local Emissions	Yes

Description: Used primarily as a precursor in styrene production. Used as a solvent in varnishes, paints, adhesives, and inks. Is also used as a gasoline additive and can be found in automobile exhaust. Also found in asphalt, naphtha, pesticides, and tobacco smoke. (EPA Hazard Summary | NIH Compound Summary)

Methyl Methacrylate

STAR Category	Reason for Monitoring	PAMS Compound
Category 4 TAC	Local Emissions	No

Description: Primarily used in polymethyl methacrylate (PMMA), acrylic plastic, and resin production. Also used to manufacture prosthetics and as a cement in dentistry. (EPA Hazard Summary | NIH Compound Summary)

Styrene

STAR Category	Reason for Monitoring	PAMS Compound
Category 4 TAC	Local Emissions	Yes

Description: Produced to make products such as rubber, plastic, insulation, fiberglass, pipes, automobile parts, food containers, and carpet backing. Primarily used in polystyrene production and as an intermediate in resin and copolymer production. (EPA Hazard Summary | NIH Compound Summary)

Tetrachloroethylene

STAR Category	Reason for Monitoring	PAMS Compound
Category 1 TAC	Identified in WLATS	Yes

Description: Used in dry cleaning. Also used as a metal degreaser and a chemical intermediate. (EPA Hazard Summary | NIH Compound Summary)

Toluene

STAR Category	Reason for Monitoring	PAMS Compound
Category 2 TAC	Local Emissions	Yes

Description: Found in gasoline and jet fuels. Used as a solvent in paints, fragrances, adhesives, and inks. Also used as a precursor in benzene production and in polymer production. (EPA Hazard Summary | NIH Compound Summary)

Trichloroethylene

STAR Category	Reason for Monitoring	PAMS Compound
Category 1 TAC	Identified in WLATS	No

Description: Primarily used as an industrial degreaser. Also used as an extraction solvent for greases, oil, fats, waxes, and tar, an intermediate in chemical production, as a refrigerant, and in paint removers, adhesives, & carpet cleaners. (EPA Hazard Summary | NIH Compound Summary)

Vinyl Chloride

STAR Category	Reason for Monitoring	PAMS Compound
Category 1 TAC	Identified in WLATS	No

Description: Primarily used to make polyvinyl chloride (PVC), which is used to make other plastic and vinyl products. Can come from waste sites and groundwater contaminated by trichloroethylene. (EPA Hazard Summary | NIH Compound Summary)

Technical Note on Auto-GC VOC Data Validation & Data Availability

Drafted by Andrea Cooley & Reviewed by Bryan Paris
3/6/2023

Background & Discussion

Auto-GC systems generate a large amount of data and reviewing, correcting, and fully validating those data take a significant amount of time. With limited staffing and resources, the number of VOCs selected by the APCD for full data validation has evolved over time. In addition, as understanding of auto-GC issues such as carryover and coelution has improved, data validation decisions related to qualifying or invalidating those data have changed. The primary goal of the auto-GC VOC monitoring program is to report ambient values that are representative of the ambient conditions during sampling and to use qualifier or null codes, when appropriate, to communicate the quality of those results.These improvements in the data validation process, along with needed modifications to the list of compounds that APCD staff can successfully manage, have resulted in some changes (over time) to the data availability of compounds and their data quality. This document is intended to provide details on the timing of these changes as well as an explanation for these changes.

Air toxic studies were performed in Louisville in 2000-2001 (West Louisville Air Toxics Study) and 2005-2013 (University of Louisville & West Jefferson County Community Task Force[3]). In 2016, the APCD began discussing implementation of their own air toxics monitoring program using equipment that could continuously monitor VOCs and provide concentration data in near-real time. With the installation of an auto-GC at the Algonquin Parkway monitoring site, the APCD's air toxics monitoring program began in late 2017. During the next two years, a field-evaluation was performed, modifications to the system were made, and QA/QC procedures were developed. Beginning in January 2020, a subset of VOCs was selected for validation. With the acquisition of a toxics cylinder standard, a larger suite of compounds was validated beginning in July 2020. In November 2020 and January 2021, some improvements were made to the data validation process.

In January 2021, an additional auto-GC was installed at the APCD's Cannons Lane air monitoring site. Following instrument evaluation and modification, routine VOC data collection began in July 2021 at the Cannons Lane site.

With two auto-GC systems online and the desire to keep up with data review such that it could be provided in a timely manner, further refinements to the data validation process were made beginning in July 2022. The auto-GC VOC data validation process is continuously evaluated to balance the work associated with the complexity and large volume of data with APCD resources to provide quality data in a timely manner.

Methodological Changes Over Time & Associated Details

During the initial stages of auto-GC monitoring at the APCD's Algonquin Parkway air monitoring site, focus was given to validating 1,3-butadiene data as this compound was of greatest interest to the community. By January of 2020, the APCD had acquired a

Photochemical Assessment Monitoring Stations (PAMS) cylinder standard for routine QC checks and set up the Data Collection System and Central Database to house auto-GC VOC data for performing routine data validation. These important steps allowed the APCD to widen their focus beyond 1,3-butadiene and begin routine monitoring and validation of a larger suite of VOCs (Table 1), which included PAMS priority VOCs, 1,3-butadiene, and cyclohexane.

Table 1 - VOCs validated from January – June 2020
(27 in total - PAMS priority + 1,3-butadiene + cyclohexane)

C_2C_6 GC	C_6C_{12} GC
ethane	benzene
ethylene	cyclohexane
propane	2,2,4-trimethylpentane
propene	toluene
isobutane	ethylbenzene
n-butane	m-xylene + p-xylene
trans-2-butene	styrene
1-butene	o-xylene
cis-2-butene	m-ethyltoluene
isopentane	p-ethyltoluene
n-pentane	o-ethyltoluene
1,3-butadiene	1,2,4-trimethylbenzene
n-hexane	1,2,3-trimethylbenzene
isoprene	

Once a toxics cylinder standard was added to the auto-GC system at the Algonquin Parkway site, VOCs in Table 2 were selected for full data validation beginning July 1, 2020. These compounds included all PAMS priority VOCs, select PAMS optional VOCs, and select APCD target compounds.

Table 2 - VOCs validated from July 2020 – June 2021
(41 in total - PAMS priority, select PAMS optional, select APCD target compounds)

C_2C_6 GC	C_6C_{12} GC
ethane	acrylonitrile
ethylene	3-methylpentane
propane	chloroform
propene	benzene
isobutane	carbon tetrachloride
n-butane	cyclohexane
acetylene	ethyl acrylate
trans-2-butene	trichloroethylene
1-butene	2,2,4-trimethylpentane

vinyl chloride	methyl methacrylate
cis-2-butene	methylcyclohexane
isopentane	toluene
n-pentane	tetrachloroethylene
1,3-butadiene	ethylbenzene
2,3-dimethylbutane + 2-methylpentane	m-xylene + p-xylene
n-hexane	bromoform
isoprene	styrene
	o-xylene
	m-ethyltoluene
	p-ethyltoluene
	o-ethyltoluene
	1,2,4-trimethylbenzene
	1,4-dichlorobenzene
	1,2,3-trimethylbenzene

On November 1, 2020, following discussions with EPA (Dr. Ingrid George), acrylonitrile and carbon tetrachloride peak identifications were updated. Prior to this change, ambient acrylonitrile and carbon tetrachloride peaks were often misidentified. Therefore, average concentrations for these two compounds are likely biased high from January through October 2020.

On January 1, 2021, the APCD began invalidating ambient results that represented contamination due to carryover from toxics standard runs. Impacted VOCs include ethyl acrylate, methyl methacrylate, tetrachloroethylene, and 1,4-dichlorobenzene. 1,4-dichlorobenzene 2020 average is certainly biased high, and 2020 averages of ethyl acrylate, methyl methacrylate, and tetrachloroethylene are likely biased high.

Also, on January 1, 2021, the APCD updated data validation decisions based on zero air blank QC results. If a zero-air blank of a given compound exceeded acceptance criteria of 0.5 ppbC and ambient concentration was not greater than 3x's the highest bracketed zero air blank result, that ambient concentration was considered mostly contamination and invalidated. This change in data validation based on zero air blank QC results impacted select VOCs on the C_2-C_6 GC channel.

Table 3 provides a summary timeline of auto-GC VOC data validation approaches and modifications from January 2020 through June 2021.

Table 3 - Summary of Algonquin Auto-GC VOC Data Validation from January 2020 – June 2021

Date	VOCs Fully Validated	Notes
January 1, 2020	PAMS priority + 1,3-butadiene + cyclohexane	With QA/QC procedures in place and routinely testing a PAMS standard, began validating 27 VOC parameters.
July 1, 2020	PAMS priority Select PAMS optional Select APCD Target compounds	Began analyzing toxics standard. Starting point of full data validation of 41 VOC parameters. Attempted to keep up with data review on a weekly basis.
November 1, 2020		Updated peak identifications of acrylonitrile & carbon tetrachloride in ambient chromatograms. January-October 2020 acrylonitrile & carbon tetrachloride averages are likely biased high.
January 1, 2021 (through June 30, 2021)		Began invalidating for carryover from toxic standard runs. Impacted ethyl acrylate, methyl methacrylate, tetrachloroethylene, and 1,4-dichlorobenzene. 2020 averages for ethyl acrylate, methyl methacrylate, and tetrachloroethylene are likely biased high. 1,4-dichlorobenzene 2020 average is biased high. Updated evaluation of zero air blanks and invalidated if contamination represented most of ambient concentrations. Impacted select C_2-C_6 VOCs.

A second auto-GC was installed at the APCD's Cannons Lane air monitoring site in January 2021. Routine data collection began in July 2021 for the 2021 EPA PAMS season. The amount of data to review from two sites became unmanageable, and a new data validation approach was discussed beginning in May 2022. In an attempt to address the current backlog of VOC

data needing review, the following data review modifications were approved by the APCD management in June 2022:

1. For Algonquin Parkway July 2021 through May 2022 data, only select APCD target compounds will be reviewed and fully validated (Table 4).

2. For Cannons Lane July & August 2021 data, only PAMS priority VOCs & 1,3-butadiene will be reviewed and fully validated (Table 5). September 2021 through May 2022 Cannons Lane auto-GC data will not be reviewed.

3. Acrylonitrile and carbon tetrachloride are no longer fully validated beginning with July 2021 data set. Coelution of these compounds in ambient chromatograms makes proper peak identification very difficult. Because the toxics cylinder contains standards for these compounds, qualitative checks for acrylonitrile and carbon tetrachloride, as well as MIBK, will be performed. Any confirmed spikes will be investigated and reported to Toxics Supervisor and Air Monitoring Program Manager.

4. 1,4-dichlorobenzene will not be reviewed in July 2021 through May 2022 data sets because ambient concentrations routinely represent carryover from toxics standard runs. However, 1,4-dichlorobenzene data are available again starting July 2022 as efforts were successful in reducing the carryover / contamination from toxics standard runs.

5. Methylcyclohexane, a PAMS optional VOC, is no longer reviewed beginning with July 2021 data sets. Cyclohexane will continue to be reviewed as it can be used as a 1,3-butadiene source indicator at the APCD's Algonquin Parkway site.

Table 4 - Algonquin Parkway VOCs validated July 2021 – May 2022
(12 in total - select APCD target compounds)

C_2C_6 GC	C_6C_{12} GC
vinyl chloride	chloroform
1,3-butadiene	benzene
	ethyl acrylate
	trichloroethylene
	methyl methacrylate
	toluene
	tetrachloroethylene
	ethylbenzene
	bromoform
	styrene

Table 5 - Cannons Lane VOCs validated July – August 2021

(26 in total - PAMS priority VOCs + 1,3-butadiene)

C_2C_6 GC	C_6C_{12} GC
ethane	benzene
ethylene	2,2,4-trimethylpentane
propane	toluene
propene	ethylbenzene
isobutane	m-xylene + p-xylene
n-butane	styrene
trans-2-butene	o-xylene
1-butene	m-ethyltoluene
cis-2-butene	p-ethyltoluene
isopentane	o-ethyltoluene
n-pentane	1,2,4-trimethylbenzene
1,3-butadiene	1,2,3-trimethylbenzene
n-hexane	
isoprene	

EPA PAMS Season 2022 marked the beginning of another new phase in auto-GC VOC data validation for the APCD. This updated approach included adjusting the number of VOCs reviewed throughout the year and streamlining the review process.

A larger set of VOCs was selected for review during PAMS season at both Algonquin Parkway and Cannons Lane sites (Table 6), and a subset of VOCs was selected for year-round review at both sites (Table 7). 1,4-dichlorobenzene was added back to the list of fully validated VOCs because the toxics standard analysis frequency changed from daily to weekly reducing carryover and therefore number of invalidated results.

Table 6 - VOCs validated during PAMS season (June-August) beginning 2022[a,b]

(38 in total - PAMS priority, select PAMS optional, select APCD target compounds)

C_2C_6 GC	C_6C_{12} GC
ethane	3-methylpentane
ethylene	chloroform
propane	benzene
propene	cyclohexane
isobutane	ethyl acrylate
n-butane	trichloroethylene
acetylene	2,2,4-trimethylpentane
trans-2-butene	methyl methacrylate
1-butene	toluene
vinyl chloride	tetrachloroethylene

cis-2-butene	ethylbenzene
isopentane	m-xylene + p-xylene
n-pentane	bromoform
1,3-butadiene	styrene
2,3-dimethylbutane + 2-methylpentane	o-xylene
n-hexane	m-ethyltoluene
isoprene	p-ethyltoluene
	o-ethyltoluene
	1,2,4-trimethylbenzene
	1,4-dichlorobenzene
	1,2,3-trimethylbenzene

Table 7 - VOCs validated year-round beginning September 2022[b]
(20 in total - select APCD target compounds, select PAMS VOCs)

C_2C_6 GC	C_6C_{12} GC
n-butane	3-methylpentane
acetylene	chloroform
vinyl chloride	benzene
isopentane	cyclohexane
1,3-butadiene	ethyl acrylate
2,3-dimethylbutane + 2-methylpentane	trichloroethylene
	2,2,4-trimethylpentane
	methyl methacrylate
	toluene
	tetrachloroethylene
	ethylbenzene
	bromoform
	styrene
	1,4-dichlorobenzene

[a]Delays in purchasing auto-GC annual maintenance kits postponed the start of PAMS season 2022 data collection for the APCD. PAMS season 2022 was limited to July and August at Cannons Lane site and to August at Algonquin site.

[b]Installation of a toxics cylinder standard at Cannons Lane site occurred in February 2022. Without a standard, select APCD target compounds cannot be fully validated from July 2022 through January 2023. These VOCs include vinyl chloride, chloroform, ethyl acrylate, trichloroethylene, methyl methacrylate, tetrachloroethylene, bromoform, and 1,4-dichlorobenzene.

In addition to the change in VOCs that are fully validated throughout the year, the air monitoring chemist's review process also changed as of July 2022. This change in the data review / data validation process was implemented in an attempt to keep up with the large and

constant flow of data. The data validation effort has shifted to focus on the most critical data validation procedures for recently collected data and leave more enhanced data validation techniques for a later time, if staffing and resources become available. As the APCD's auto-GC monitoring program has grown over the years and APCD staff have learned the effort and rigor needed to produce high quality data, the data validation process has been constantly tweaked and refined. This refinement is done in an attempt to find a balance between producing high quality data while also being able to manage the large flow of data. Additional refinements will likely be needed in the future.

The graphic below provides a visual of the APCD's auto-GC data validation status at the time this technical note was written. The numbers that appear in each box represent the VOCs under review (refer to the Tables in this document for applicable list).

[1] Table 1 VOCs - 27 in total = PAMS priority + 1,3-butadiene + cyclohexane
[2] Table 2 VOCs - 41 in total = PAMS priority, select PAMS optional, select APCD target compounds
[4] Table 4 VOCs - 12 in total = select APCD target compounds
[5] Table 5 VOCs - 26 in total = PAMS priority + 1,3-butadiene
[6] Table 6 VOCs - 38 in total = PAMS season VOCs including PAMS priority, select PAMS optional, select APCD target compounds
[7] Table 7 VOCs - 20 in total = year-round VOCs including select APCD target compounds, select PAMS VOCs

Brief explanations of the symbols used in graphic above:

- "-" VOC data will not be reviewed
- "X" VOC data have not been reviewed but are slated to be reviewed
- "*" VOC data review process has begun
- "→" VOC data have been subjected to several levels of review and validation; data may be shared as preliminary results
- "✓" VOC data have been subjected to all levels of review and validation

Auto-GC sensitivity

Auto-GC raw data contain both signal noise and peaks. Signal noise is the random fluctuation of the baseline while peaks provide information about the identity of a VOC and the magnitude of the concentration. Auto-GC sensitivity represents the lowest concentration in which a VOC peak can confidently be distinguished from signal noise.

The APCD's auto-GC software allows a user to set thresholds for peak integration parameters - slope, drift, and peak area. An explanation of slope and drift can be found in the APCD's Auto-GC VOC Data Handling SOP. For a peak to be integrated by the auto-GC software, that peak must meet the drift and slope parameters and have a peak area that is greater than or equal to the defined peak area threshold. Integration parameters are generally selected during initial GC set up and are not routinely changed. Integration parameter selection must balance integration of peaks representing low VOC concentrations with minimizing integration of signal noise or fluctuations in baseline. Each auto-GC system may use different integration parameter thresholds depending on the signal noise for that system.

If all auto-GC peak integration parameters are met, a peak is integrated. If that peak has a retention time that falls within a defined retention time window, the peak is identified, and a concentration result is calculated by the auto-GC software. When no peak is integrated within a defined retention time window, the auto-GC software returns a 0 ppbv value for that VOC. Therefore, 0 ppbv can represent no detectable amount of VOC or the VOC concentration was below one or more peak integration parameter thresholds (i.e. not distinguishable from signal noise). Note that for APCD target compounds regulated under the APCD's Strategic Toxic Air Reduction (STAR) program, the Benchmark Ambient Concentration (BAC) for cancer for an air toxic VOC may fall below the lowest quantifiable concentration by the auto-GC. Table 8 provides the lowest quantifiable concentrations for each VOC based on the currently selected peak area parameters and experimentally determined calibration parameters for each auto-GC system. An asterisk (*) is used to identify instances when the VOC's STAR BAC for cancer is below the auto-GC's lowest quantifiable concentration level.

Table 7 - APCD Auto-GC Lowest Quantifiable VOC Concentrations (as of 3/1/2023)

Compound	Algonquin Pkwy. auto-GC Lowest Quantifiable Concentration (ppbv)	Cannons Lane auto-GC Lowest Quantifiable Concentration (ppbv)
1,2,3-trimethylbenzene	0.01	0.01
1,2,4-trimethylbenzene	0.01	0.01
1,3-butadiene	0.02*	0.06*
1,4-dichlorobenzene	0.01	0.02*
1-butene	0.01	0.06
2,2,4-trimethylpentane	0.01	0.01
2,3-dimethylbutane + 2-methylpentane	0.01	0.04
3-methylpentane	0.01	0.01
acetylene	0.03	0.13

benzene	0.01	0.01
bromoform	0.10*	0.21*
chloroform	0.07*	0.13*
cis-2-butene	0.01	0.06
cyclohexane	0.01	0.01
ethane	0.03	0.11
ethyl acrylate	0.03	0.03
ethylbenzene	0.01	0.01
ethylene	0.03	0.12
isobutane	0.01	0.06
isopentane	0.01	0.05
isoprene	0.01	0.05
methyl methacrylate	0.03	0.03
m-ethyltoluene	0.01	0.01
m-xylene + p-xylene	0.01	0.01
n-butane	0.01	0.06
n-hexane	0.01	0.04
n-pentane	0.01	0.05
o-ethyltoluene	0.01	0.01
o-xylene	0.01	0.01
p-ethyltoluene	0.01	0.01
propane	0.02	0.08
propene	0.02	0.08
styrene	0.01	0.01
tetrachloroethylene	0.03	0.04
toluene	0.01	0.01
trans-2-butene	0.01	0.06
trichloroethylene	0.03	0.04
vinyl chloride	0.04	0.19*

* APCD's Strategic Toxics Air Reduction (STAR) Benchmark Ambient Concentration for cancer (BAC_c) is below the auto-GC's lowest quantifiable concentration level.

As time permits, a Method Detection Limit (MDL) Study will be performed to provide additional information about Auto GC detection limits. Briefly put, an MDL study is an experimental determination and statistical estimate of the lowest concentration at which there is a 99% chance that the concentration is greater than zero. MDL studies are described in detail in 40 CFR Part 136 Appendix B. Once MDLs have been established for each VOC of interest, low level auto-GC results will be evaluated against these MDLs. Therefore, while the auto-GC system may be able to detect/quantify down to the concentrations provided in Table 8, there is some uncertainty in concentrations that fall below the determined MDL, the lowest level in which concentrations can be accurately quantified with 99% confidence.