

NEW HAMPSHIRE DEPARTMENT OF ENVIRONMENTAL SERVICES 2021 PAMS SUMMARY

Photochemical Assessment Monitoring Station (PAMS)



June 8, 2022

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**NEW HAMPSHIRE DEPARTMENT OF
ENVIRONMENTAL SERVICES
2021 PAMS SUMMARY**

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TABLE OF CONTENTS

1.	INTRODUCTION	6
2.	DATA VALIDATION	9
3.	QUALITY CONTROL.....	9
4.	DATA COMPLETENESS.....	9
5.	DATA ANALYSIS	10
5.1	PAMS Compounds and Major Species	10
5.2	Diurnal, Weekly, and High-Low Elevation Variation	15
5.3	Compound Groups	23
5.3.1	Gasoline Related Compounds	23
5.3.2	Motor Vehicle Tracers.....	26
5.3.3	Secondary Organic Aerosol Precursors (SOAP).....	28
5.4	Other Species	29
5.4.1	Hazardous Air Pollutants.....	29
5.4.2	Toxic Species	30
5.4.3	Liquefied Petroleum Gas Constituents	33
5.4.3	Naturally Emitted VOCs	34
5.5	Forest Fire Events.....	39
5.5.1	Exceptional PM Event Analysis	39
6.	CARBONYL ANALYSIS	47
7.	PAMS SEASON OZONE – 2021	52
7.1	Ozone Attainment and NAAQS Exceedances at New Hampshire PAMS Sites.....	52
7.2	Ozone Monitoring Summary for the New Hampshire PAMS Sites	52
8.	MIXING HEIGHT.....	57
9.	CONCLUSION.....	64

LIST OF FIGURES

Figure 1.1:	Map of PAMS stations in New Hampshire.....	6
Figure 1.2:	Nonattainment/Maintenance Areas in or near New Hampshire.....	8
Figure 4.1:	Data Capture Rates New Hampshire PAMS Sites, 2015-2021.....	10
Figure 5.1:	Seasonal Average PAMS Compound Trends New Hampshire PAMS Sites, 2005-2021	10
Figure 5.2:	10 Most Abundant Species Yearly Averages at Miller PAMS (2015-2021)	13
Figure 5.3:	10 Most Abundant Species Yearly Averages at Londonderry PAMS (2015-2021).....	14
Figure 5.4:	Five Most Abundant Species Monthly Averages at Miller, 2021	15

Figure 5.5: Five Most Abundant Species Monthly Averages at Londonderry, 2021.....	15
Figure 5.6: 2021 Average Diurnal Pattern and Max for Isoprene at both New Hampshire PAMS Sites.....	16
Figure 5.7: 2021 Average and Maximum Diurnal Variation for α -pinene at Londonderry.....	16
Figure 5.8: 2021 Diurnal Pattern for Average and Maximum Hourly Values for Ethane at New Hampshire PAMS Sites.....	17
Figure 5.9: 2021 Diurnal Pattern for Average and Maximum Hourly Values for Propane at New Hampshire PAMS Sites.....	17
Figure 5.10: 2021 Diurnal Pattern for Average and Maximum Hourly Values for Isopentane at New Hampshire PAMS Sites.....	18
Figure 5.11: 2021 Diurnal Pattern for Average and Maximum Hourly Values for n-Butane at New Hampshire PAMS Sites.....	18
Figure 5.12: 2021 Diurnal Pattern for Average and Maximum Hourly Values for Toluene at New Hampshire PAMS Sites.....	19
Figure 5.13: 2021 Diurnal Pattern for Average and Maximum Hourly Values for p-Ethyltoluene at New Hampshire PAMS Sites.....	19
Figure 5.14: 2021 Diurnal Pattern for Average and Maximum Hourly Values for Pentane at Londonderry.....	20
Figure 5.15: 2021 Diurnal Pattern for Average and Maximum Hourly Values for Benzene at New Hampshire PAMS Sites.....	20
Figure 5.16: 2021 Diurnal Pattern for Average and Maximum Hourly Values for 1-Butene at Miller.....	21
Figure 5.17 : 2021 Diurnal Pattern for Average and Maximum Hourly Values for 1,2,3-Trimethylbenzene at Miller.....	21
Figure 5.18: Average Weekday v. Average Weekend VOC Trends at Londonderry in 2021.....	22
Figure 5.19: Weekday v. Weekends VOC Trends at Miller in 2021.....	22
Figure 5.20: Yearly Averages of BTEX Compounds.....	23
Figure 5.21: 2021 Diurnal Hourly Averages for BTEX Compounds.....	24
Figure 5.22: 2021 Benzene/Toluene and Xylene/Toluene ratios at Londonderry and Miller.....	25
Figure 5.23: 2021 Diurnal CO Values at Londonderry and Miller.....	26
Figure 5.24: 2020 VOC/NO _x Ratio for PAMS Season at Londonderry, 6:00 - 9:00 AM.....	28
Figure 5.25: Trends of Secondary Organic Aerosol Precursor (SOAP) Compounds.....	29
Figure 5.26: Trends of HAP Compounds.....	30
Figure 5.27: 24-hour Averages of Benzene, p-Ethyltoluene, and 1,2,3-Trimethylbenzene during 2021 PAMS season at Miller.....	32
Figure 5.28: Monthly Averages of Benzene, and Toluene during 2021 PAMS season at Londonderry and Miller.....	32
Figure 5.29: Yearly LPG Averages in PPBC.....	33
Figure 5.30: Annual Averages of Propane for Londonderry and Miller.....	33
Figure 5.31: Isoprene Monthly 2021 Averages.....	34
Figure 5.32: Isoprene Average Concentrations Since 2006 at NH PAMS Locations.....	35
Figure 5.33: Biogenic Compound Average Concentrations at Londonderry Since 2018.....	36
Figure 5.34: 24-Hour Average Isoprene, α - and β -pinene, Temperature and Solar Radiation at Londonderry 2021.....	36
Figure 5.35: Diurnal Average Isoprene, UV Radiation and Temperature at Londonderry, 2021.....	37
Figure 5.36: 2021 Diurnal Average Isoprene, α - and β -pinene at Londonderry.....	37
Figure 5.37: 2021 Monthly Averages, Isoprene, α - and β -pinene at Londonderry.....	38
Figure 5.38: 24 Hour Average Temperature and Isoprene at Miller in 2021.....	38
Figure 5.39: 2021 Diurnal Average and Maximum Isoprene with Average Temperature Miller.....	39
Figure 5.40: July 20, 2021 PM _{2.5} Concentrations at Londonderry and Miller with CO and Mixing Height.....	40

Figure 5.41: July 20, 2021 Wind Direction Frequency for Londonderry and Miller	40
Figure 5.42: July 20, 2021 Benzene and Toluene Concentrations with Mixing Height and PM _{2.5} Values for Londonderry and Miller	41
Figure 5.43: July 20, 2021 VOC Groups with Mixing Height and PM _{2.5} Values for Londonderry and Miller	42
Figure 5.44: July 20, 2021 VOC Carbon Ranges compared to PM _{2.5} Values for Londonderry and Miller	42
Figure 5.45: July 26, 2021 PM _{2.5} Concentrations at Londonderry and Miller with CO and Mixing Height	43
Figure 5.46: July 26, 2021 Wind Direction Frequency for Londonderry and Miller	43
Figure 5.47: July 26, 2021 Benzene and Toluene Concentrations with Mixing Height and PM _{2.5} Values for Londonderry and Miller	44
Figure 5.48: July 26, 2021 VOC Groups with Mixing Height and PM _{2.5} Values for Londonderry and Miller	44
Figure 5.49: July 26, 2021 VOC Carbon Ranges compared to PM _{2.5} Values for Londonderry and Miller	45
Figure 5.50: July 20 and 26, 2021 Average Temperature (deg F), Solar Radiation (W/m ²) and Percent Biogenics at Londonderry and Miller	45
Figure 5.51: July 20 and 26, 2021 Wind Direction Charts for Miller and Londonderry	46
Figure 6.1: Total 24-Hour Reportable Carbonyl Concentrations with 8-Hour Ozone Max and Average Solar Radiation at Londonderry PAMS in 2021	47
Figure 6.2: Total 24-Hour Reportable Carbonyl Concentrations with daily Rainfall and Average Relative Humidity at Londonderry PAMS in 2021	48
Figure 6.3: June-August, 2021 Total Reportable Formaldehyde Concentrations at Lynn, MA and Londonderry, NH	49
Figure 6.4: Total 24-Hour Required Carbonyl Concentrations at Londonderry PAMS in 2021	49
Figure 6.5: 8-Hour Average Carbonyls by Time of Day at Londonderry PAMS in 2021	50
Figure 6.6: Carbonyl Compound Averages by Year - Londonderry PAMS	50
Figure 6.7: Carbonyl Totals by Sampling Event- Londonderry PAMS	51
Figure 7.1: Average Seasonal Diurnal Ozone Concentrations for Londonderry and Miller in 2021	53
Figure 7.2: Hourly TNMOC/Ozone at Londonderry PAMS Site, 2021	53
Figure 7.3: Hourly TNMOC/Ozone at Miller, 2021	54
Figure 7.4: PAMS Monitoring Station Seasonal Ozone Averages	54
Figure 7.5: Hourly Ozone, PAMS and Meteorological Conditions at Londonderry and Miller on June 18, 2021	56
Figure 7.6: Wind Frequencies and 3-Day Back-Trajectory for Londonderry and Miller on June 18, 2021	56
Figure 8.1: Londonderry PAMS Season Averages of Ozone, Temperature, Solar Radiation, TNMOC and Mixing Layer Height 2021	58
Figure 8.2: June 5, 2021 Hourly Ozone, Temperature, Mixing Height, and TNMOC	58
Figure 8.3: 2021 PAMS Season Averages of PM _{2.5} and Mixing Height at Londonderry	59
Figure 8.4: July 26, 2021 Wildfire Event - Hourly PM _{2.5} , Ozone, Temperature and Mixing Height at Londonderry	59
Figure 8.5: Mixing Height Scatter Plots with Various Parameters at Londonderry	61
Figure 8.6 Average of Various Parameters by Mixing Height at Londonderry	62
Figure 8.7: Average Mixing Height Levels by Meteorological Season	63

LIST OF TABLES

Table 1.1: List of PAMS organic compounds and their AQS codes	8
Table 5.1: Top 10 Most Abundant Compounds New Hampshire PAMS Sites 2021*	11
Table 5.2: Seasonal Maximum 24-hour Averages at Londonderry for Toxic Species vs. AAL	31
Table 5.3: Seasonal Maximum 24-hour Averages at Miller for Toxic Species vs. AAL	31
Table 7.1: 2021 Average and Maximum Monthly Ozone Concentrations	55

Table 7.2: 2021 1-Hour Ozone Measurements Greater Than 70 ppb at Londonderry and Miller.....55

APPENDIX A: 2021 VOC MDL's FOR MILLER AND LONDONDERRY PAMS

.....64

ACRONYMS USED IN THIS REPORT

AAL	Ambient Air Limits, a health-based air limit
AQS	Air Quality System, repository for air pollution information
BTEX	Benzene, Toluene, Ethylbenzene, and Xylene (inherent to gasoline)
CFR	Code of Federal Regulations
CO	Carbon monoxide
EMP	Enhanced Monitoring Plan
EPA	U.S. Environmental Protection Agency
ETP	External temperature, temperature outside of the monitoring station
HAPs	Hazardous Air Pollutants, substances that are defined as hazardous
LP	Liquefied propane
LPG	Liquid petroleum gas
MDL	Method Detection Limit
MIR	Maximum Incremental Reactivity factor
MLH	Mixing Layer Height
mph	miles per hour
NAAQS	National Ambient Air Quality Standards, health-based ambient air standard
NCORE	National Core, an air monitoring network
NHDES	New Hampshire Department of Environmental Services
NO ₂	Nitrogen Dioxide
NO ₃	nitrate radical
NO _x	Nitrogen Oxides
NO _y	Aged nitrogen oxides
O ₃	Ozone, a chemically reactive air pollutant
OH	Hydroxy radical
PAMS	Photochemical Assessment Monitoring Station
PM	Particulate Matter
PM _{2.5}	Particulate Matter less than 2.5 microns
PM ₁₀	Particulate Matter less than 10 microns
ppb	parts per billion, a measure of concentration
ppbC	parts per billion times carbon, a measure of concentration
ppm	parts per million, a measure of concentration
QAPP	Quality Assurance Project Plan
R ²	coefficient of determination
SOA	Secondary Organic Aerosols
SOAP	Secondary Organic Aerosol Precursors
TNMOC	Total Non-Methane Organic Compounds
µg/m ³	Micrograms per cubic meter (concentration)
UMBC	University of Maryland, Baltimore County
UV	Ultraviolet (radiation), a type of light from the sun
VOCs	Volatile organic compounds
W/m ²	Watt per square meter

1. INTRODUCTION

In 2021, monitoring for the Photochemical Assessment Monitoring Stations (PAMS) was completed for the 7th summer season at the Moose Hill School site in Londonderry, New Hampshire (Londonderry), and the 16th season at Miller State Park located at the top of Pack Monadnock in Peterborough, New Hampshire (Miller). The combination of the two sites provides a unique high-low look (elevation 345 ft. vs. 2290 ft.) at ozone precursors within the state. PAMS monitoring locations have changed throughout the years, but the current locations in Londonderry and Miller are likely to continue in the foreseeable future. Both sites are National Core (NCORE) air monitoring stations. This is advantageous because it provides information that is useful for the analysis of ozone formation, such as carbon monoxide (CO), oxides of nitrogen (NO_x), ozone and meteorology at different elevations. PAMS monitoring stations collect information on a select group of Volatile Organic Compounds (VOCs) in addition to other parameters. The PAMS sites in the state are operated and maintained by the New Hampshire Department of Environmental Services (NHDES) PAMS Program and the locations of these stations are shown in **Figure 1.1**.

The 2015 revision of the ozone National Ambient Air Quality Standard (NAAQS) changed the criteria for federally required PAMS sites across the country effective in 2021.¹ NHDES elected to implement many of the mandated changes at the Londonderry location prior to the required date as an early adopter, while continuing the monitoring at the Miller location under the Enhanced Monitoring Plan (EMP) for the Ozone Transport Region.

The Londonderry VOC equipment was upgraded to meet the new requirements in 2018. This equipment generally improves detection limits for PAMS target compounds and includes additional biogenic compounds.

The new VOC equipment at Londonderry includes a Markes Unity thermal desorption system and Agilent 7890B gas chromatograph and companion software. The thermal desorption unit includes a Markes KORI-xr drier, which removes moisture from sampled air much more effectively than the Nafion dryer used at Miller State Park. The Markes KORI dryer not only allows

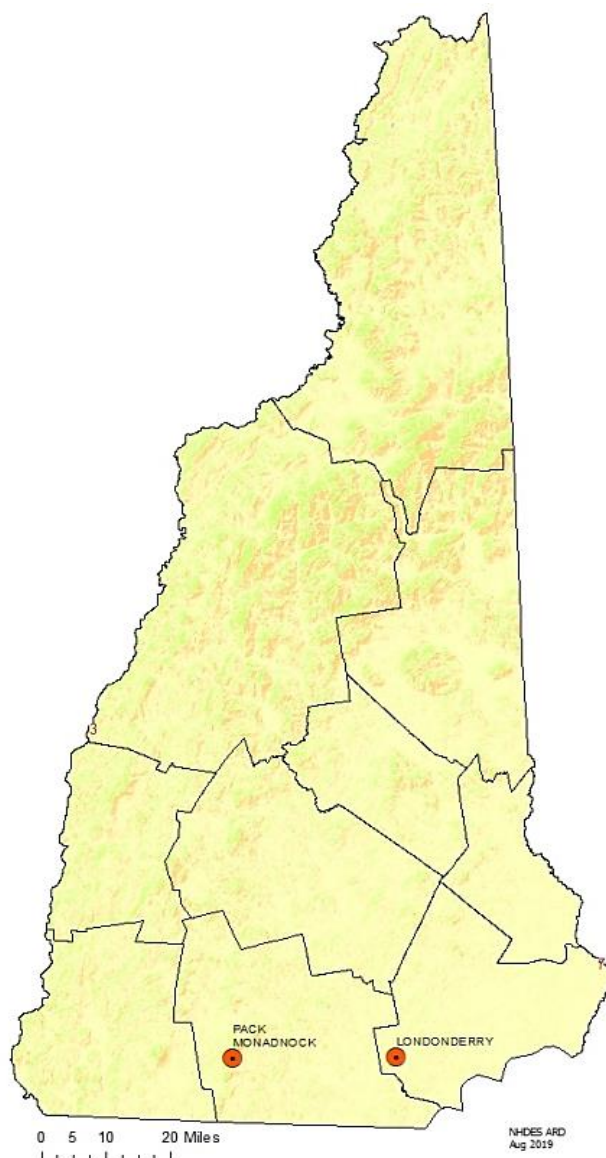


Figure 1.1: Map of PAMS stations in New Hampshire

¹ The EPA has revised the start date to June 1, 2021 [\[84 FR 25221\]](#).

the passage of certain compounds (notably, α - and β -pinene) to enter the gas chromatograph that the Nafion dryer does not, it also increases the sensitivity of compound detection. As a result, the magnitude of VOCs captured at this location has increased, as expected. In addition, the Londonderry site added the analysis of carbonyl compounds and mixing height measurement in 2019. New Hampshire continued PAMS monitoring at the Miller site using the current PerkinElmer VOC system under the approved EMP PAMS Quality Assurance Project Plan (QAPP), however the instrumentation there has now been upgraded for the 2022 monitoring season with a Markes Agilent system identical to the one at the Londonderry required site.

The objectives of the PAMS program are to help verify ozone precursor emission inventories, identify their trends and distribution, and provide critical information for improving photochemical model performance. PAMS is also intended to help states identify potential emission control strategies and to help characterize population exposure to VOCs and ozone. PAMS monitoring was initially required under the Clean Air Act's provision for enhanced monitoring in certain regions that have measured ozone concentrations high enough to be designated in non-attainment areas classified as serious, severe, or extreme.

The first PAMS sites were operational in 1994 and have been collecting data for more than 25 years. Since inception, there have been many changes to the nature and scope of the ozone problem in the U.S. as well as our understanding of it. As a result, the ozone standard has been revised many times, most recently in September of 2015 when the standard was lowered from 0.075 parts per million (ppm) to 0.070 ppm (or 75 parts per billion (ppb) to 70 ppb) [\[80 FR 65292\]](#). Included in the 2015 revision of the ozone standard were changes to the monitoring requirements in 40 CFR part 58, Appendix D Section 5, "Network Design for PAMS and Enhanced Ozone Monitoring."

Under the updated requirements, NCORE sites in a Core Based Statistical Metropolitan Area with a population of 1,000,000 or more require PAMS monitoring regardless of ozone attainment status to provide spatial coverage to meet national model evaluation needs. This change became effective June 1, 2021, however, NHDES took proactive measures to accommodate the new regulations concerning the relocation of the PAMS site from Nashua to Londonderry in 2014. A revision of the VOC list and the addition of both mixing height and carbonyl sampling is also effective in 2021. Carbonyl sampling is required at the Londonderry site on a one and three-day basis with three, eight-hour samples from June through August. As early adopters, NHDES applied these changes effective in 2019. New technologies have been developed that to improve data quality and further our knowledge base on the topic.

Ozone concentrations in New Hampshire have trended downward since 1990. However, the area in which the PAMS stations are located is a chemically complicated air region, and higher ozone concentration areas exist near the New Hampshire border: the New Hampshire ozone maintenance area that includes portions of three counties in the southern portion of the state within the Boston-Manchester-Portsmouth area (Southeastern), and the Boston-Lawrence-Worcester (Eastern) Massachusetts nonattainment area – both related to the 1997 ozone standard, **Figure 1.2**.

Figure 1.2: Nonattainment/Maintenance Areas in or near New Hampshire²

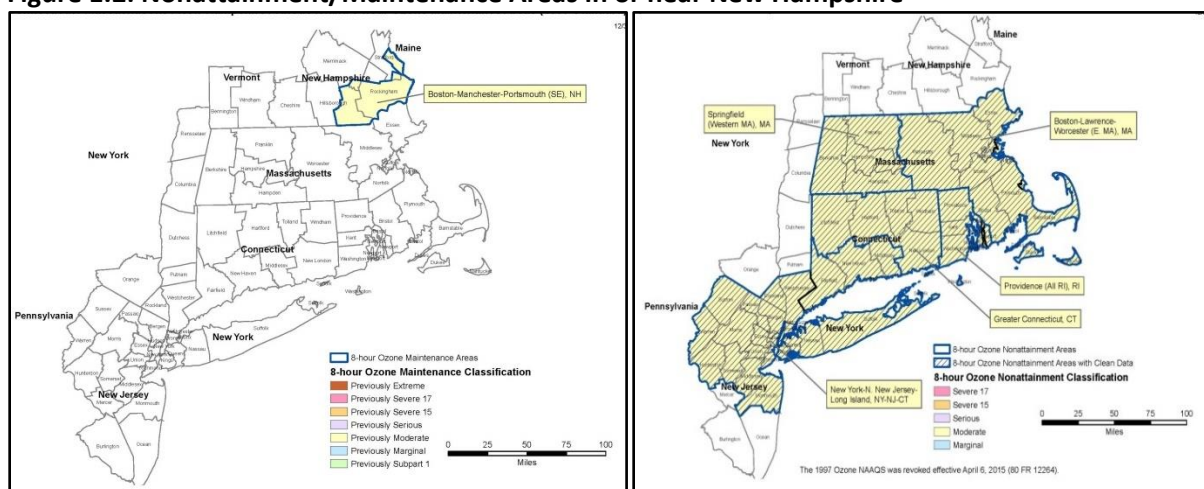


Table 1.1 lists the current PAMS VOC target compounds along with the chemical species' Air Quality System (AQS) codes. The PAMS program entails collection of data in accordance with 40 CFR 58 Appendix D, Part 5. This report summarizes that data and examines VOC concentration patterns, meteorological conditions, and a comparison of ozone values with PAMS compounds associated with New Hampshire's 2021 PAMS program data collection.

Table 1.1: List of PAMS organic compounds and their AQS codes

VOC	AQS	VOC	AQS	VOC	AQS	VOC	AQS
Ethane	43202	Ethylene	43203	Propane	43204	Propylene	43205
Isobutane	43214	1, 3 -Butadiene	43218	n-Butane	43212	Acetylene	43206
trans-2-Butene	43216	1-butene	43280	cis-2-Butene	43217	Cyclopentane	43242
Isopentane	43221	n-Pentane	43220	trans-2-Pentene	43226	1-Pentene	43224
cis-2-Pentene	43227	2,2-Dimethyl- butane	43244	2,3-Dimethyl-butane	43284	2-Methylpentane	43285
3-Methylpentane	43230	Isoprene	43243	n-Hexane	43231	Methylcyclopentane	43262
2,4-Dimethyl-pentane	43247	Benzene	45201	Cyclohexane	43248	2-Methylhexane	43263
2,3-Dimethyl-pentane	43291	3-Methyl-hexane	43249	2,2,4-Tri-methylpentane	43250	n-Heptane	43232
Methylcyclohexane	43261	2,3,4-Tri-methylpentane	43252	Toluene	45202	2-Methylheptane	43960
3-Methylheptane	43253	n-Octane	43233	Ethylbenzene	45203	m&p-Xylene	45109
Styrene	45220	o-Xylene	45204	n-Nonane	43235	Isopropylbenzene	45210
n-Propylbenzene	45209	Alpha-Pinene*	43256	m-Ethyltoluene	45212	p-Ethyltoluene	45213
1,3,5-Trimethyl-benzene	45207	o-Ethyltoluene	45211	1,2,4-Trimethyl-benzene	45208	Beta-Pinene*	43257
n-Decane	43238	1,2,3-Trimethyl-benzene	45225	m-Diethylbenzene	45218	p-Diethyl-benzene	45219
n-Undecane	43954	Total Non-Methane Organic Compounds	43102	Sum PAMS Target Species	43000		

*new compounds added in 2018 at the Londonderry site

² <https://www3.epa.gov/airquality/greenbook/gbca.html> (April 2020)

2. DATA VALIDATION

Data validation is necessary to identify data with errors, biases, and physically unrealistic values before they are used for identification of exceedances, analyses, or modeling. Data validation for the 2021 season was conducted in accordance with the NHDES Required Site and EMP QAPP.³ AirVision and VOCdat were the software platforms used for PAMS data validation and reporting. Values that fail to meet the acceptance criteria and their associated data are flagged in the Air Quality System (AQS). Blank exceedances and Continuing Calibration Verification (CCV) qualifiers were applied to the 2021 data but are unlikely to have any major influence on the hourly data, though a handful of compounds at the Londonderry site were flagged for a large portion of the season with a “QX.” This indicates that the CCV criteria were outside of control limits and was due to a faulty lot of KORI traps purchased from the vendor, lowering the percent deviation, therefore skewing some of the data low. Any major quality deviations with the data were invalidated with the appropriate NULL codes. The full list of data flags and invalidation can be found within the Air Quality System ([AQS](#)).

3. QUALITY CONTROL

NHDES performs PAMS monitoring in accordance with the Environmental Protection Agency’s (EPA) PAMS Technical Assistance Document. Quality control procedures are documented in the NHDES approved QAPPs, which ensures certain quality control processes are in place to maintain high quality PAMS data. With new regulations effective in 2021, additional quality assurance/quality control procedures are being developed and will include a performance evaluation study, increased calibration certification frequency and use of a second source standard.

A Method Detection Limit (MDL) study is run prior to the start of each PAMS season using the Retention Time (RT) cylinder received from EPA. A predetermined concentration of this standard is run 7 times over the course of three days to determine the MDL for each compound. These values change yearly per site and are recorded in AirVision. Values reported below the MDL are flagged as such for the Required Site. The 2021 MDL’s are attached as part of Appendix A of this report.

4. DATA COMPLETENESS

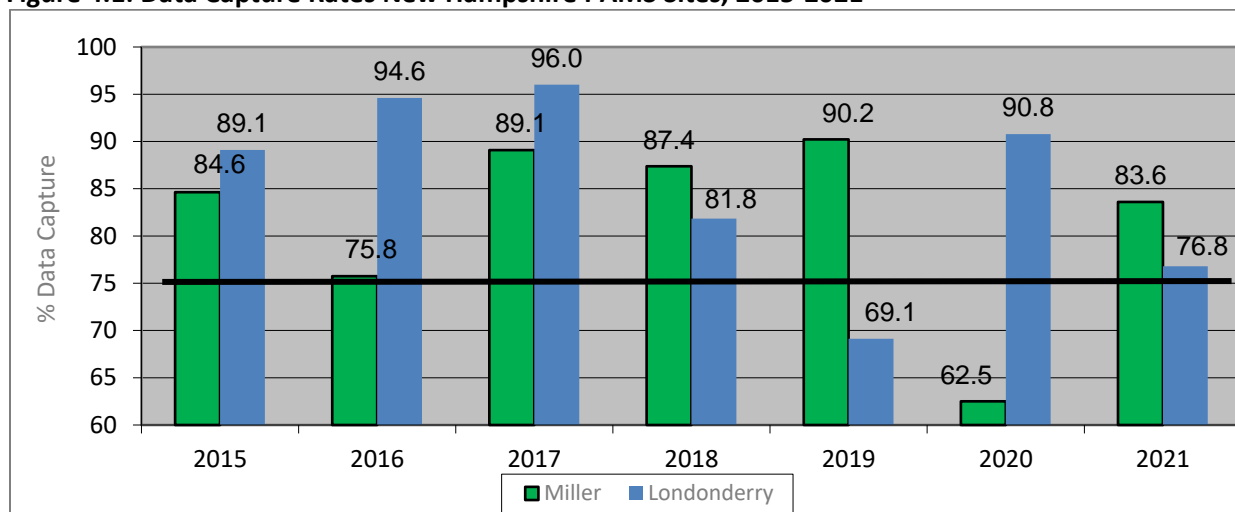
Data capture rates met the EPA acceptance criteria of 75% at both PAMS locations for 2021 (black line in **Figure 4.1**). Data collection rates at the sites are impacted by periods of instrument down time due to equipment issues, and to a lesser degree, running QC samples. The VOC analytical system at Miller was retired at the end of the 2021 ozone season, providing 16 years of service at that location.

Problems with the Perkin Elmer system at Miller started in late August. A new collector was needed for one of the flame ionization detectors (FID). Once the replacement was delivered and installed, a blockage occurred in one of the nafion driers leading to inadequate air supply. That was repaired on September 3rd and the system ran smoothly for the rest of the season.

The required Londonderry site, operating with the updated Markes Agilent equipment, saw a nearly 77% data completeness rate in 2021. Most of the data loss came late June into July when the CIA Advantage portion of the system became unable to sample. At first, the rotor was changed which got the system operating for a few days, but ultimately the entire actuator needed replacement. Data capture at Miller is expected to improve in 2022 now that the new GC is operational.

³ State of New Hampshire, Photochemical Assessment Monitoring Station Quality Assurance Project Plan (PAMS QAPP), Revision #9, August 24, 2017

Figure 4.1: Data Capture Rates New Hampshire PAMS Sites, 2015-2021

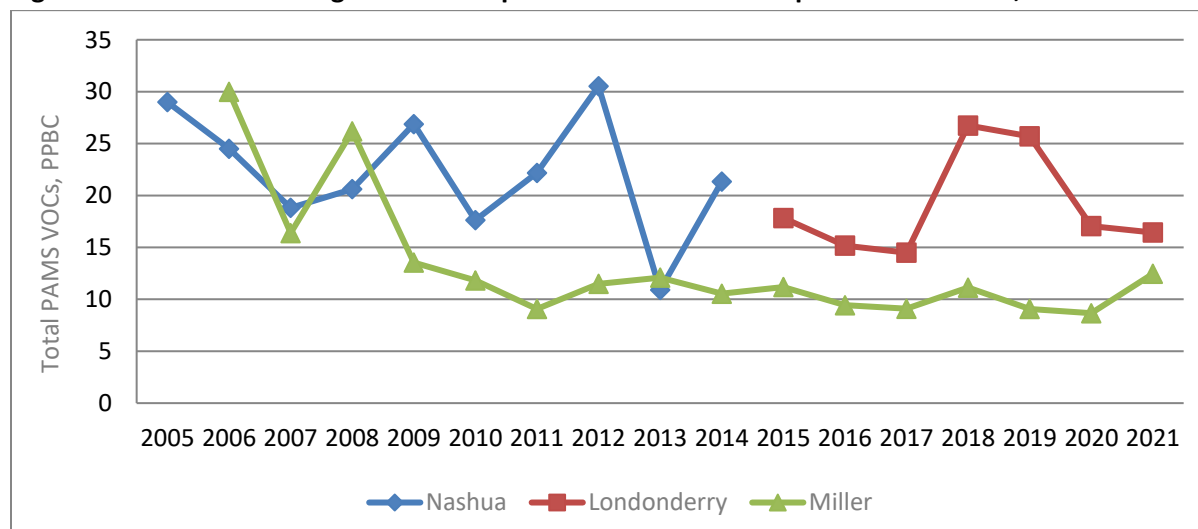


5. DATA ANALYSIS

5.1 PAMS Compounds and Major Species

Figure 5.1 represents the seasonal average PAMS compound concentrations measured at the Nasua Gilson Road, Miller, and Londonderry sites since 2005. Although PAMS sampling discontinued at Gilson Road in 2013 when measurements at Londonderry began, the data is retained in some of the trending charts for the purpose of comparison.

Figure 5.1: Seasonal Average PAMS Compound Trends New Hampshire PAMS Sites, 2005-2021⁴



Concentrations of PAMS VOC target compounds were variable at the Gilson Road site in Nashua over the first 10 years of monitoring. The Nashua site was replaced by Londonderry in 2015 as part of the NHDES NCore plan. At the current PAMS sites, the target VOC compounds have generally trended downward since 2015 until 2018. In 2018, there was a dramatic increase in the seasonal average VOC at Londonderry:

⁴ 2008 Miller data are biased high due to the installation of new instrumentation and contamination of high molecular weight compounds; 2009 Gilson Road (Nashua) data are biased high due to influence from a local paving project that took place that year; 2014 Gilson Road data only includes September data up until September 18. 2019 Londonderry data and 2020 Miller data has less than 75% data capture.

an 84% increase for both total non-methane organic compounds (TNMOCs) and PAMS compounds. This increase is attributable to the addition of α - and β -pinene to the compound list which are both major VOC contributors at the Londonderry site. Data for 2021 showed a decrease for the sum of PAMS from 2020 concentrations at Londonderry. VOC concentrations at Miller have been stable since 2009 but saw a modest increase in 2021. In 2021, PAMS concentration averages were reduced by 3.7% at Londonderry and increased 36% at Miller from 2020. The increase at Miller is partially due to the increased data capture compared to the previous year when a large portion of data was lost during the months of June and July which is usually when New Hampshire experiences maximum VOC concentrations. Trends in PAMS parameters including ozone and summer weather patterns are examined later in this report.

Table 5.1 summarizes the 10 most abundant PAMS volatile organic compounds measured at each New Hampshire PAMS site. The lists of compounds are generally consistent but the changes in the top 10 most plentiful compounds from 2020 to 2021 are highlighted in green. At Miller, the most abundant compounds for 2021 were similar to what was measured in 2020, except benzene, 1-butene and pentane replaced ethylene, toluene and isobutane in the top 10. Most compounds at Londonderry remained in the top 10 in 2021 from 2020, however, benzene replaced β -pinene.

Table 5.1: Top 10 Most Abundant Compounds New Hampshire PAMS Sites 2021*

Miller	Seasonal Daily Average Concentration (ppbC)	Seasonal Maximum Concentration (ppbC)
ISOPRENE (43243)	2.99	27.45
ETHANE (43202)	2.58	10.40
PROPANE (43204)	1.56	35.76
1,2,3-TRIMETHYLBENZENE (45225)	1.47	6.22
BENZENE (45201)	0.77	5.35
P-ETHYLTOLUENE (45213)	0.68	2.84
BUTANE (43212)	0.55	3.29
ISOPENTANE (43221)	0.52	2.74
1-BUTENE (43280)	0.40	0.84
PENTANE (43220)	0.30	1.41
Londonderry	Seasonal Daily Average Concentration (ppbC)	Seasonal Maximum Concentration (ppbC)
ISOPRENE (43243)	4.40	9.22
ETHANE (43202)	2.85	7.26
PROPANE (43204)	2.78	27.25
ISOPENTANE (43221)	0.81	5.85
TOLUENE (45202)	0.75	9.35
P-ETHYLTOLUENE (45213)	0.63	8.42
BUTANE (45212)	0.63	3.71
ALPHA-PINENE (43256)**	0.56	14.06
PENTANE (43220)	0.56	4.57
BENZENE (45201)	0.39	3.87

* Green highlighted compounds unique to this site ** Not measured at Miller

Based on **Table 5.1**, there are several compounds commonly seen in New Hampshire. These include:

- **Isoprene** (C_5H_8) is a major biogenic volatile hydrocarbon that reacts with nitrogen oxides to create tropospheric ozone by photolysis. Most isoprene is released into the atmosphere by terrestrial plants.
- **p-Ethyltoluene** (C_9H_{12}) is added to fuels to increase performance. This compound is also used in the manufacture of a variety of other chemicals, plastics and coatings, printing materials and inks, solvents and cleaning products, and pesticides. p-Ethyltoluene in the environment comes from petroleum refineries and gas stations. It may also be released in vehicle exhaust fumes.

Relatively very small amounts of the compound are released naturally to the environment from crude oil and coal tar, and it is found in some natural plant oils. It can be transported significant distances from its point of release and its pollution is of concern at a global level, as well as local.

- **Butane** (C_4H_{10}) is a paraffin that can be used for gasoline blending, as a fuel gas, and extraction solvent. When blended with propane and other hydrocarbons, it is referred to as LPG or liquefied petroleum gas. It may be released into the atmosphere by evaporative and exhaust emissions from liquefied propane (LP) gas and vehicle exhaust.
- **Ethane** (C_2H_6) is the second most abundant atmospheric hydrocarbon and the second most important constituent of natural gas. It also occurs dissolved in petroleum oils and as a byproduct of oil refinery operations and of the carbonization of coal. It has been reported that a single U.S. shale oil field is responsible for much of the past decade's increase in global atmospheric levels of ethane. Researchers found that the Bakken Formation, an oil and gas field in North Dakota and Montana, is emitting roughly two percent of the globe's ethane, or 250,000 tons per year.⁵
- **Propane** (C_3H_8) is a byproduct of natural gas processing and petroleum refining and is commonly used as a fuel. Propane is one of a group of LPGs that also includes butane, propylene, butadiene, butylene, isobutylene, and mixtures thereof. Propane emitted during combustion processes accumulate in the atmosphere. Propane in the Northeast is believed to largely come from leaking gas barbecues.
- **Alpha-pinene**, or **α -pinene**, ($C_{10}H_{16}$) is found in the oils of many species of coniferous trees, notably pine. New Hampshire is 81% forested, with 4.8 million acres. Among the most predominate tree species are hemlock, spruce, balsam fir and white pine.⁶ Alpha-pinene is emitted in substantial amounts by vegetation, and these emissions are affected by temperature and light intensity. In the atmosphere, α -pinene undergoes reactions with ozone, the hydroxyl radical (OH) or the nitrate radical (NO_3), leading to low-volatility species that partly condenses on existing aerosols, thereby generating secondary organic aerosols (SOA). This compound plays a significant role in ozone chemistry in rural areas.⁷ Secondary organic aerosol precursors (SOAP) are discussed later in this section. **Beta-pinene** (**β -pinene**) is a similarly common compound emitted by coniferous trees.
- **Toluene** (C_7H_8) occurs naturally at low levels in crude oil and is a byproduct in the production of gasoline and from the production of coke from coal. Toluene is used as an octane booster in gasoline. Toluene reaches the air from a variety of sources such as combustion of fossil fuels and evaporative emissions. It is also used as a common solvent in many products like paint. It is a member of the BTEX group of pollutants, which refers to benzene, toluene, ethyl benzene and xylene. The main source of BTEX in the atmosphere is the volatilization of the BTEX components of gasoline that commonly occurs when fueling vehicles. Other sources of BTEX contamination include releases from large bulk facilities, surface spills and pipeline leaks. Measurement of the BTEX compound group at New Hampshire PAMS sites is discussed later in this report.
- **Isopentane** (C_5H_{12}) is a significant component of natural gas. It is also used in the chemical industry as a refrigerant in air conditioning and refrigerators, a solvent, and a blowing agent in making plastics. In the environment, isopentane may come from releases from industry manufacturing or use during the disposal of products containing it, however, most of it comes from natural gas emissions.

⁵ University of Michigan, "[One oil field a key culprit in global ethane gas increase.](#)" Science Daily. Science Daily, 26 April 2016.

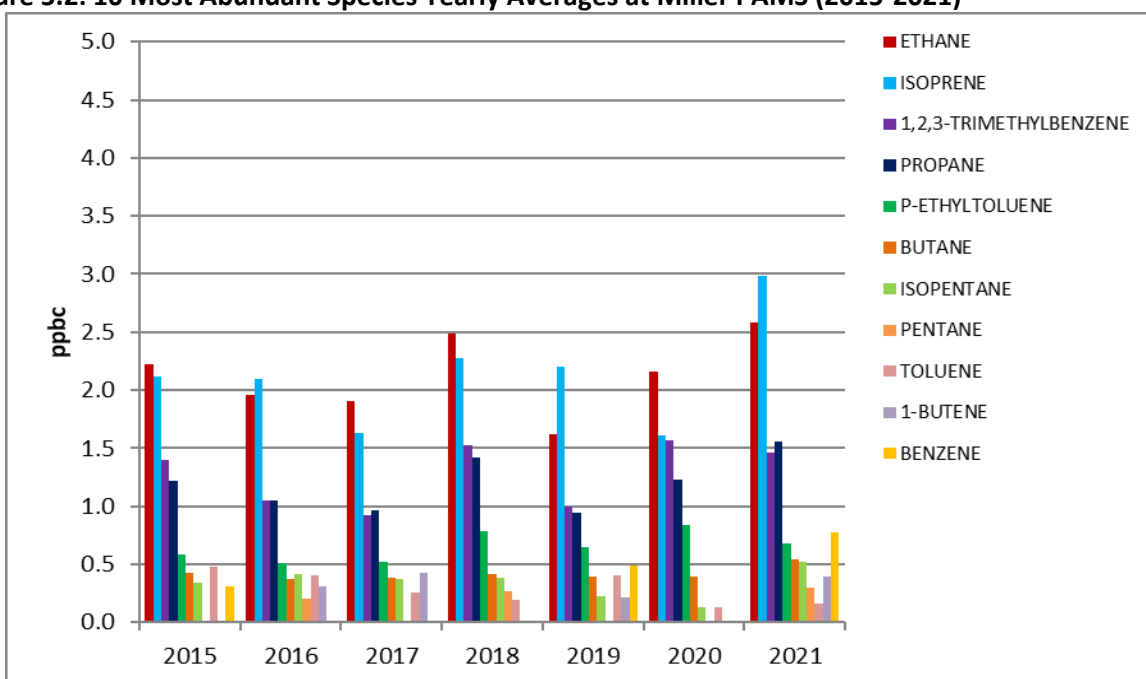
⁶ NH Department of Resources and Economic Development, Division of Forests and Lands. 2012 Inventory

⁷ Pathak, R. K., C. O. Stanier, N. M. Donahue, and S. N. Pandis (2007), Ozonolysis of α -pinene at atmospherically relevant concentrations: Temperature dependence of aerosol mass fractions (yields), *J. Geophys. Res.*, 112, D03201, doi:10.1029/2006JD007436.

- **Ethylene** (C_2H_4) emission sources include both natural gas and petroleum, and it is released in vehicle exhaust fumes and from waste incineration plants. Most of the ethylene in ambient air comes from mobile sources.
- **Benzene** (C_6H_6) is formed from both natural processes and human activity. Natural sources of benzene include volcanoes and forest fires. Benzene is also a natural part of crude oil, gasoline, and cigarette smoke.

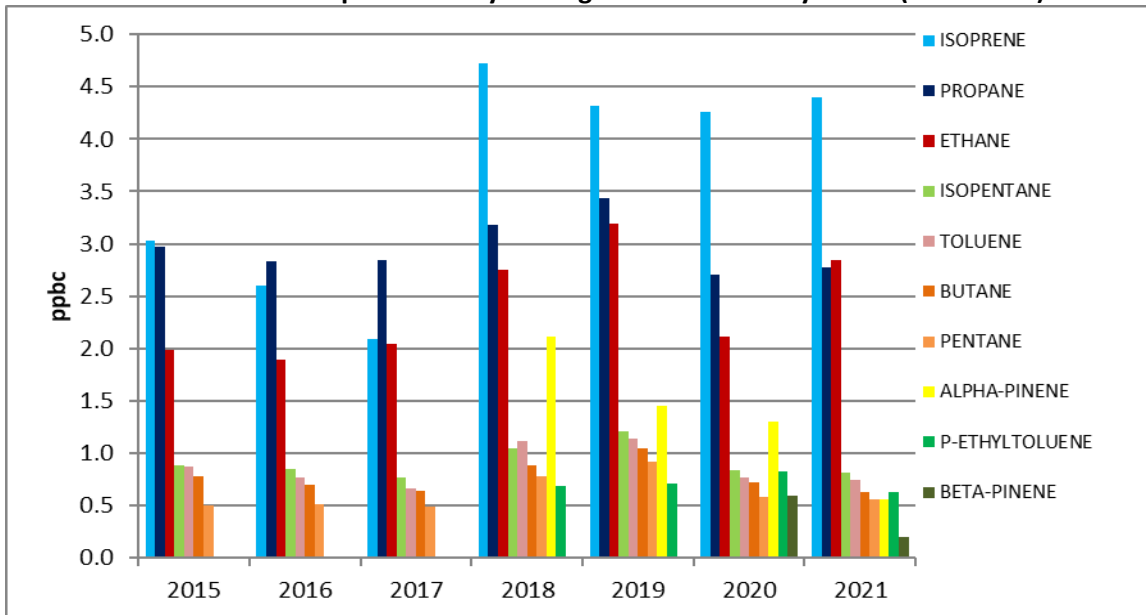
Looking at the 10 most abundant compounds at Miller over the last several years (**Figure 5.2**), the top five have been consistent, and the differences in the remainder have been minimal, minus the significant increase in benzene for 2021. The change is more dramatic at the Londonderry site since 2018, for the reasons previously noted (improved measurements for natural emissions) (**Figure 5.3**).

Figure 5.2: 10 Most Abundant Species Yearly Averages at Miller PAMS (2015-2021)



Apart from ethane (discussed further in Section 5.2), the highest concentrations of the remaining top 5 species occurred during the warmer months of the year at Miller in 2021, shown in **Figure 5.4**, coinciding with the highest average temperatures.

Figure 5.3: 10 Most Abundant Species Yearly Averages at Londonderry PAMS (2015-2021)



** Data loss occurred during portions of peak season 2020.*

P-Ethyltoluene measured slightly lower as a seasonal average at Miller compared to 2020 as did 1,2,3-Trimethylbenzene as seen in Figure 5.3. Ethane is measured approximately 18% higher at Miller this year and 29% higher at Londonderry compared to last year. Propane measured slightly higher this year at Londonderry (a 2% increase) while isopentane and toluene were 3.6% and 2.6% lower respectively. Benzene was 188% higher in 2021 at Miller and Isoprene was 3% higher at Londonderry and 60% higher at Miller (part in due to low capture rates in 2020 at Miller during the peak of the season).

Isoprene production is highest in the warmest months that also have the strongest sunlight: product shows a strong positive correlation with light and temperature. As shown in **Figure 5.4** and **Figure 5.5**, isoprene production was highest during the warmest month at both sites. During 2021, this compound measured higher at Miller and Londonderry compared to 2020. The drastic increase seen at Miller is indicative again of the large loss of data capture that occurred during the warmest period of the PAMS season during 2020. Isoprene’s chemical structure makes it a highly reactive substance with a short atmospheric lifetime and large ozone forming potential. The amount of isoprene emissions (and the pinenes (α and β) from oaks and conifers varies seasonally, with emissions increasing as length of daylight and temperature increase.

Figure 5.4: Five Most Abundant Species Monthly Averages at Miller, 2021

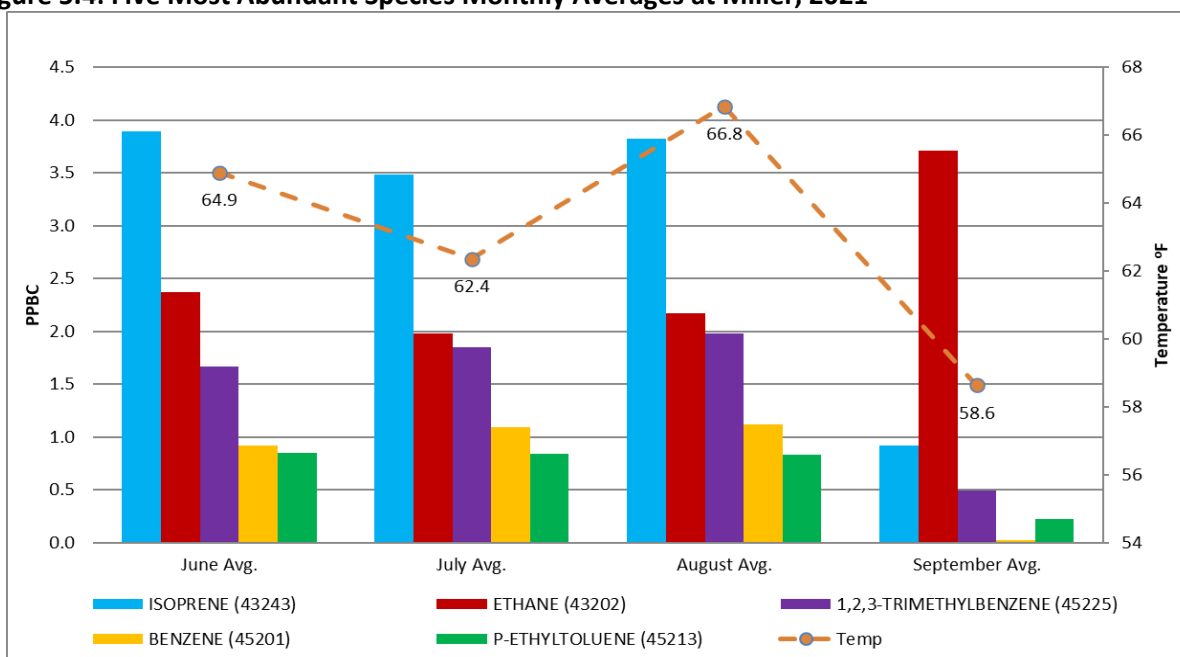
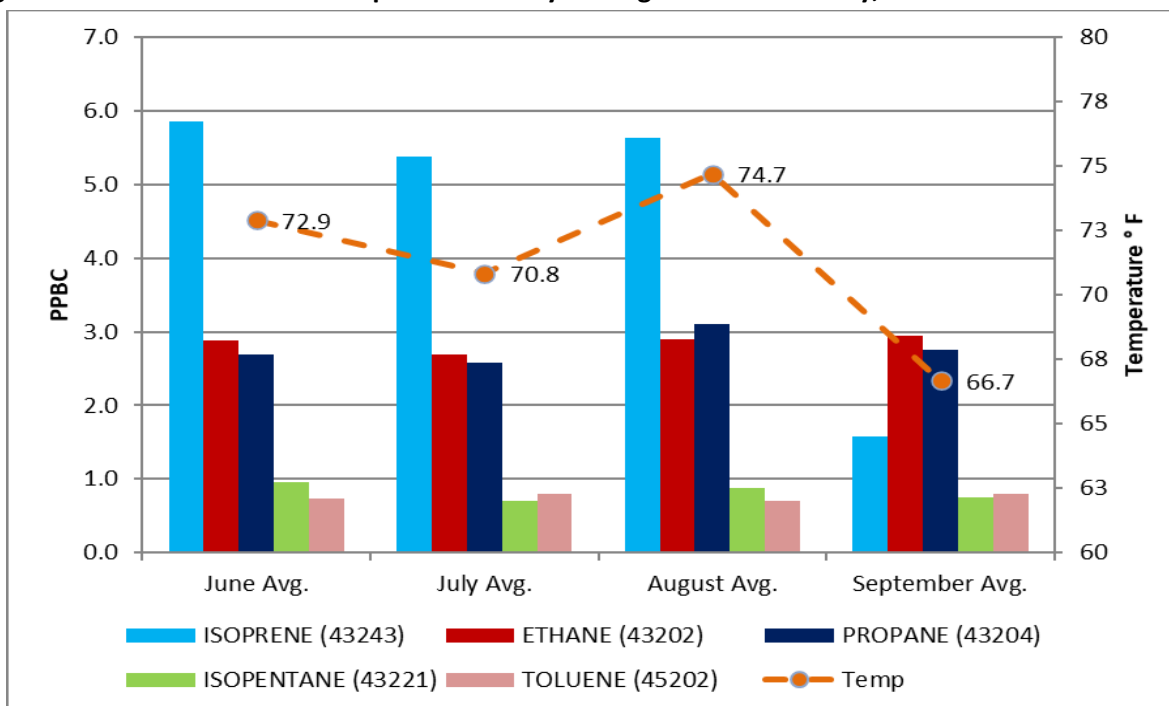


Figure 5.5: Five Most Abundant Species Monthly Averages at Londonderry, 2021

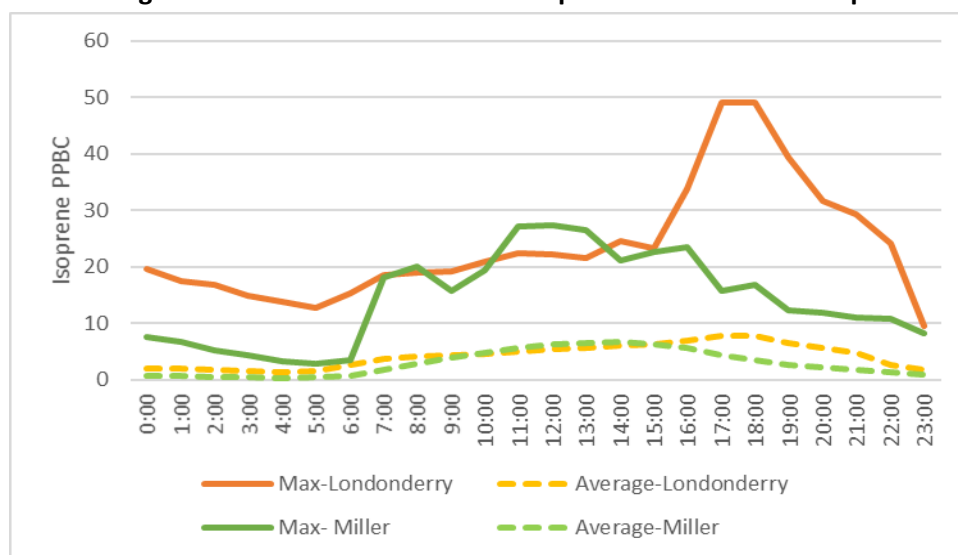


5.2 Diurnal, Weekly and High-Low Elevation Variation

The next series of graphs compare the top 10 compounds at each site with their diurnal patterns and hourly maximum concentrations. These figures compare two relatively close monitoring stations with an elevation difference (a high elevation site - Miller compared to a low elevation site - Londonderry) where applicable. In general, the average values (average for an hour for the entire monitoring season) exhibit a weaker diurnal pattern than the maximum values for that hour for the entire monitoring season.

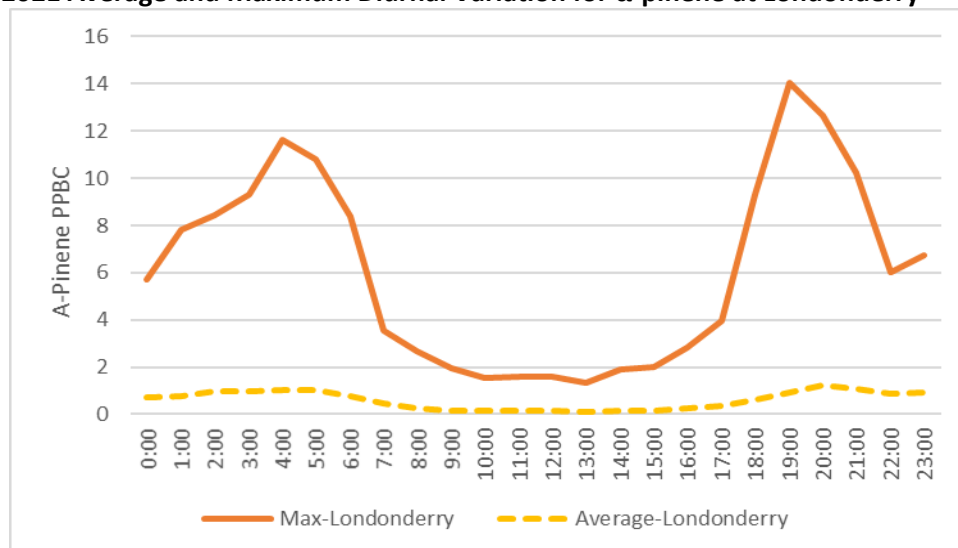
Isoprene was the most abundant species at both the Londonderry and Miller sites in 2021, with Londonderry showing higher values compared to Miller. The species shows a distinct diurnal pattern (**Figure 5.6**), with the highest maximum concentration peaking at the former site on June 6 at 6:00 PM (49.2 parts per billion carbon [ppbC]), and on June 21 at 12:00 PM (27.5 ppbC) at the latter site. The average concentration is similarly delayed. The low elevation site, Londonderry, exhibits higher concentrations and later diurnal peak of isoprene concentrations compared to the high elevation of Miller.

Figure 5.6: 2021 Average Diurnal Pattern and Max for Isoprene at both New Hampshire PAMS Sites



α - and β -pinene were first measured at Londonderry in 2018 as part of the required site equipment upgrades and α -pinene has been in the top 10 at Londonderry since monitoring for it began (**Figure 5.7**). α -pinene and β -pinene are organic compounds of the terpene class. Similar to isoprene, they are biogenic VOCs emitted from plants. As the name suggests, both forms are important constituents of pine resin; they are also found in the resins of many other conifers, as well as in non-coniferous plants. α - and β -pinene show a diurnal pattern indicating that these species are emitted in the evening hours and their concentration decreases during the day as they react photochemically.

Figure 5.7: 2021 Average and Maximum Diurnal Variation for α -pinene at Londonderry



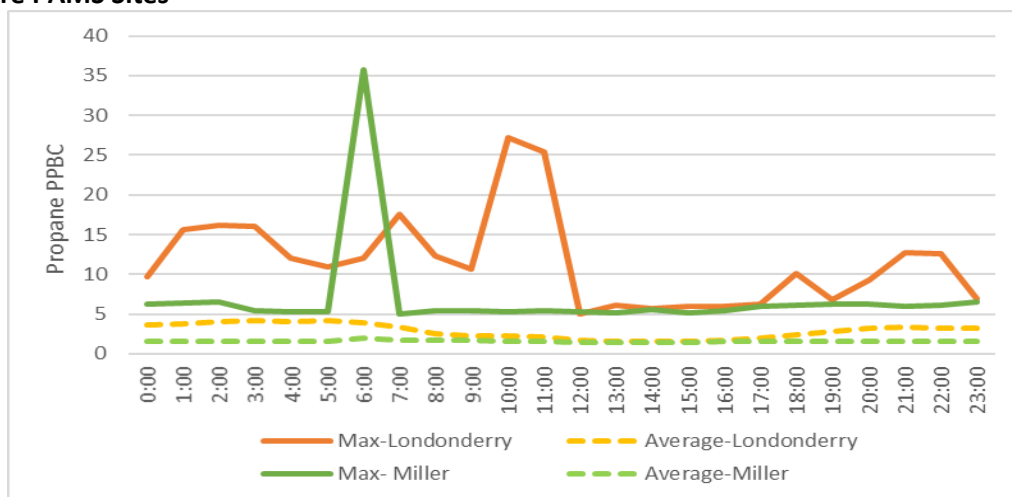
Ethane was the second most abundant compound measured at both Miller and Londonderry and there is not much of a diurnal pattern seen at either site (**Figure 5.8**). Hourly average ethane emissions at both sites were consistent in 2021 indicating they do not necessarily react to the warming of the day. Interestingly, peaks representing maximum values occurred on September 13 at 2:00 AM at both sites. Backwards trajectories and wind data indicate that the air mass traveled from the west to both Miller and Londonderry on this date. This trend is mirrored in the figure below; maximum ethane values occur earlier in the day and pick up again later in the afternoon.

Figure 5.8: 2021 Diurnal Pattern for Average and Maximum Hourly Values for Ethane at New Hampshire PAMS Sites



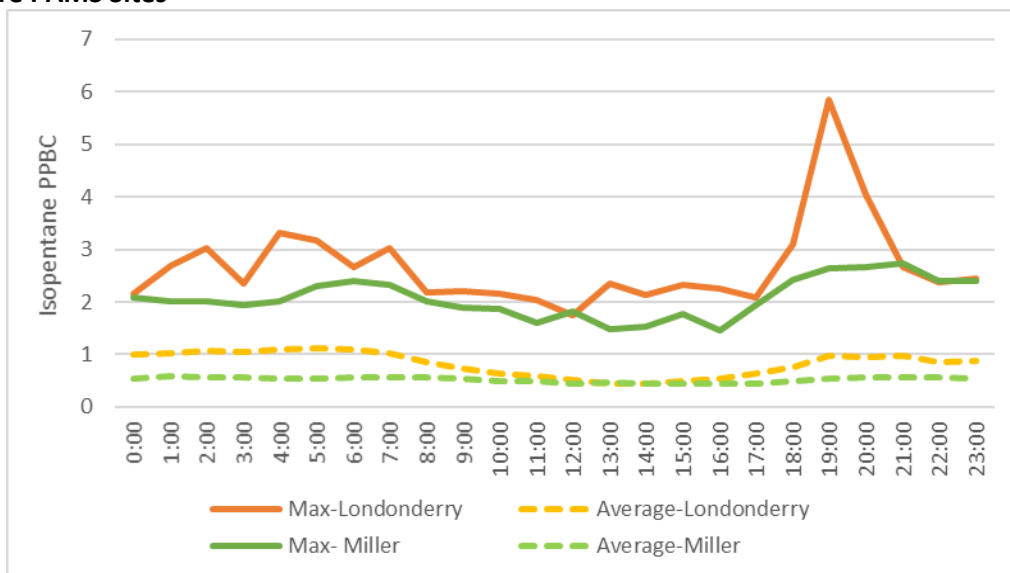
Propane is very persistent in the air in New Hampshire and most emissions are believed to come from natural gas leakage and combustion of liquid petroleum gas (LPG). Propane tends to accumulate in the atmosphere, with higher concentrations occurring overnight and early morning at lower elevations (Londonderry) and more evenly distributed concentrations throughout the day at higher elevations (Miller) (**Figure 5.9**). This tendency may even be seen at higher concentrations during the colder months, when PAMS is not running, due to its use as a heating fuel. Propane concentrations are stable at Miller and show a variable, diurnal pattern at Londonderry, which is situated in a more urban locale. The low elevation site exhibits higher concentrations of propane compared to the high elevation site.

Figure 5.9: 2021 Diurnal Pattern for Average and Maximum Hourly Values for Propane at New Hampshire PAMS Sites



Isopentane is an alkane and can be a more stable indicator of long-range transport (**Figure 5.10**). Miller shows a subtle diurnal pattern with a slight increase in the early morning and late afternoon. Isopentane at Londonderry shows a more exaggerated pattern than what is seen at Miller, with the nadir occurring midday. Londonderry exhibited higher concentrations of isopentane but is on both sites top ten abundant list for 2021.

Figure 5.10: 2021 Diurnal Pattern for Average and Maximum Hourly Values for Isopentane at New Hampshire PAMS Sites



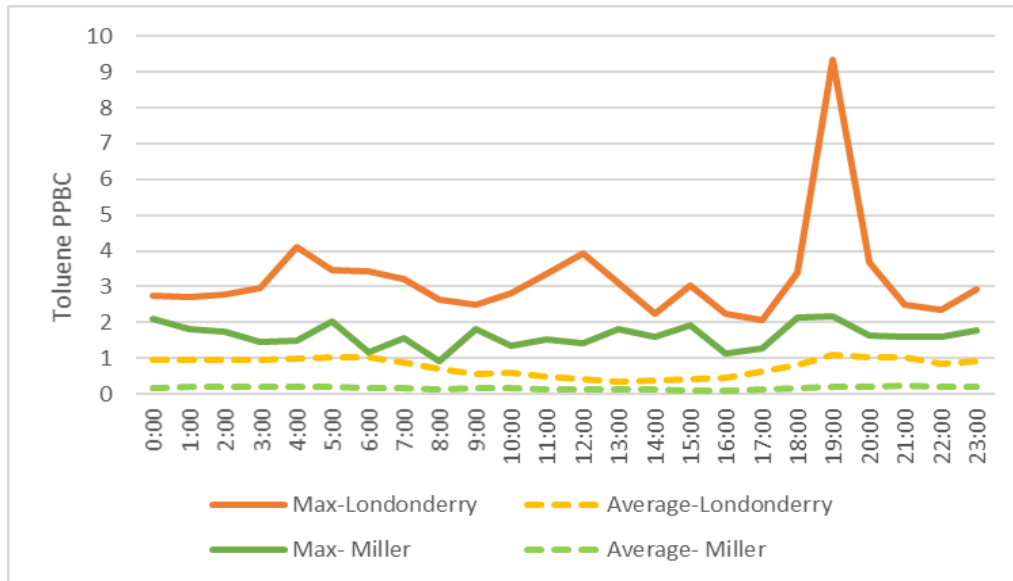
n-butane is used in the blending of gasoline, as a fuel gas, lighter fluid, an extraction solvent and is also a constituent of LPG. Maximum n-butane concentrations had various peaks throughout the day at both sites but were not necessarily indicative of a daytime pattern, although the average concentrations at Londonderry do show a mid-day dip (**Figure 5.11**). Both locations showed slightly elevated overnight concentrations of n-Butane. Londonderry averaged higher concentrations while Miller often had higher hourly peaks.

Figure 5.11: 2021 Diurnal Pattern for Average and Maximum Hourly Values for n-Butane at New Hampshire PAMS Sites



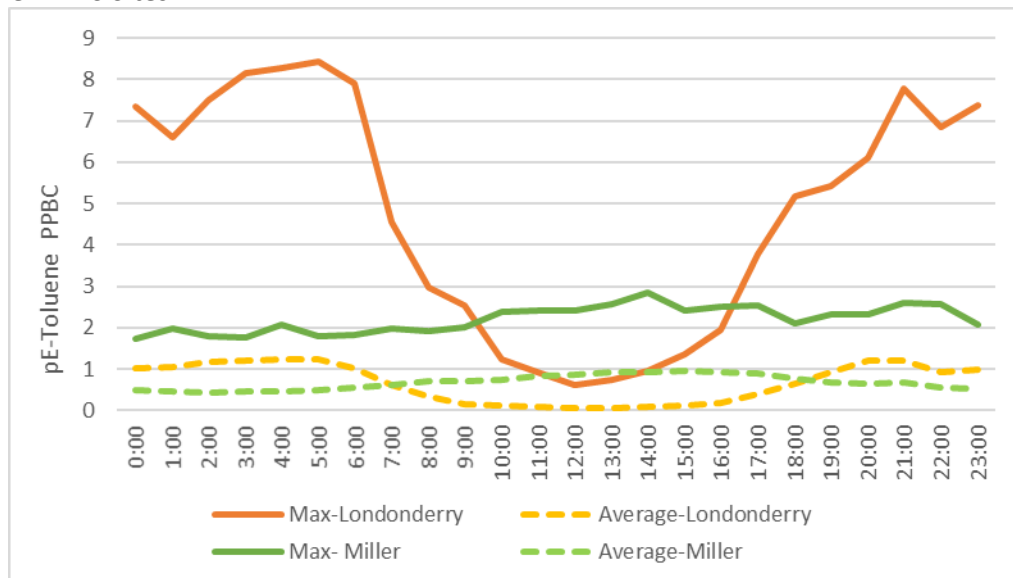
Toluene is a major indicator of motor vehicle exhaust and is usually from a local influence (**Figure 5.12**). Londonderry shows patterns associated with traffic increases building in the early morning and then again in the afternoon and evening. Toluene was not seen in the top ten most abundant compounds at Miller for 2021 perhaps due in part to its location away from heavily traveled roadways but included in the figure for reference.

Figure 5.12: 2021 Diurnal Pattern for Average and Maximum Hourly Values for Toluene at New Hampshire PAMS Sites



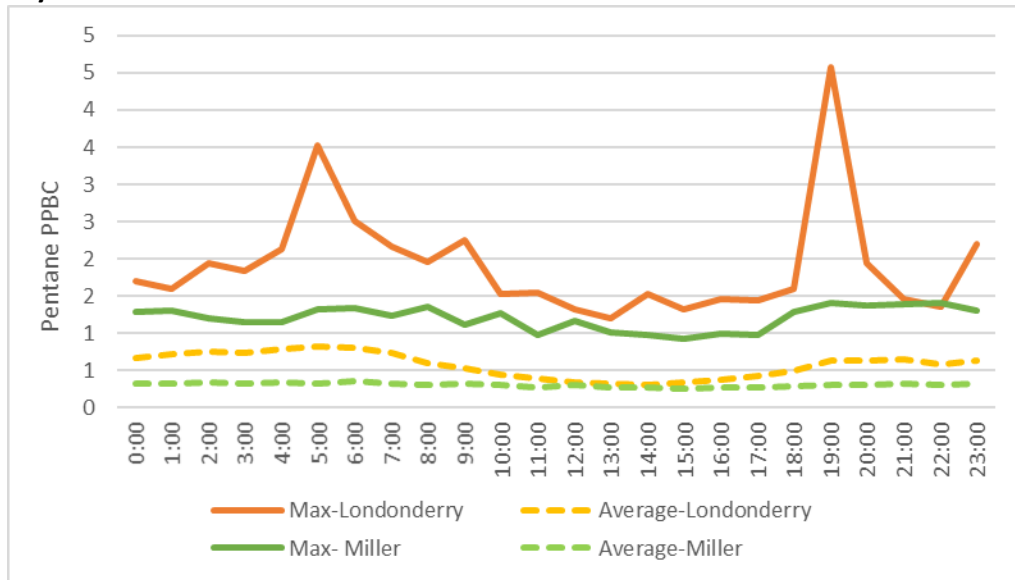
P-Ethyltoluene is a heavy hydrocarbon associated with gas and diesel tailpipe emissions. The diurnal patterns are opposite each other at the two PAMS sites (**Figure 5.13**). P-Ethyltoluene maximums peak in the morning and evening at Londonderry and midday at Miller. This may be in response to increased vehicular traffic on the auto road during the daytime at Miller or a delay in the response to the morning commute. The diurnal profile for Londonderry was significantly more enhanced than Miller overnight and lower during the day.

Figure 5.13: 2021 Diurnal Pattern for Average and Maximum Hourly Values for p-Ethyltoluene at New Hampshire PAMS Sites



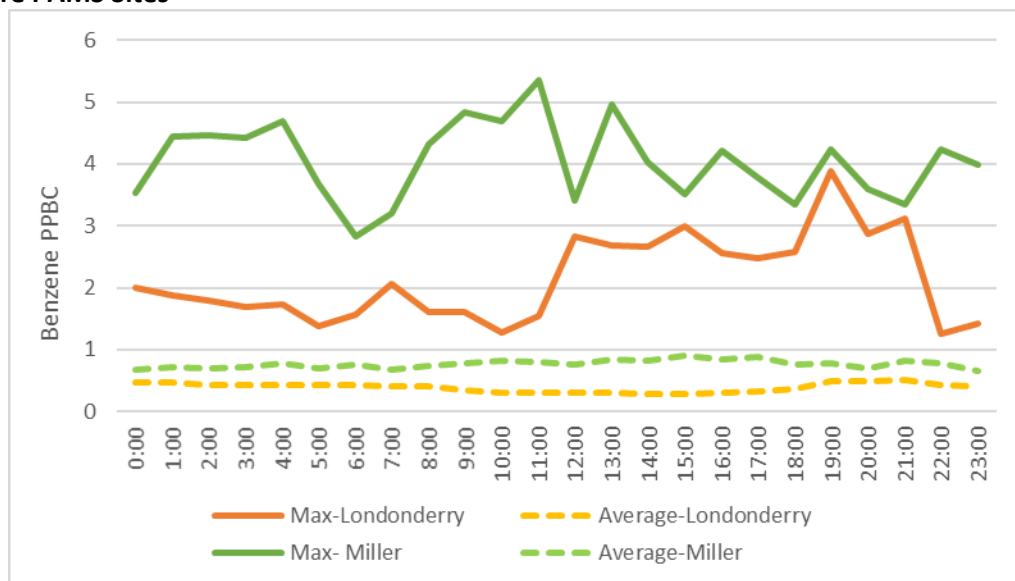
Pentane was among the top 10 compounds at both Londonderry and Miller during 2021 and is associated with petroleum and natural gas products (**Figure 5.14**). Pentane maximums coincide with likely increases in vehicular activity, especially during the early morning hours. Concentrations of pentane are mostly stable throughout the day at Miller, unlike those seen at the Londonderry site. Londonderry is located at Moose Hill Elementary School and these peaks may correlate with traffic patterns.

Figure 5.14: 2021 Diurnal Pattern for Average and Maximum Hourly Values for Pentane at Londonderry



Benzene is widely used throughout the world in a multitude of different processes. It also occurs naturally from volcanoes and forest fires; the latter contributing to the increase in benzene seen at both PAMS sites in 2021 (**Figure 5.15**). Otherwise, average diurnal patterns for both PAMS locations typically remain fairly stable throughout the day.

Figure 5.15: 2021 Diurnal Pattern for Average and Maximum Hourly Values for Benzene at New Hampshire PAMS Sites



1-Butene and 1,2,3-Trimethylbenzene (1,2,3 TMB) are two PAMS compounds that were in the top 10 most abundant compounds at Miller but not at Londonderry. 1-Butene is used in the production of many industrial materials and its vapor is heavier than air making it capable of traveling long distances (Figure 5.16). As a result, it shows a very slight diurnal pattern, characteristic of many of the PAMS compounds at that elevated site. 1,2,3 TMB is an aromatic hydrocarbon occurring naturally in coal tar and petroleum; it is used in jet fuel and gasoline as well as an industrial solvent (Figure 5.17). This compound does show more of a pattern than most at Miller, peaking during the mid-afternoon.

Figure 5.16: 2021 Diurnal Pattern for Average and Maximum Hourly Values for 1-Butene at Miller

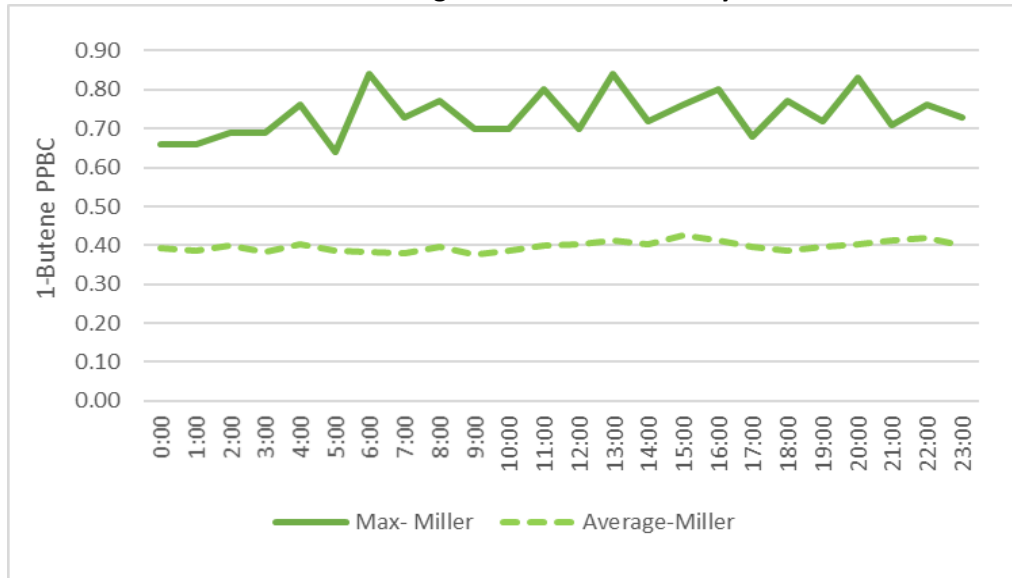


Figure 5.17 : 2021 Diurnal Pattern for Average and Maximum Hourly Values for 1,2,3-Trimethylbenzene at Miller



The data were then examined to determine if there was any variation between weekday and weekend emissions. First, different categories of VOCs were analyzed to look for patterns. The maximum TNMOC value appears on weekdays at Miller and weekends at Londonderry. Otherwise, maximum value trends are split at both sites (Figure 5.18 and

Figure 5.19).

When looking at average values, there is not much of a difference between weekdays and weekends at Londonderry. Average concentrations at Miller are generally higher on weekdays and lower on weekends. Olefins include compounds such as isoprene, butane, and ethylene. Alkanes include ethane, propane, butane and isopentane, and aromatics include heavier hydrocarbons such as benzene and toluene.

Figure 5.18: Average Weekday v. Average Weekend VOC Trends at Londonderry in 2021

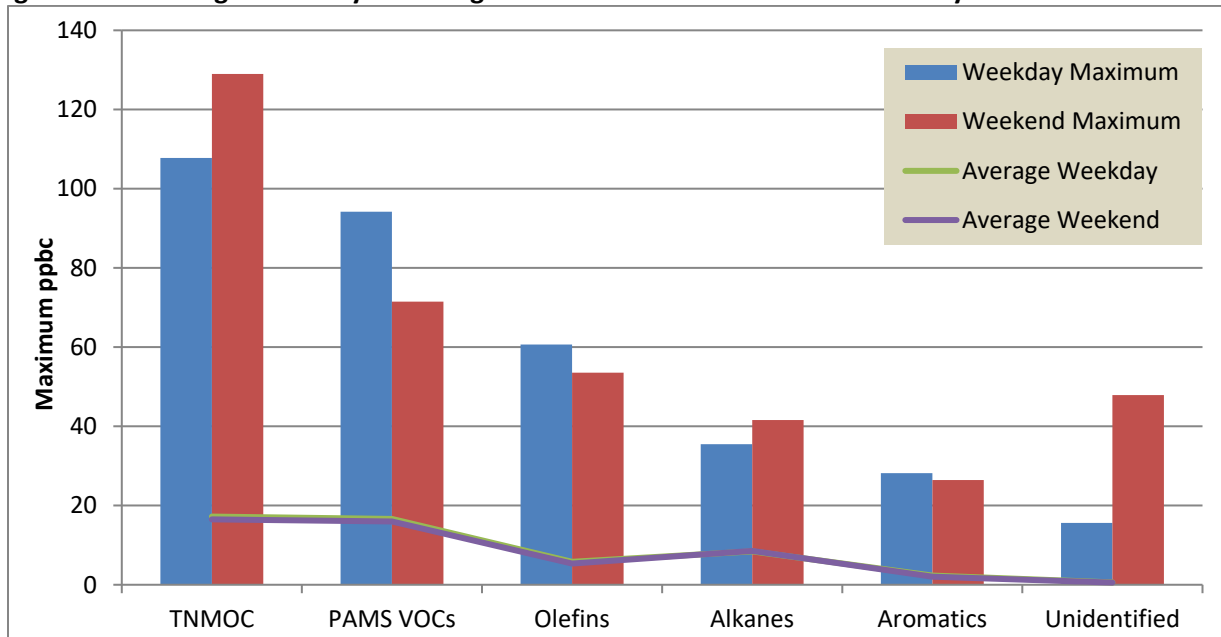
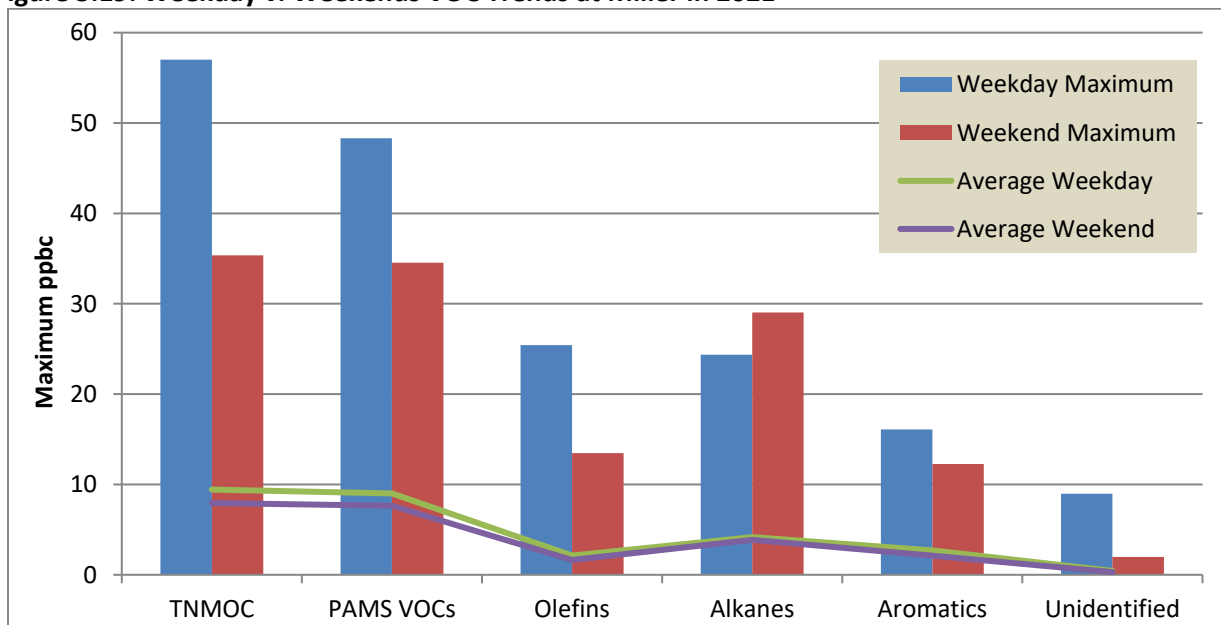


Figure 5.19: Weekday v. Weekends VOC Trends at Miller in 2021



5.3 Compound Groups

Trending of select compound groups is another useful way to analyze PAMS data. Compounds associated with certain types of emission sources are grouped to determine how emissions of related compounds trend over time and how they appear to affect ozone forming potential.

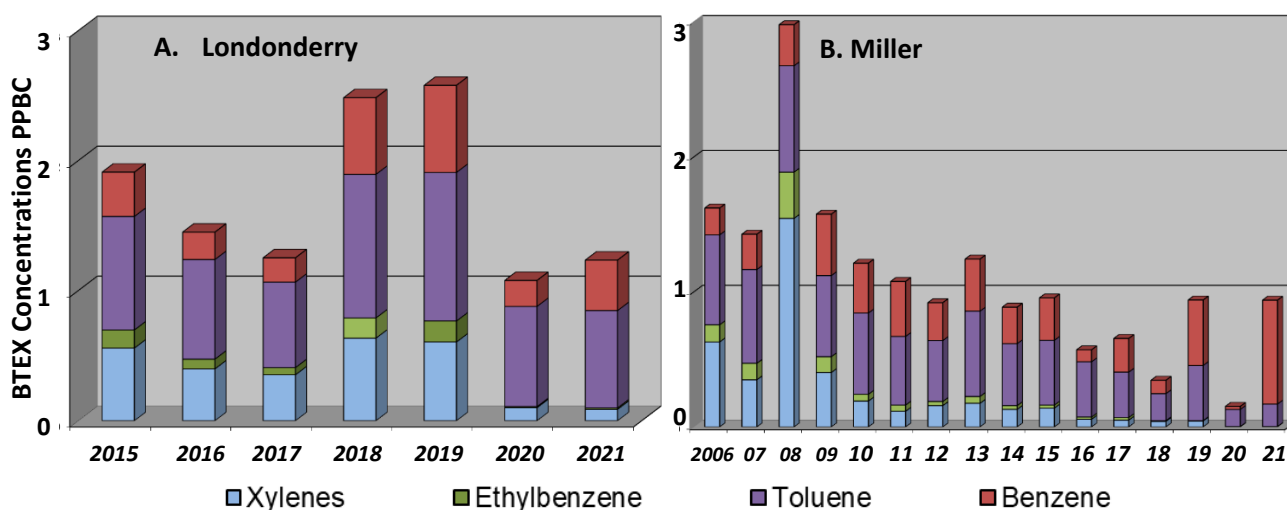
5.3.1 Gasoline Related Compounds

The BTEX gasoline related compound group includes benzene, toluene, ethylbenzene, and xylene, which are all organic compounds that are emitted from petroleum derivatives among other sources. BTEX gives a great indication of VOC emissions from a range of sources.

As expected, the Londonderry location experiences higher concentrations of BTEX compounds compared to Miller, due in part to its location in a suburban area where vehicle traffic is more common than at the more remote Miller location (**Figure 5.20**). Though still rural, its proximity to heavily traveled roadways, an airport and an industrial park have an influence on compound concentrations. BTEX compounds at this site were similar between 2018 and 2019, but we see a drastic reduction in 2020 likely due to the COVID-19 pandemic and decreased traffic throughout the summer. This trend however carried over to 2021 with only a slight increase in toluene values and more of an increase of Benzene, presumably due to the prevalence of benzene in wildfire smoke seen throughout portions of the summer.

The Miller site is in a much more rural location and at a higher elevation. As a result, this site measures lower BTEX concentrations than Londonderry. Despite year-to-year variability, **Figure 5.20** shows BTEX compound concentrations have clearly trended downward since 2006 at this site. Concentrations of the BTEX group show a significant drop in 2020, most likely due to a combination of reduced vehicular travel during the COVID-19 pandemic and from data loss during portions of peak season, however Benzene values make a comeback in 2021 which is further detailed in section 5.5 of this report.

Figure 5.20: Yearly Averages of BTEX Compounds



**2008 Miller data are biased high due to the installation complications of new instrumentation and contamination of high molecular weight compounds. Data loss occurred during portions of peak season 2020.*

BTEX concentrations at Londonderry display a typical diurnal pattern for reactive, anthropogenic VOCs with emissions generally dominated by automotive-related sources (**Figure 5.21**). This pattern is interpreted as follows:

- The morning maximum is associated with high emissions from morning rush hour traffic and limited vertical mixing in the lower atmosphere.
- The midday minimum is associated with decreased mobile source emissions and a rapid growth of the daytime boundary layer which leads to increased vertical mixing and increased reaction rates due to higher temperatures and maximum solar radiation.
- The early evening maximum is associated with gradual buildup of emissions in the boundary layer over the course of the day, increased mobile source emissions during the afternoon culminating in an early evening commute traffic peak, and decreased vertical mixing.⁸

BTEX concentrations at Miller shows a different scenario and ethylbenzene and the xylenes are not routinely seen at this higher elevation. In addition, benzene concentrations are, in many cases, higher than toluene, which is not typical in ambient air in most urban settings.

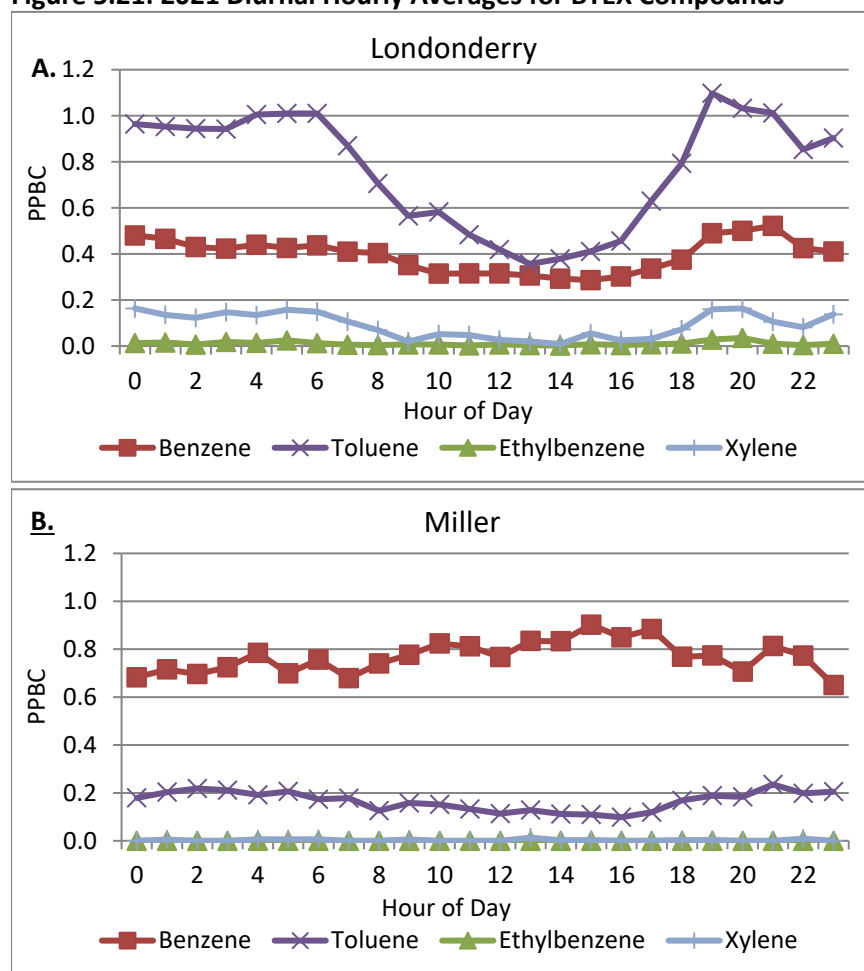
Figure 5.21 exhibits the diurnal pattern seen with the Miller data (B.) is not to the same extent as Londonderry (A.). In 2021, benzene is seen at a much higher rate than in the past and is stable throughout the day, though the benzene concentrations drop significantly in September which is not represented in this graph.

The majority of benzene emissions come from combustion, whereas toluene (along with ethylbenzene and xylenes) is mostly found as a solvent in gasoline and industrial uses. According to the works carried out by Atkinson (1990) and Simpson (1995), the lifetimes of benzene and toluene are 56.5 hours and 11.7 hours, respectively. The longer lifespan of benzene does correlate with a more aged air mass which is frequently seen at the Miller site due to its higher elevation.

The scatter plot of benzene and xylene ratios to toluene (

Overall, xylenes and ethylbenzene had higher concentrations at Londonderry (low elevation) than at Miller (high elevation). But benzene concentrations at Miller were higher than at the lower elevation Londonderry location. Toluene was about the same at both locations. Correlations between toluene and

Figure 5.21: 2021 Diurnal Hourly Averages for BTEX Compounds



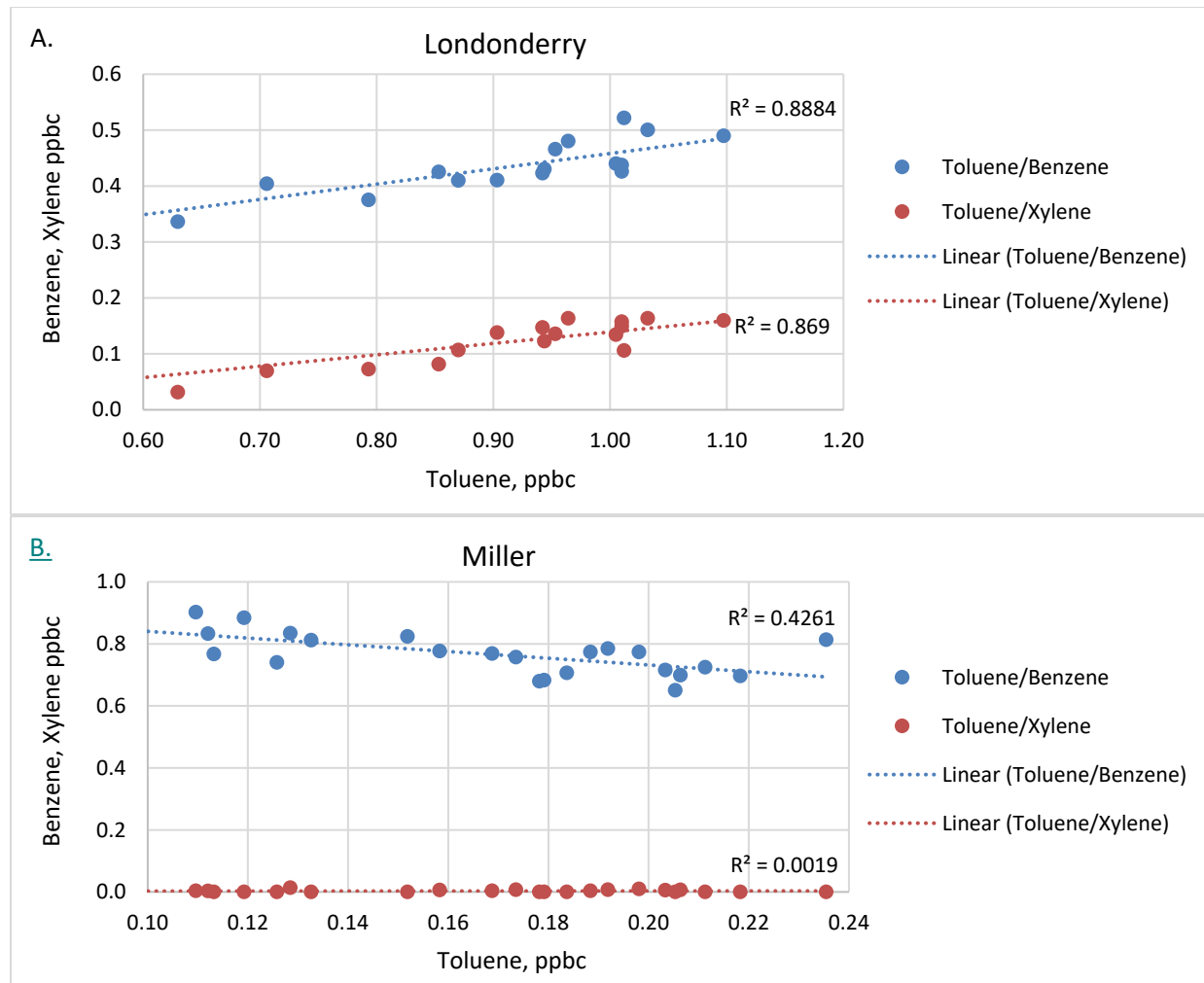
⁸ EPA, PAMS Data Analysis Results Report, EPA-454/R-96-006, November 1996

benzene, and toluene and xylene were relatively strong at Londonderry and weak at Miller. This supports the observation that these VOC compounds are fresher at Londonderry and more aged and transported at Miller.

Figure 5.22), representing average hourly emissions for the season, shows that toluene concentrations at Londonderry were well correlated with both benzene and xylenes, which is consistent with fresh emissions. The lack of xylene concentrations at Miller makes this determination harder, though the benzene toluene ratio shows the opposite pattern as Londonderry, again emphasizing a more aged air mass at this location.

Overall, xylenes and ethylbenzene had higher concentrations at Londonderry (low elevation) than at Miller (high elevation). But benzene concentrations at Miller were higher than at the lower elevation Londonderry location. Toluene was about the same at both locations. Correlations between toluene and benzene, and toluene and xylene were relatively strong at Londonderry and weak at Miller. This supports the observation that these VOC compounds are fresher at Londonderry and more aged and transported at Miller.

Figure 5.22: 2021 Benzene/Toluene and Xylene/Toluene ratios at Londonderry and Miller

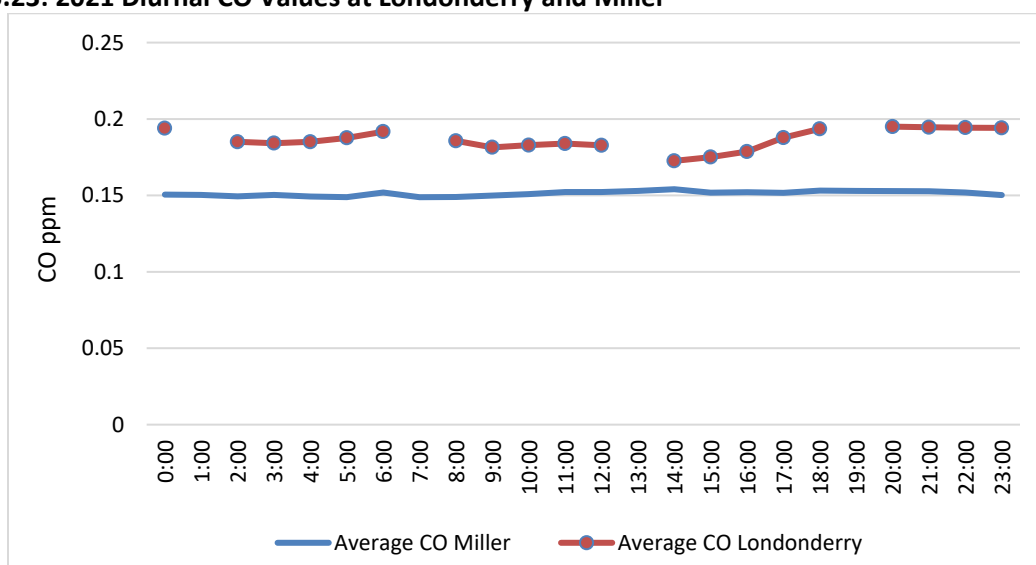


5.3.2 Motor Vehicle Tracers

Typically, nitrogen oxides (NO_y) and carbon monoxide (CO) are collected at the two NH PAMS sites as part of the NCORE requirements. These compounds are good motor vehicle tracers where higher concentrations occur during commuting times. NO_x is oxidized in the hours and days after emission to various organic and inorganic nitrates. NO_y comprise of these product species plus unreacted NO_x. CO has a relatively long lifetime and generally has a flat diurnal pattern in New Hampshire, especially at the low concentrations being measured. Unfortunately, instrument challenges resulted in no reportable data for NO_y, NO or NO_x data during the 2021 PAMS season at either location.

Figure 5.23 outlines hourly CO average values at Londonderry and Miller during the 2021 PAMS season. The Londonderry site demonstrates periodic dips during the 1:00 AM/PM and 7:00 AM/PM hours due to a feature on the analyzer which skews those hours' low, therefore they have been removed from the graph. A pattern can still be seen, however, where CO values increase slightly during the 6:00 AM and 6:00 PM time frames correlating with traffic patterns. Additionally, CO values are higher at Londonderry than Miller also indicating influence from local traffic. This result was expected since CO is relatively stable in the air and Londonderry is closer to fresh emission than Miller.

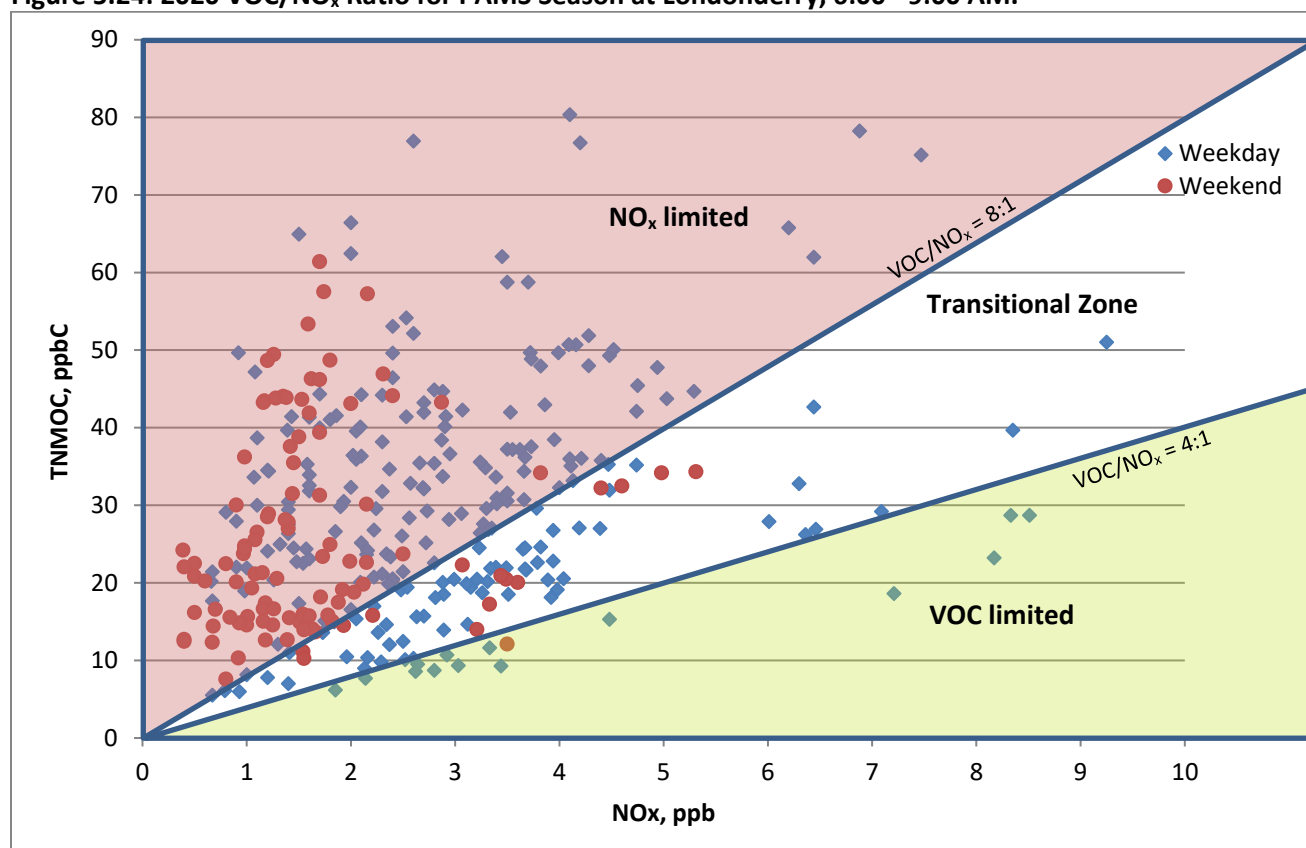
Figure 5.23: 2021 Diurnal CO Values at Londonderry and Miller



The ratio of TNMOC to NO_x is used to understand the relative importance of TNMOC and NO_x precursors to ozone formation. In general, when TNMOC/NO_x is low (below four), the atmosphere is "VOC-limited," which infers that a VOC-based emission control strategy is helpful to reduce high ozone concentrations. Conversely, when ratios are well above eight, the atmosphere is "NO_x-limited," and NO_x emission controls will be more effective than VOC emission controls in reducing ozone. The zone in between is called the Transitional Zone and either NO_x and/or VOC emission controls can be helpful in reducing high ozone concentrations. However, in the actual atmosphere, wide variations in the measured TNMOC/NO_x ratio occur and it's constantly shifting, thus emission controls are normally targeted to the category where most data points reside when high ozone conditions occur.

Figure 5.24 shows the VOC/NO_x ratios for the hours of 6:00-9:00 AM at the Londonderry site for both weekdays and weekends. The 6:00-9:00 AM TNMOC/NO_x ratios tend to emphasize the importance of motor vehicle exhaust, since the emissions from this source grouping peak during these morning hours. Other VOC sources such as biogenic hydrocarbons, non-road mobile sources, and evaporative sources of all types, peak at midday or in the afternoon. The chart shows both weekday and weekend emissions heavily tilted toward being NO_x-limited. New Hampshire is a mostly rural state that is heavily forested which produces large quantities of natural VOC emissions, especially on warmer days conducive to ozone production, tipping the TNMOC/NO_x ratio in favor of being NO_x-limiting. Stagnation or changes in wind direction have the potential to cause significant buildup of emissions, or transport of aged emissions, at that site.

Figure 5.24: 2020 VOC/NO_x Ratio for PAMS Season at Londonderry, 6:00 - 9:00 AM.



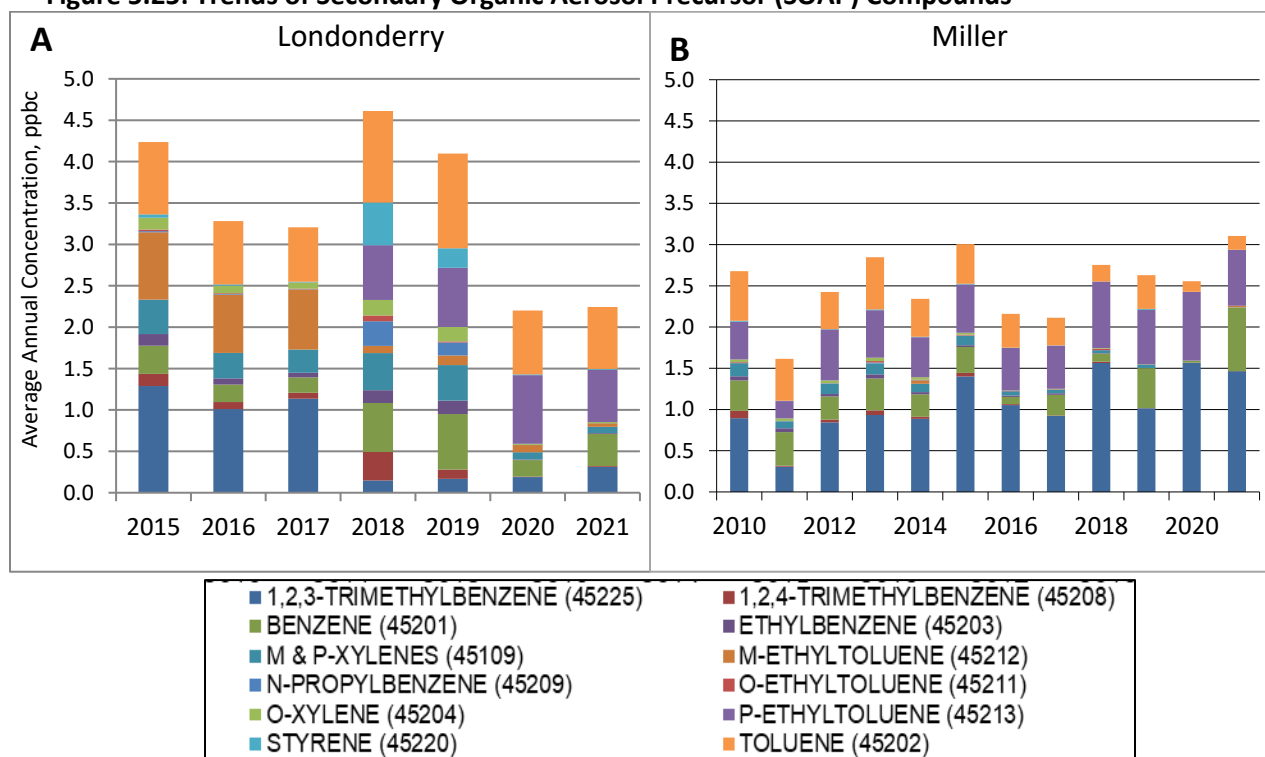
Note: Figure 5.24 uses 2020 data due to the lack of NO_x data for 2021

5.3.3 Secondary Organic Aerosol Precursors (SOAP)

Secondary organic aerosols (SOA) are formed from the atmospheric oxidation of precursor gas emissions of organic compounds that can develop into solid form particulate matter. Because SOA emissions are so common, SOA precursors (SOAP) are a major component of fine particle pollution (particulate matter less than 2.5 microns, PM_{2.5}), which has been found to cause lung and heart problems among other health effects. Fine particles (including SOAP) are also the leading cause of reduced visibility (haze) in parts of the United States. Anthropogenic and biogenic VOCs can react in the atmosphere to form SOA and are considered secondary organic aerosol precursors. Several PAMS compounds fall into this category and are examined for their overall trend at the New Hampshire PAMS sites.

At Londonderry (**Figure 5.25A**), average total concentrations of these precursors decreased in 2020 compared to the prior years and that trend continued into 2021. Concentrations of SOAP at Miller State Park (**Figure 5.25B**) have been relatively consistent since 2010, though individual compounds have varied considerably. Of note at both sites is the decrease over time of compounds like 1,2,4-trimethylbenzene and m/p-xylene. This group of compounds is now dominated by toluene, p-Ethyltoluene and benzene at both sites and 1,2,3-trimethylbenzene at Miller.

Figure 5.25: Trends of Secondary Organic Aerosol Precursor (SOAP) Compounds



* Data loss occurred during portions of peak season 2020 at Miller site.

5.4 Other Species

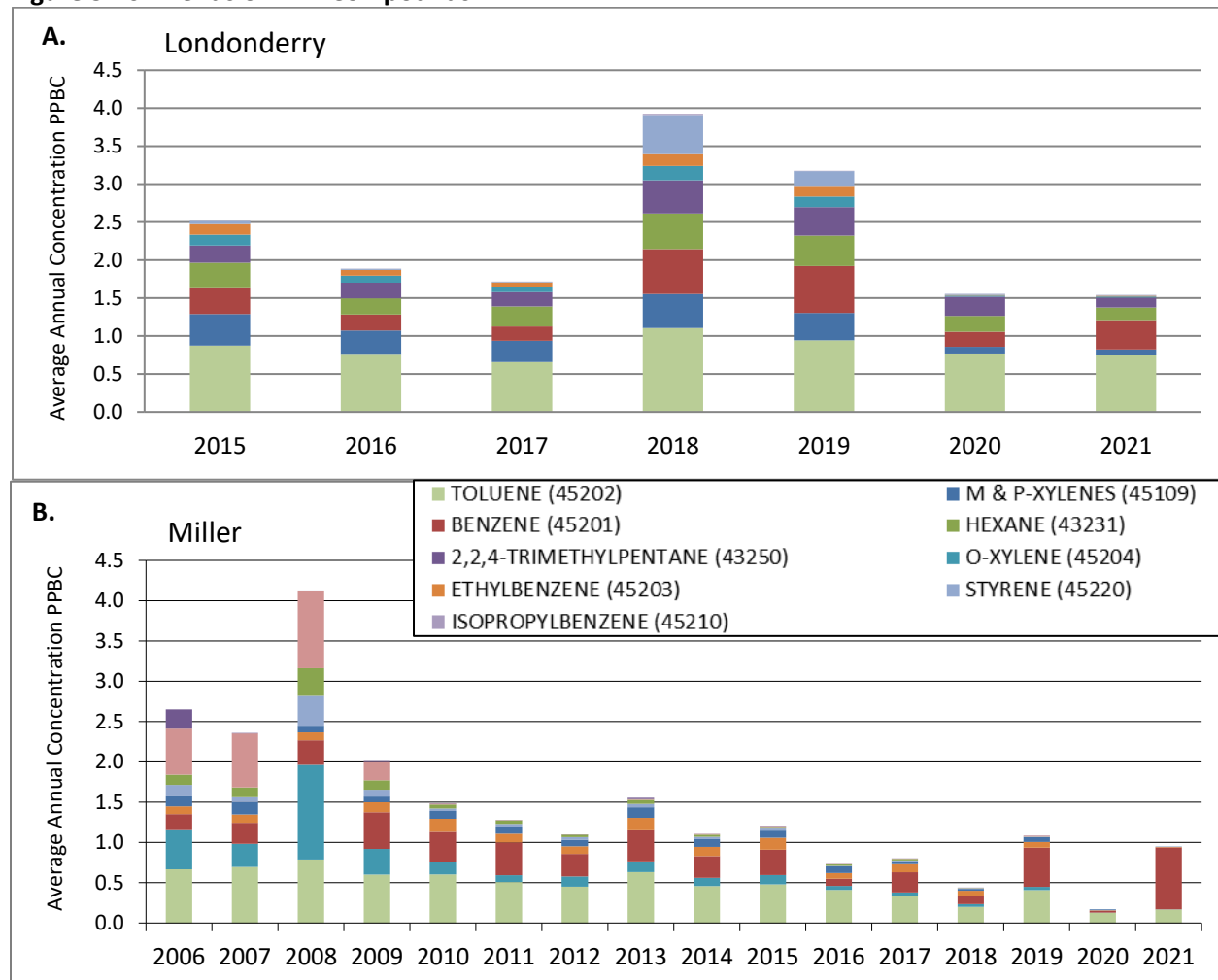
5.4.1 Hazardous Air Pollutants

Hazardous Air Pollutants (HAPs) are chemicals that can cause adverse effects to human health and the environment. The EPA currently lists [187 compounds](#)⁹ in this group including substances that are known or suspected to cause cancer or other serious health effects, such as reproductive effects, birth defects or adverse environmental effects. Nine of the PAMS compounds are listed HAPs. PAMS monitoring is currently the only consistent method to measure these compounds routinely in ambient air in New Hampshire. HAP concentrations at Londonderry appear to have increased dramatically in 2018 (**Figure 5.26**), for styrene¹⁰ in particular. These increases are a function of the new equipment installed there, rather than changes in emission sources, although trace amounts of styrene are known to be present in vehicle exhaust. The drastic reduction of these compounds at both sites in 2020 was likely a result of less emissions during the COVID-19 pandemic. This trend did continue at Londonderry for 2021, but rebounded at Miller, mostly due to increased benzene concentrations.

⁹ [Hazardous Air Pollutants | US EPA](#)

¹⁰ Styrene was found in the blanks, therefore skewed the results high for this compound. It was flagged in the reported AQS data for this reason.

Figure 5.26: Trends of HAP Compounds



* Data loss occurred during portions of peak season 2020 at Miller.

5.4.2 Toxic Species

The NHDES Air Toxics Control Program regulates HAP emissions as well as over 800 regulated toxic air pollutants (RTAPs), which have a health-based risk to humans. The aim of the regulatory program is to protect public health and the environment by establishing ambient air limits (AALs) and requiring businesses in the state to reduce their emissions of any of the RTAPs, such that they do not affect the downwind air quality at levels that may exceed the established AALs. The list of RTAPs, published in New Hampshire Code of Administrative Rules Chapter Env-A 1400 Regulated Toxic Air Pollutants includes: (1) those compounds listed as HAPs by EPA; (2) those chemical substances for which a threshold limit value has been established by the American Conference of Governmental Industrial Hygienists; and (3) those compounds not otherwise included that are regulated by the Occupational Safety and Health Administration. The AALs are reviewed and updated every year as new scientific data on toxicity becomes available. As with HAPS, PAMS is the only consistent means of measuring these compounds in ambient air in New Hampshire.

Tables 5.2 and 5.3 summarize the AALs for the relevant PAMS compounds at each site. Measured benzene concentrations at Londonderry and Miller are 15.98% and 26.99%, respectively, of the AAL for 2021. Londonderry increased by 73% and Miller up by 149% from 2020 values. The increase of benzene concentrations at Miller is discussed below and summarized in Figure 5.27 and Figure 5.28, as well as throughout the report. All other PAMS compounds with an assigned AAL have consistently measured less than 1% of their AAL.

Table 5.2: Seasonal Maximum 24-hour Averages at Londonderry for Toxic Species vs. AAL

202

PAMS Parameter	AAL ug/m ³	Max 24 Hr. Avg. (ug/m ³)							2021 Max % of AAL	2021 Change
		2015	2016	2017	2018	2019	2020	2021		
PROPYLENE (43205)	35,833	0.37	0.21	0.28	0.41	0.56	0.39	0.34	0.00%	=
CYCLOPENTANE (43242)	25,595	0.11	0.15	0.07	0.13	0.17	0.03	0.02	0.00%	=
ISOPENTANE (43221)	36,875	1.17	1.73	1.27	1.09	1.26	0.95	1.02	0.00%	=
PENTANE (43220)	36,875	0.59	0.73	0.73	0.86	0.81	0.62	0.70	0.00%	=
2-METHYLPENTANE (43285)	36,875	0.16	0.25	0.13	0.42	0.53	0.39	0.33	0.00%	=
3-METHYLPENTANE (43230)	36,875	0.16	0.29	0.11	0.34	0.44	0.29	0.14	0.00%	=
HEXANE (43231)	885	0.44	0.64	0.50	0.52	0.54	0.60	0.33	0.04%	↓
BENZENE (45201)	6	0.53	0.27	0.33	0.69	0.53	0.42	0.91	15.98%	↑
CYCLOHEXANE (43248)	6,000	0.12	0.18	0.10	0.17	0.15	0.02	0.03	0.00%	=
HEPTANE (43232)	8,249	0.18	0.44	0.11	0.25	0.36	0.10	0.13	0.00%	=
METHYLCYCLOHEXANE (43261)	23,958	0.12	0.24	0.07	0.15	0.16	0.02	0.03	0.00%	=
TOLUENE (45202)	5,000	1.11	1.65	1.17	1.07	1.10	1.14	0.93	0.02%	=
OCTANE (43233)	7,000	0.11	0.15	0.04	0.12	0.14	0.02	0.01	0.00%	=
ETHYLBENZENE (45203)	1,000	0.18	0.22	0.16	0.20	0.25	0.07	0.08	0.01%	=
M & P-XYLENES (45109)	1,550	0.51	0.61	0.53	0.52	0.47	0.28	0.38	0.02%	=
STYRENE (45220)	1,000	0.17	0.07	0.07	0.47	0.44	0.17	0.11	0.01%	↓
O-XYLENE (45204)	1,550	0.20	0.21	0.21	0.23	0.29	0.09	0.15	0.01%	=
NONANE (43235)	15,625	0.13	0.11	0.12	0.10	0.12	0.03	0.15	0.00%	=
1,3,5-TRIMETHYLBENZENE (45207)	619	0.10	0.12	0.07	0.07	0.03	0.01	0.06	0.01%	↑
1,2,4-TRIMETHYLBENZENE (45208)	619	0.21	0.27	0.19	0.33	0.23	0.04	0.20	0.03%	↑

* Some data flagged for quality control purposes. All data in micrograms per cubic meter (µg/m³). Pandemic may affect the 2020 levels.

Table 5.3: Seasonal Maximum 24-hour Averages at Miller for Toxic Species vs. AAL

PAMS Parameter	AAL ug/m ³	Max 24 Hour Avg. (ug/m ³)							2021 Max % of AAL	2021 Change
		2015	2016	2017	2018	2019	2020	2021		
PROPYLENE (43205)	35,833	0.28	0.29	0.23	0.61	0.47	0.29	0.21	0.00%	=
CYCLOPENTANE (43242)	25,595	0.23	0.11	0.11	0.09	0.07	0.03	0.06	0.00%	=
ISOPENTANE (43221)	36,875	0.96	0.68	1.34	0.74	0.50	0.54	0.94	0.00%	=
PENTANE (43220)	36,875	0.51	0.38	0.69	0.55	0.41	0.19	0.60	0.00%	=
2-METHYLPENTANE (43285)	36,875	0.12	0.07	0.09	0.07	0.04	0.04	0.19	0.00%	=
3-METHYLPENTANE (43230)	36,875	0.05	0.03	0.02	0.02	0.00	0.52	0.01	0.00%	=
HEXANE (43231)	885	0.40	0.16	0.18	0.29	0.23	0.03	0.03	0.00%	=
BENZENE (45201)	6	0.64	0.18	0.45	0.32	0.48	0.23	1.54	26.99%	↑
CYCLOHEXANE (43248)	6,000	0.09	0.01	0.06	0.03	0.04	0.00	0.03	0.00%	=
HEPTANE (43232)	8,249	0.14	0.04	0.04	0.03	0.03	0.00	0.01	0.00%	=
METHYLCYCLOHEXANE (43261)	23,958	0.10	0.04	0.03	0.02	0.04	0.01	0.00	0.00%	=
TOLUENE (45202)	5,000	0.67	0.53	0.54	0.54	0.53	0.43	0.41	0.01%	=
OCTANE (43233)	7,000	0.02	0.02	0.02	0.01	0.03	0.00	0.00	0.00%	=
ETHYLBENZENE (45203)	1,000	0.08	0.05	0.09	0.04	0.02	0.00	0.00	0.00%	=
M & P-XYLENES (45109)	1,550	0.25	0.13	0.12	0.20	0.14	0.02	0.03	0.00%	=
STYRENE (45220)	1,000	0.04	0.03	0.02	0.02	0.07	0.00	0.00	0.00%	=
O-XYLENE (45204)	1,550	0.06	0.04	0.04	0.06	0.04	0.00	0.00	0.00%	=
NONANE (43235)	15,625	0.09	0.06	0.03	0.03	0.02	0.01	0.01	0.00%	=
1,3,5-TRIMETHYLBENZENE (45207)	619	0.09	0.01	0.02	0.04	0.02	0.01	0.02	0.00%	=
1,2,4-TRIMETHYLBENZENE (45208)	619	0.15	0.04	0.04	0.06	0.01	0.01	0.02	0.00%	=

*All data in micrograms per cubic meter (µg/m³). Pandemic and data loss may affect the 2020 levels.

Benzene concentrations at Miller increased 188% in 2021 over 2020. The increase was not seen with the other BTEX compounds as shown in Section 5.3 above. Seeing consistent amounts of xylenes and ethylbenzene is rare at Miller, however, there has been a trend at this location in the past to see higher levels of benzene over toluene, which is contrary to other PAMS sites, including Londonderry (Figure 5.28). Figure 5.27 shows average 24-hour concentrations of three aromatic compounds over the entire PAMS season at Miller: benzene, p-Ethyltoluene, and 1,2,3-Trimethylbenzene. Benzene concentrations and patterns seem to resemble more closely 1,2,3-Trimethylbenzene and p-Ethyltoluene. These heavier molecular weight compounds have a longer atmospheric life and can travel long distances in air. Benzene concentrations noticeably spiked during the days where forest fire smoke had made its way into the area, however, it was seen throughout much of the summer until a drastic decrease occurred at the beginning of September. There was a period of instrument down time from 8/20-8/31. Once the instrument issues were resolved, the decrease was noted. None of the QC measures indicate that this change was systemic, rather it could have been the result of changing weather or atmospheric conditions occurring during the late summer.

Figure 5.27: 24-hour Averages of Benzene, p-Ethyltoluene, and 1,2,3-Trimethylbenzene during 2021 PAMS season at Miller

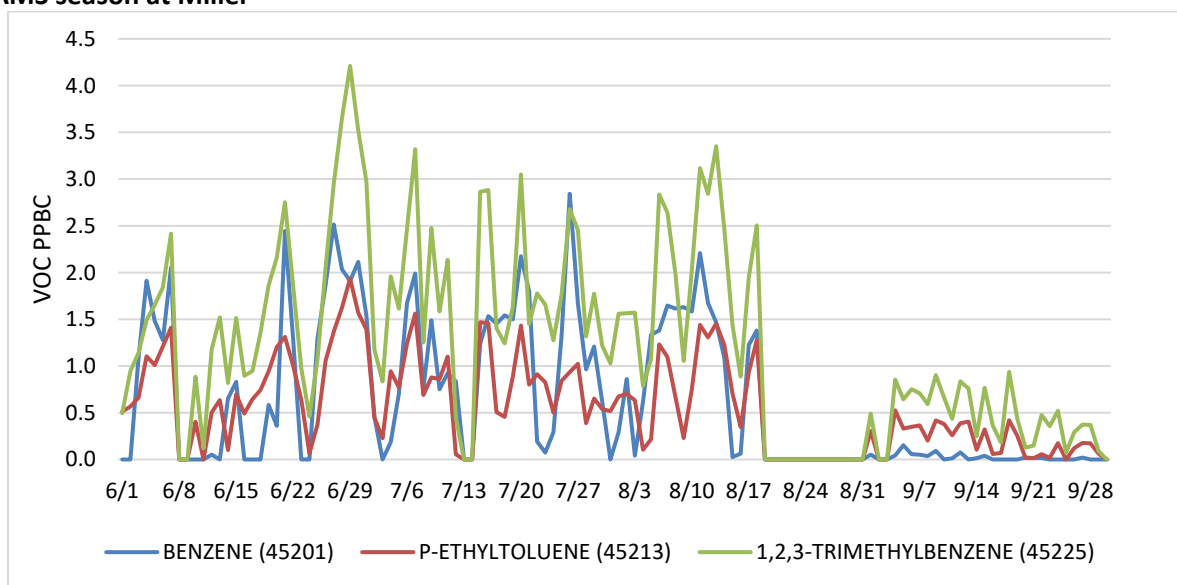
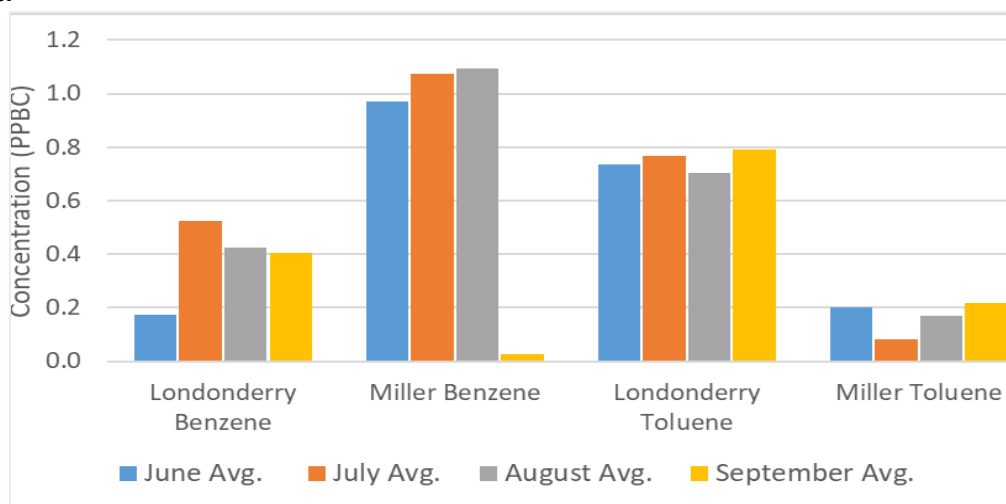


Figure 5.28: Monthly Averages of Benzene, and Toluene during 2021 PAMS season at Londonderry and Miller

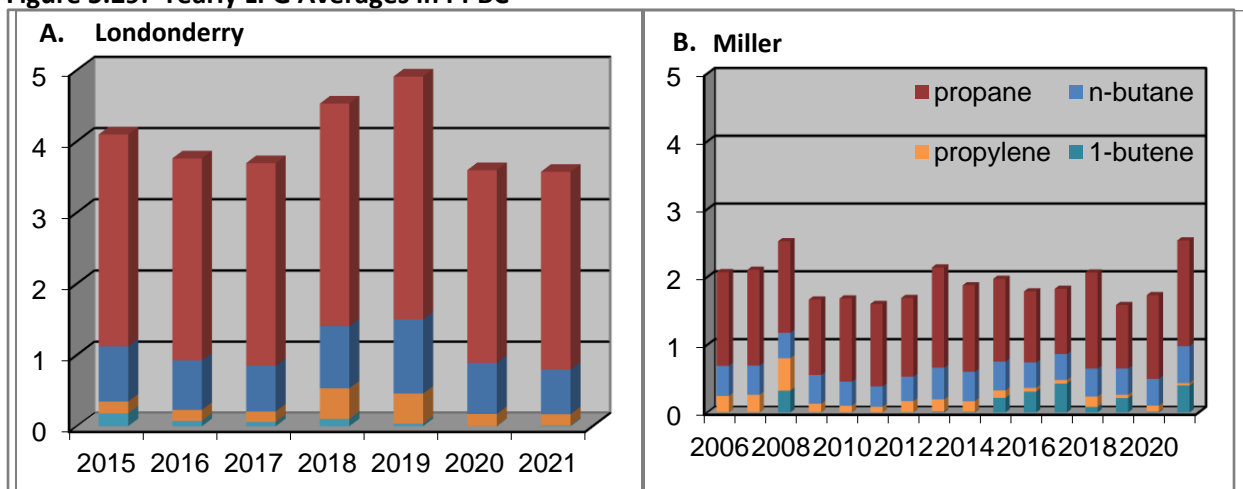


5.4.3 Liquefied Petroleum Gas Constituents

Liquified Petroleum Gas (LPG) is generally stored in bottles and is used widely throughout the U.S. as a fuel for heating, cooking, hot water, vehicle transportation and many other applications. **Figure 5.29** show average LPG constituent emissions per year for Londonderry and Miller, respectively. As shown in the figures, propane is the predominant compound followed by n-butane.

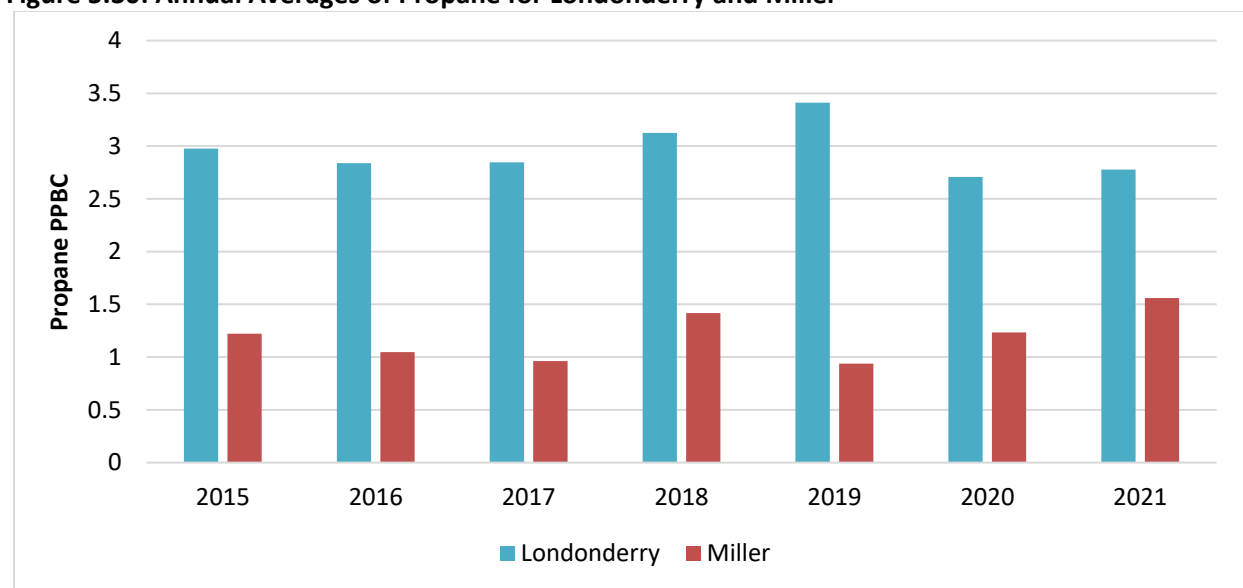
Figure 5.30 looks specifically at propane for both sites dating back to 2015. Propane values at Londonderry average higher than at Miller. Propane is a highly volatile compound and monitoring indicates that it is a widely occurring pollutant. It is presumed to be a good indicator of oil and gas activities.

Figure 5.29: Yearly LPG Averages in PPBC



* Data loss at Miller may affect the 2020 levels.

Figure 5.30: Annual Averages of Propane for Londonderry and Miller



* Data loss at Miller may affect the 2020 levels.

5.4.3 Naturally Emitted VOCs

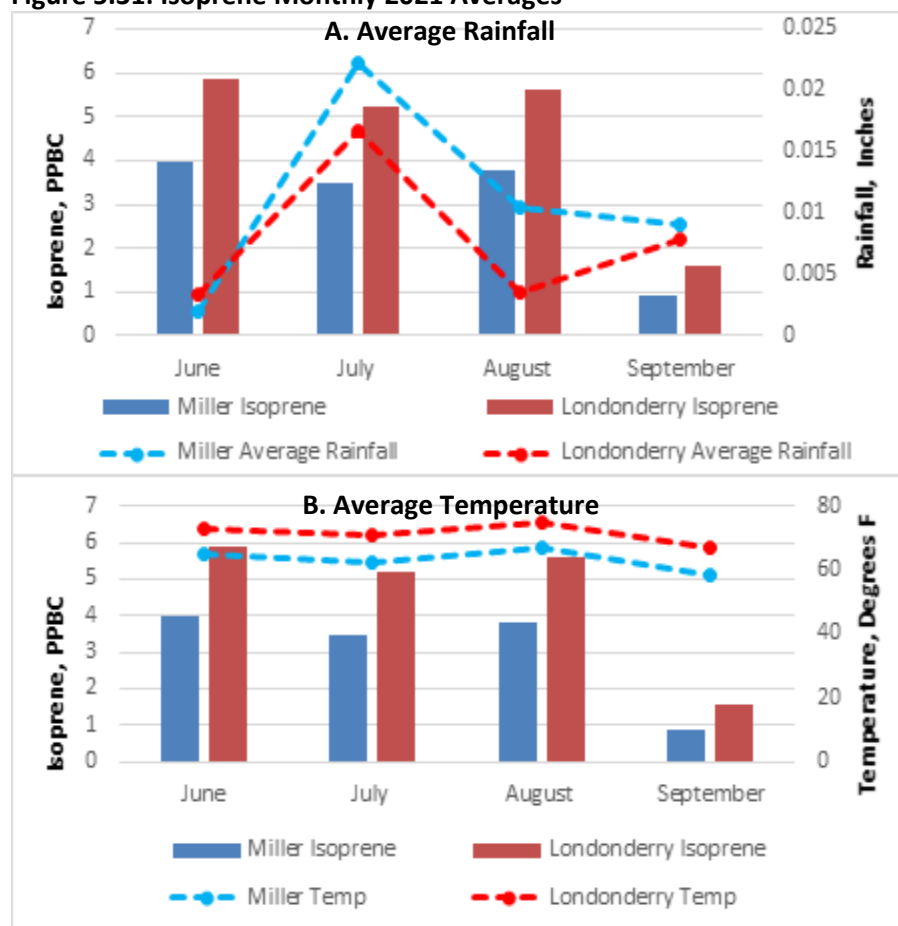
On a global scale, biogenic emissions dominate the organic carbon budget, with anthropogenic emissions contributing greater than 15%.¹¹ Biogenic VOCs include isoprene and other terpenoids including α - and β -pinene, among others. Due to its photochemical reactivity, isoprene and other biogenic VOCs can account for a significant amount of the ozone-forming potential, especially in non-urban areas. Isoprene concentrations are usually highest during the middle of the day when solar ultraviolet (UV) radiation and air temperatures are highest, and because isoprene is highly photochemically reactive, it is conducive to ozone formation.

Isoprene is emitted by many types of vegetation, notably deciduous trees, and emissions are thought to be influenced by factors that affect tree health and growth, such as rainfall and temperature. Isoprene emissions are comparable with worldwide natural emissions of methane, another natural gas, at around 500 million tons into the air each year.¹² The majority of isoprene emissions in the Northeast comes from oak trees, and pinenes largely come from pine trees, as the name indicates.

Figure 5.31 shows the average 2021 summer monthly isoprene concentrations with average temperature and rainfall at Londonderry and Miller.

The higher temperatures at Londonderry likely contribute to the difference in isoprene concentrations at that site, as isoprene emissions vary with temperature: cool temperatures result in decreased isoprene emissions as they are thought to have a protective effect on plants not just from insects, but also from other dangers like heating and drought that interfere with photosynthesis.¹³ In addition, an abnormally wet July had an impact on isoprene levels in NH as solar radiation levels at Londonderry

Figure 5.31: Isoprene Monthly 2021 Averages



¹¹ Goldstein, A. H. (2007), Known and unexplored organic constituents in the earth's atmosphere, Environ. Sci. Technol., 41(5), 1514-1521.

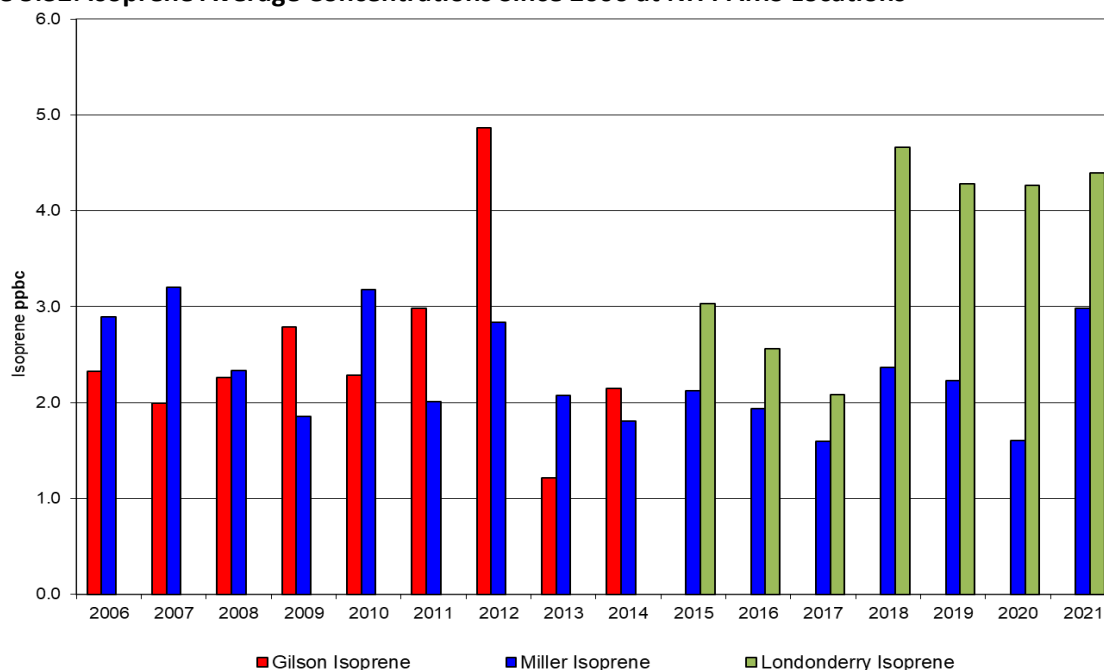
¹² Cotton, S. (2015, August, 25) Chemistry World, "[Isoprene](#)". [2017, March, 6].

¹³ Ibid.

were 34% lower than in July 2020.

Figure 5.32 depicts average isoprene concentrations at three New Hampshire monitoring sites since 2006. Cooler, wetter summers were experienced in 2013 and 2014. Average isoprene increased at both PAMS monitoring sites in 2021. Despite a cooler and rainier July, isoprene concentrations were higher during the remainder of the summer months, making up the difference. Temperatures during the PAMS season in 2021 varied anywhere between 3.7 °F above normal in June to 2.2°F below normal in July, while in 2020 temperatures were 1.5 - 4.5°F above normal for the entire season. 2021 tied for the third warmest year on record and rainfall amounts were 2.07 inches above normal putting an end to drought conditions that had persisted for the previous few years. Weather and isoprene values are discussed in detail below.

Figure 5.32: Isoprene Average Concentrations Since 2006 at NH PAMS Locations



**2014 Gilson Road (Nashua) data only include September data up until September 10. 2020 Miller data does not include the second half of June and most of July.*

The PAMS target species list has included naturally emitted isoprene since inception, but the new protocols add α - and β -pinene, which are also biogenically emitted compounds (**Figure 5.33**). NHDES began collection of the pinene compounds in 2018 after the Londonderry site completed its equipment upgrade.

Though isoprene levels have been stable since 2018, α - and β -pinene concentrations show a significant reduction in 2021; this is to be expected if there are large variations in rainfall, temperature, sunlight, and/or land use. However, data at Londonderry does not show this trend apart from July. Each month showed a decrease in the average α - and β -pinene concentrations despite warmer average temperatures and relative humidity values were also higher during each of those months. Solar radiation values were slightly lower during July, August and September when compared to 2020. Considering the meteorological factors did not impact isoprene levels, it is assumed that issues with methodology may have caused the decrease in pinene concentrations.

Both α - and β -pinene are qualified in AQS with QX codes, meaning the QC did not meet criteria for the entire PAMS season. The yearly retention time cylinder received from EPA in 2021 could not confirm stability in the cylinder for these two compounds and therefore were either not detected, or

concentrations could not be confirmed. Problems with the KOR1 trap over the season could have also contributed to lower amounts, but this cannot be confirmed as the compounds were not verified in the calibration cylinder, so there was no standard available to compare them to.

Figure 5.33: Biogenic Compound Average Concentrations at Londonderry Since 2018

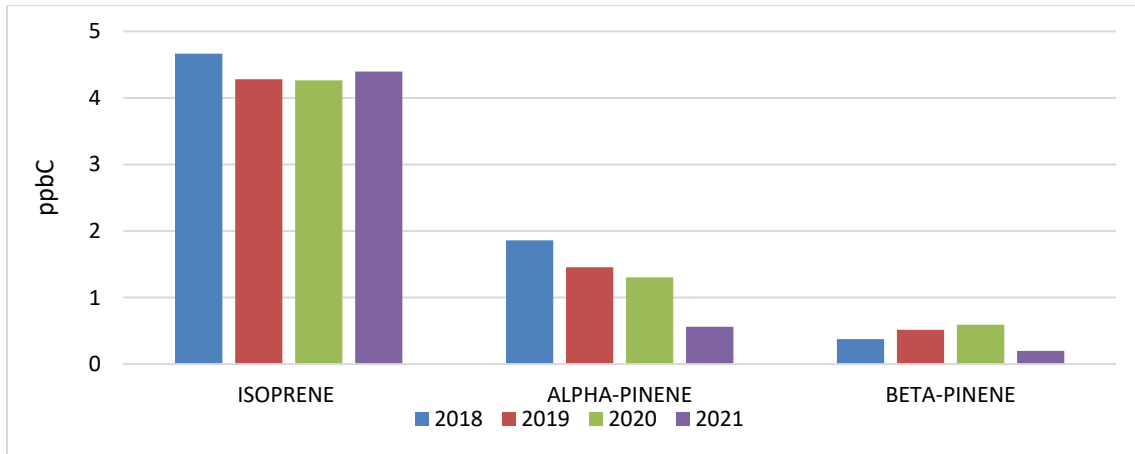


Figure 5.34 illustrates how hourly measured isoprene and pinene concentrations vary with temperature and UV radiation at Londonderry during the 2021 PAMS season. Note how UV radiation peaks around the first day of summer in late June and decreases through later summer months as daylight slowly decreases.

Figure 5.34: 24-Hour Average Isoprene, α - and β -pinene, Temperature and Solar Radiation at Londonderry 2021

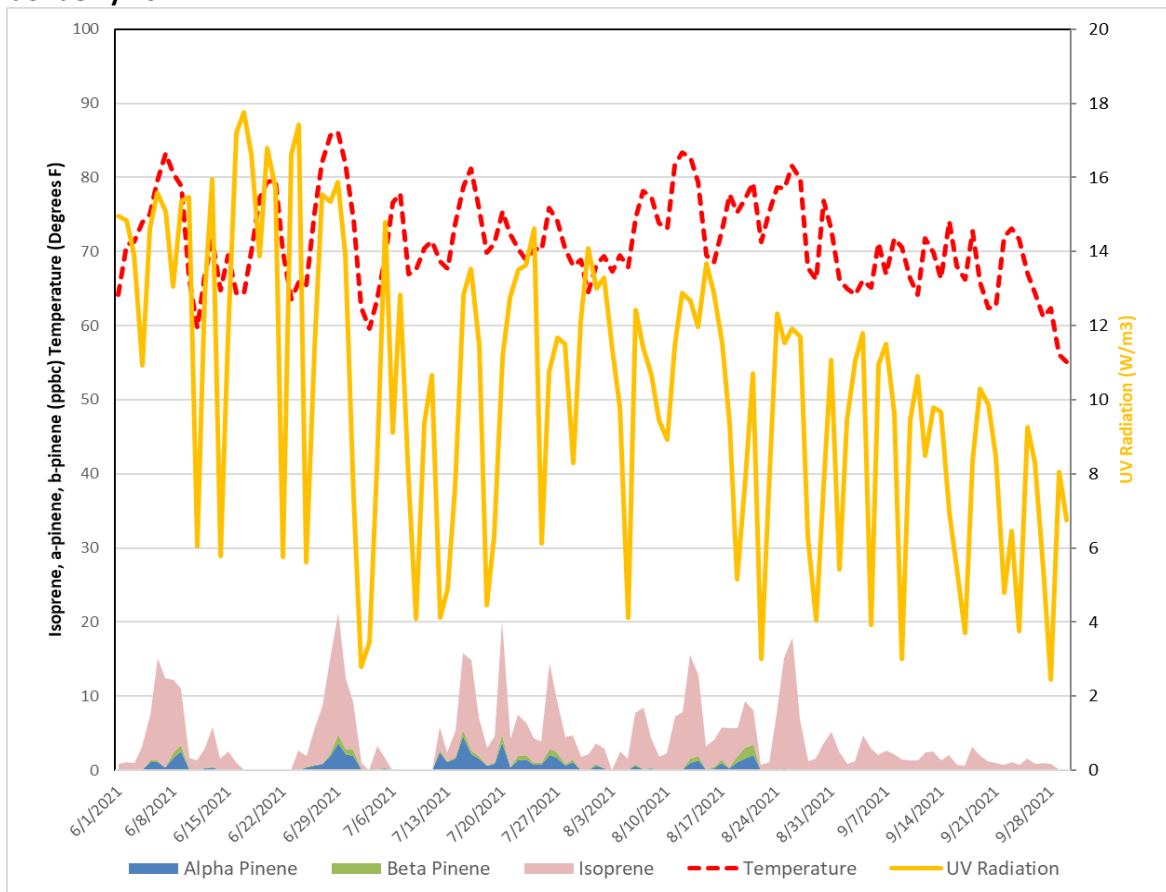
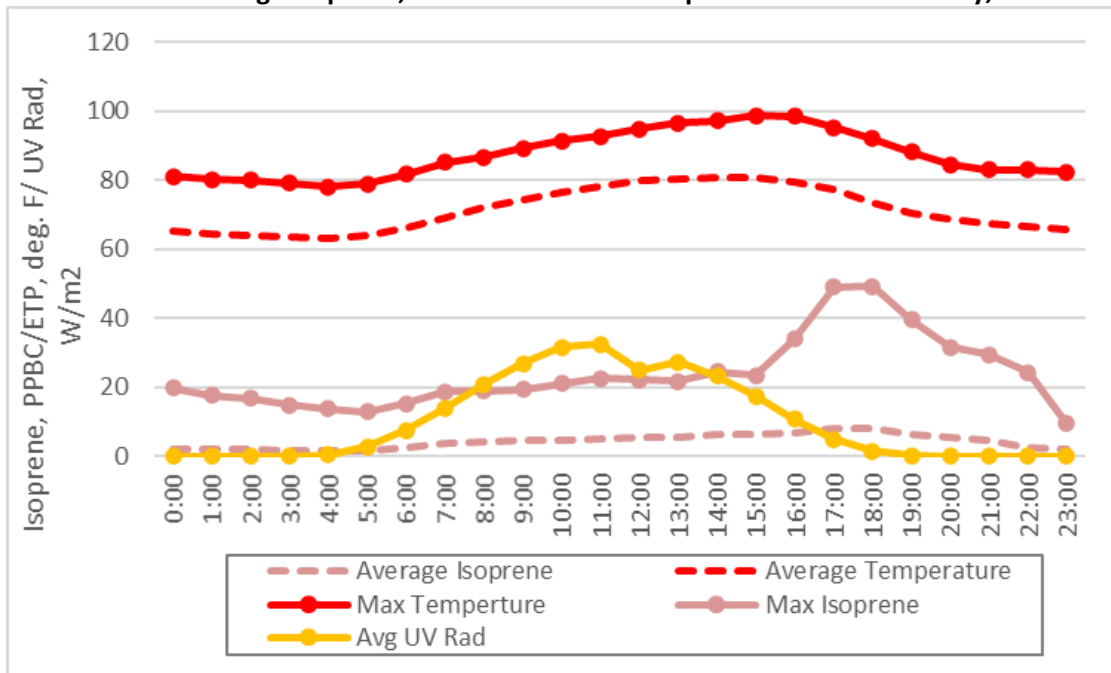


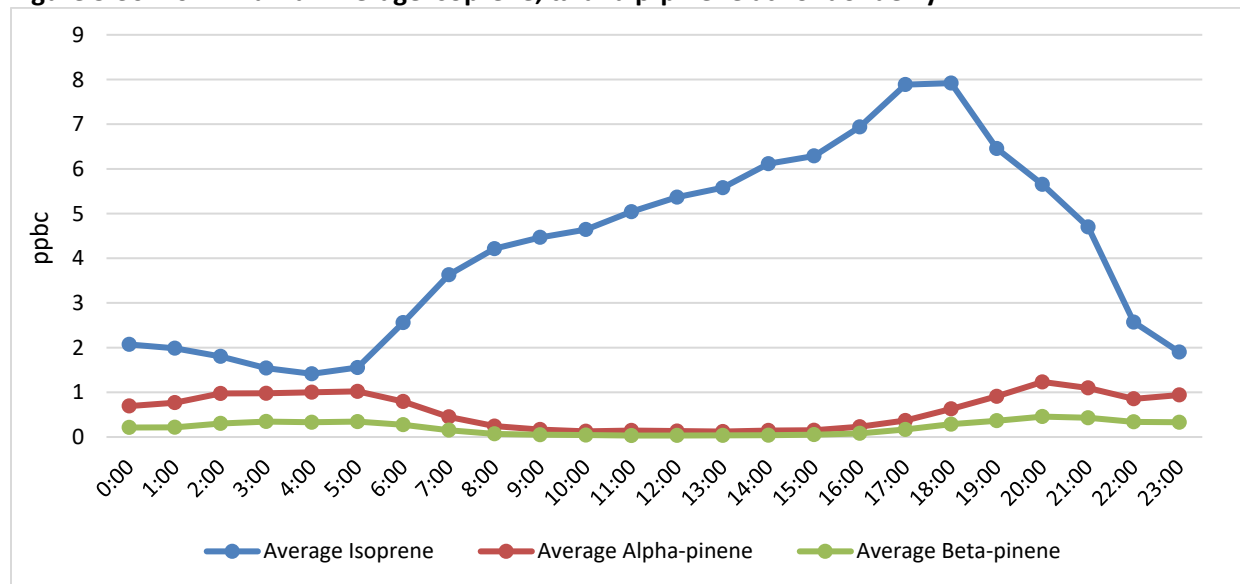
Figure 5.35 shows the 2021 PAMS season diurnal pattern of isoprene and temperature at Londonderry. Isoprene builds in the atmosphere as the temperature increases and peaks as the temperature begins to drop. The highest isoprene values were measured at 6:00 PM (49.10 ppbC) and 7:00 PM (49.22 ppbC) on June 6th.

Figure 5.35: Diurnal Average Isoprene, UV Radiation and Temperature at Londonderry, 2021



In contrast to isoprene, α - and β -pinene show a diurnal pattern indicating that these species are emitted in the evening hours and their concentration decreases during the day as they react photochemically (Figure 5.36).

Figure 5.36: 2021 Diurnal Average Isoprene, α - and β -pinene at Londonderry



In addition to a different diurnal pattern, they seem to respond differently to the higher average temperatures, as seen in **Figure 5.37**. The highest monthly average temperatures occurred in August of 2021 rather than July, which is what is typically seen, yet average isoprene values peaked during June while α - and β -pinene values peaked in July. This is a deviation in comparison with prior years.

Figure 5.37: 2021 Monthly Averages, Isoprene, α - and β -pinene at Londonderry

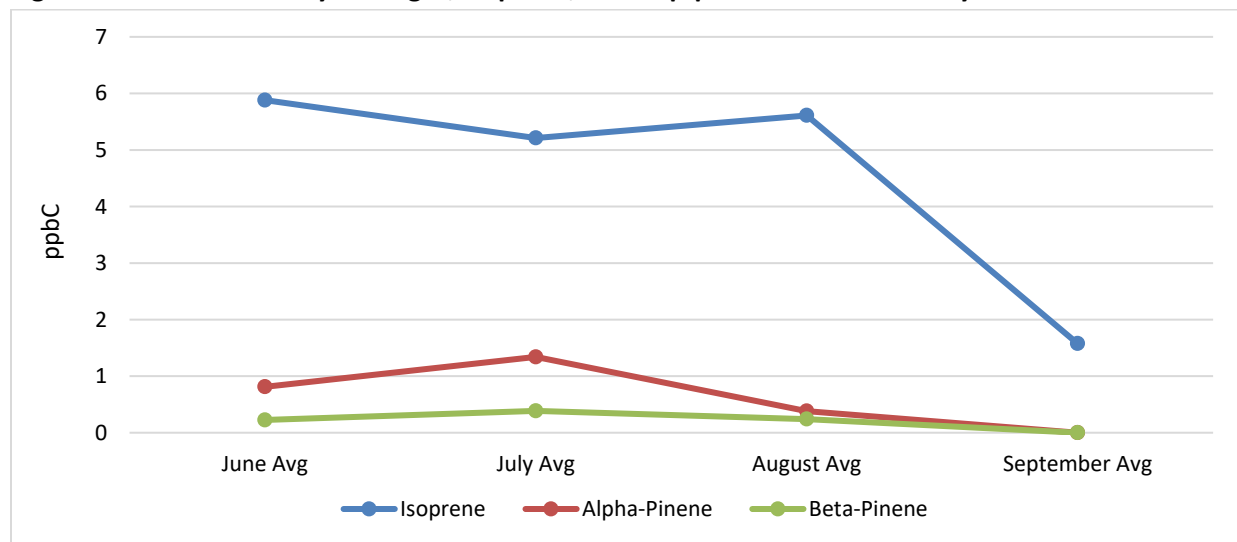


Figure 5.38 shows the relationship between isoprene and temperature at Miller. Isoprene peaked on June 29th with a corresponding temperature of 76.7°F. UV radiation, and α - and β -pinene are not measured at Miller, though the pinenes will be added to the compound list for the 2022 PAMS season.

Figure 5.38: 24 Hour Average Temperature and Isoprene at Miller in 2021

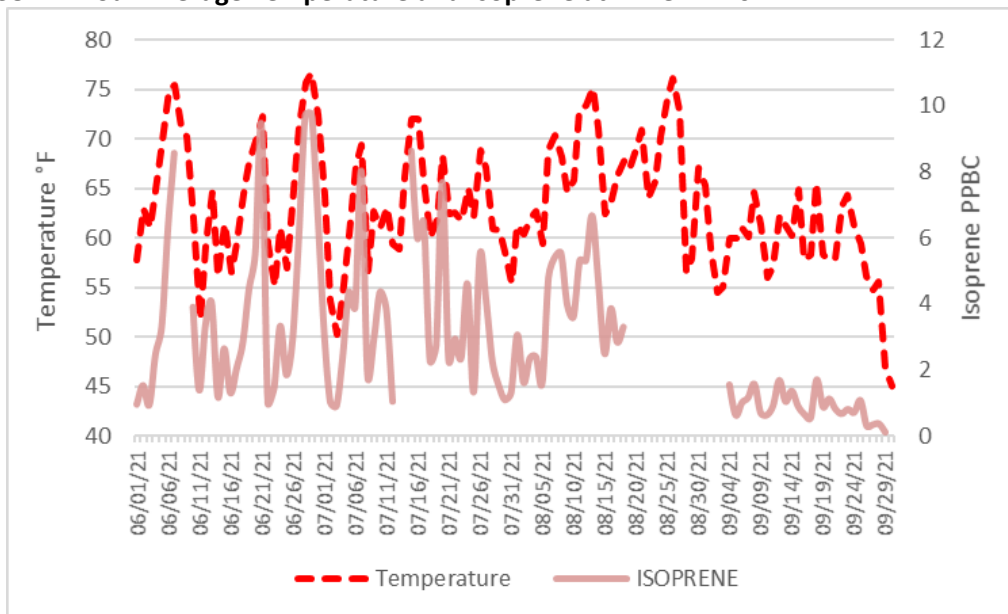
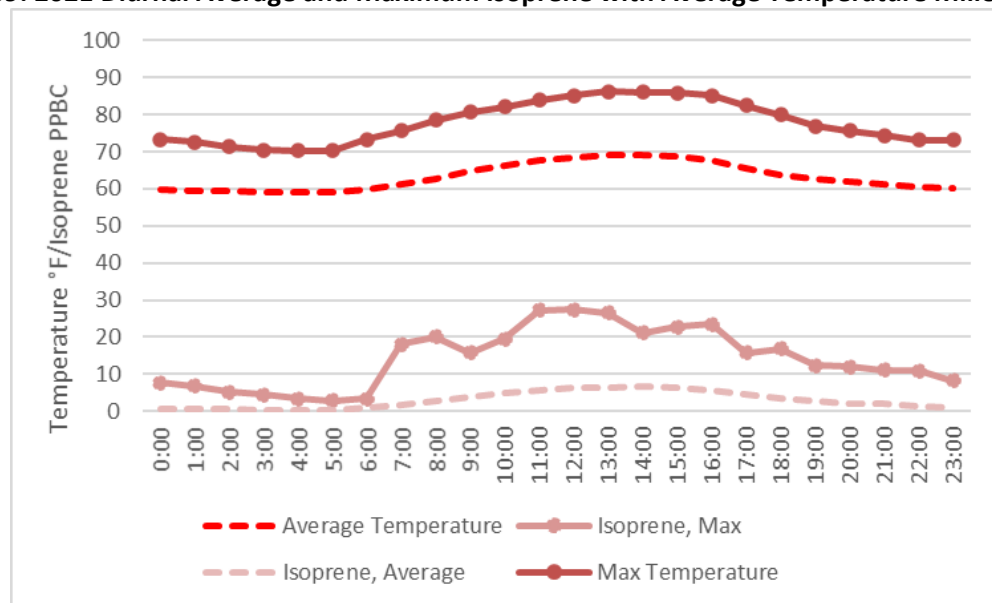


Figure 5.39 shows the average diurnal and maximum isoprene concentrations at Miller and how they relate with temperature during the 2021 summer season. At ground level (Londonderry), isoprene concentrations top shortly after temperatures peak and into the early evening hours. At the higher elevation site, average isoprene concentrations correlate better with average temperatures during the day. On an individual day, hourly isoprene patterns are not as smooth as the average values over a

season because peak concentrations often result from brief, isolated events; however, there is an obvious decline once the sun sets. At Londonderry, maximum isoprene values peak at 6:00 PM after air temperatures have peaked. Average and maximum isoprene values at Miller, unlike Londonderry, peak between midday and early afternoon, correlating more closely with temperature.

Figure 5.39: 2021 Diurnal Average and Maximum Isoprene with Average Temperature Miller



5.5 Forest Fire Events

5.5.1 Exceptional PM Event Analysis

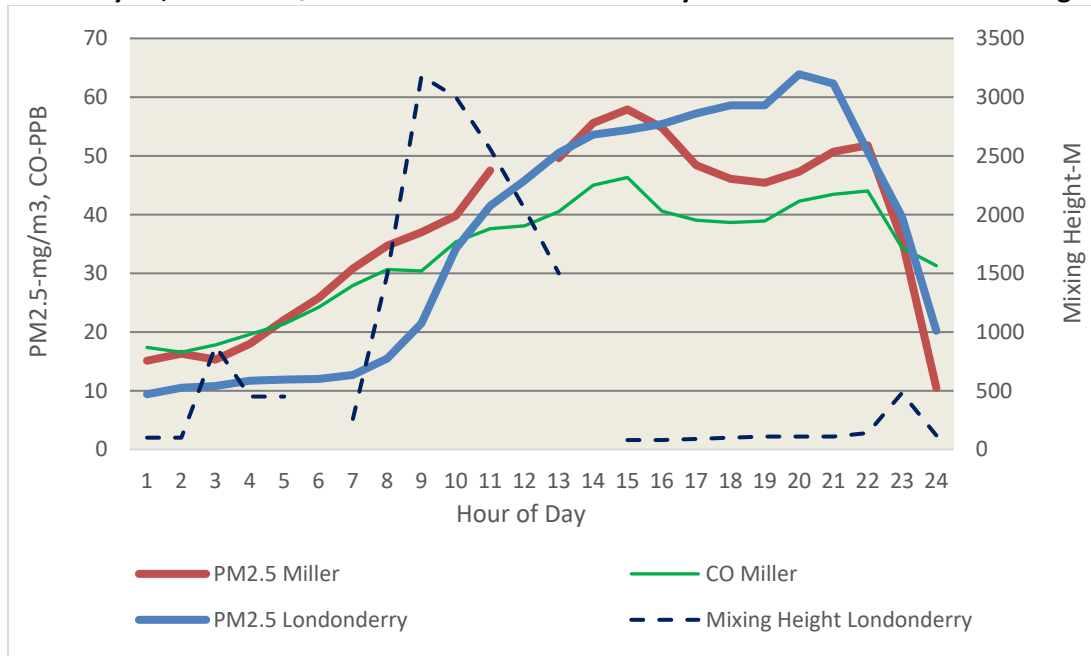
The summer of 2021 was notable for a few reasons in New Hampshire. July was exceptionally wet and cool and yet experienced a very unusual smoke event from forest fires in the Western US and Canada that made their way to the Northeast. This caused widespread 24-hour PM_{2.5} exceedances of the National Ambient Air Quality Standard (NAAQS). High concentrations of smoke limited visibility and produced a strong smell of smoke that lingered in the air for a few days. Highest concentrations of wood smoke reached New Hampshire on July 20th and 26th. The Londonderry monitoring site recorded 24-hour PM_{2.5} averages of 35.9 and 54.1 µg/m³, respectively, while Miller recorded 37.4 and 53 µg/m³ for the two dates in July. With the increase in PM_{2.5} levels, came an increase in certain VOC concentrations as well.

According to EPA, designated Exceptional Events are unusual or naturally occurring events that can affect air quality but are not reasonably controllable using techniques that tribal, state or local air agencies may implement in order to attain and maintain the NAAQS. NHDES intends to request designation of the influence of this high PM_{2.5} concentration smoke event as an Exceptional Event because it was heavily influenced by a combination of western wildfires and unusually cohesive transport patterns that enabled long-range transport at unprecedented concentrations in the state. Because the PAMS units were operating, this event creates an interesting scenario to study the ozone precursor influences at two different elevations.

As seen in **Figure 5.40**, PM_{2.5} concentrations rose steadily at both NH PAMS locations on July 20, peaking in the early afternoon before sharply decreasing at around 9:00 PM. Carbon monoxide (CO) was not captured at Londonderry during this time frame, but concentrations of CO measured at Miller tracks well with the PM_{2.5} plume. Mixing height measured at Londonderry rapidly increased during the morning, from 260 to 3,180 meters, allowing the transported smoke to move into the area at higher

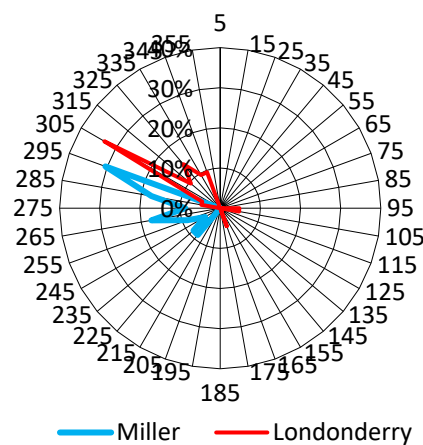
altitudes. By early afternoon it rapidly decreased, trapping high concentrations of smoke close to ground level.

Figure 5.40: July 20, 2021 PM_{2.5} Concentrations at Londonderry and Miller with CO and Mixing Height



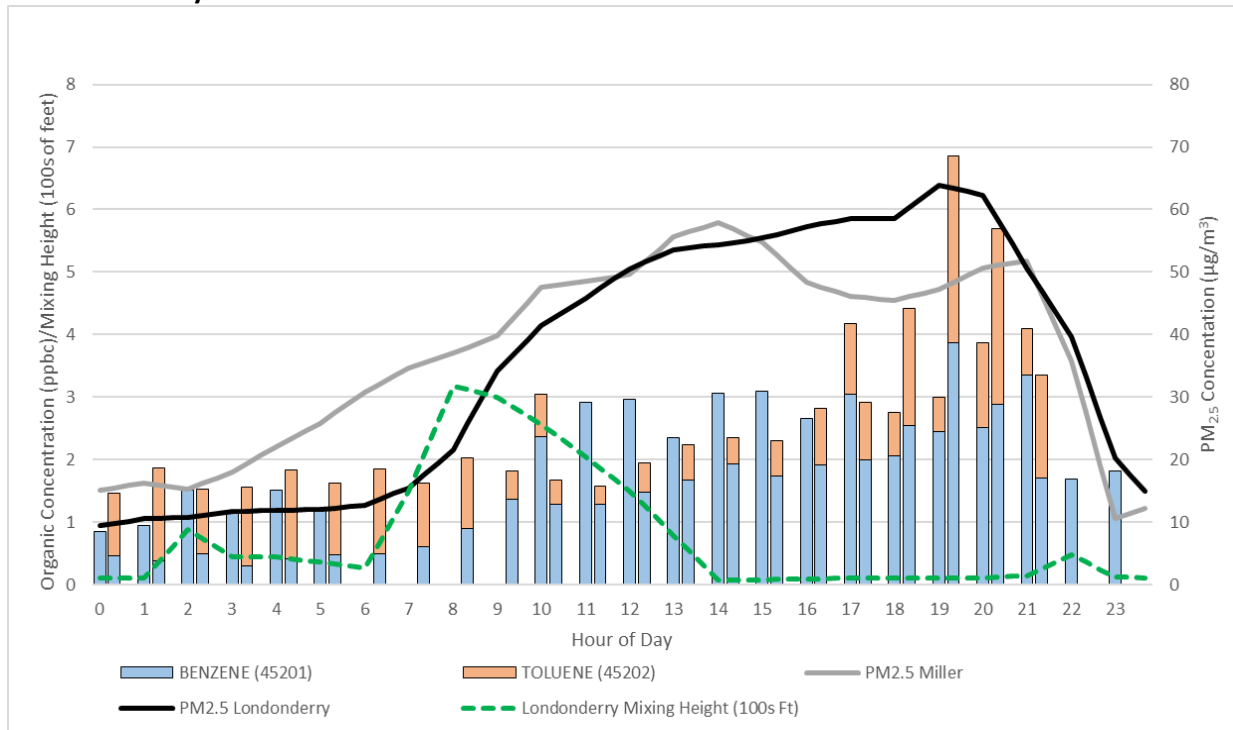
Wind data indicates the air mass approached the state from the west and west-northwest (**Figure 5.41**). Wind speeds were generally in the 2-5 mph range and did not top 8 mph at either location. Long range trajectory strongly connects the smoke event with the locations of the western wildfires.

Figure 5.41: July 20, 2021 Wind Direction Frequency for Londonderry and Miller



Certain VOCs are typically associated with wood smoke, namely benzene and toluene. Benzene’s longer lifetime in ambient air correlates with an aged air mass, making toluene an indicator of fresher emissions. **Figure 5.42** shows the relationship of these compounds compared to PM_{2.5} concentrations. At Londonderry, a shift in the ratio of benzene and toluene is seen at around 8:00 AM correlating with the influx of the more aged PM_{2.5} coming into the region. A more aged airmass is typically seen at Miller due to its elevation and it is not until the dip in PM_{2.5} seen at around 5:00 PM where toluene contributes to the total VOCs at that site.

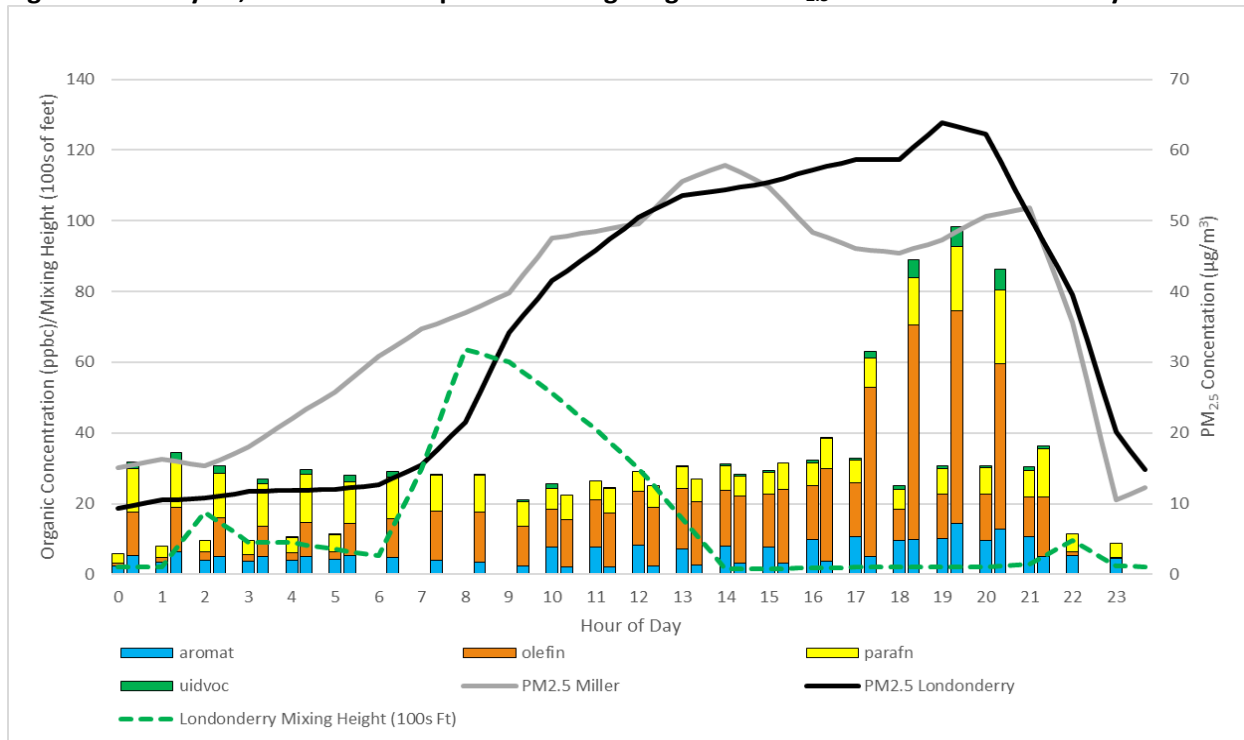
Figure 5.42: July 20, 2021 Benzene and Toluene Concentrations with Mixing Height and PM_{2.5} Values for Londonderry and Miller



***Benzene/toluene stack Miller Left, Londonderry Right**

Another look at the VOC composition of forest fire smoke is seen in **Figure 5.43**. Olefins are naturally higher at Londonderry due to the additional analysis of α - and β -pinene at this location, however this compound group makes a significant contribution to the VOC presence at both sites. Biogenic VOCs play a significant part in this group and since the half-life of these compounds is generally in the range of 4-6 hours, it is assumed that the plume caused an unexpected amount of stress on the trees that emit them. Other compounds in this group include the butenes, pentenes and ethylene, though a vast majority of concentrations are coming from isoprene and α - and β -pinene. Aromatics play a much bigger role in the total VOCs at Miller. These are compounds which contain a benzene ring and include the benzenes, toluenes and xylenes. Paraffins make up a small, but steady amount of the hourly VOC totals. This group consists of alkanes and the majority of what is seen during this PM_{2.5} comes from propane, the butanes and ethane.

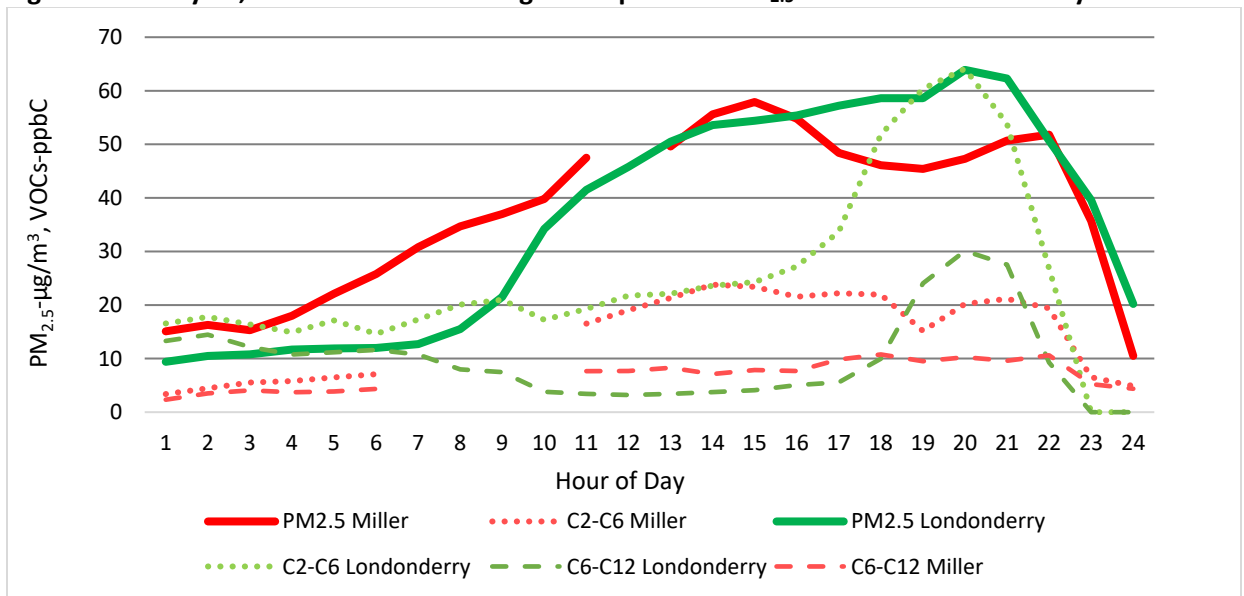
Figure 5.43: July 20, 2021 VOC Groups with Mixing Height and PM_{2.5} Values for Londonderry and Miller



*Benzene/toluene stack Miller Left, Londonderry Right

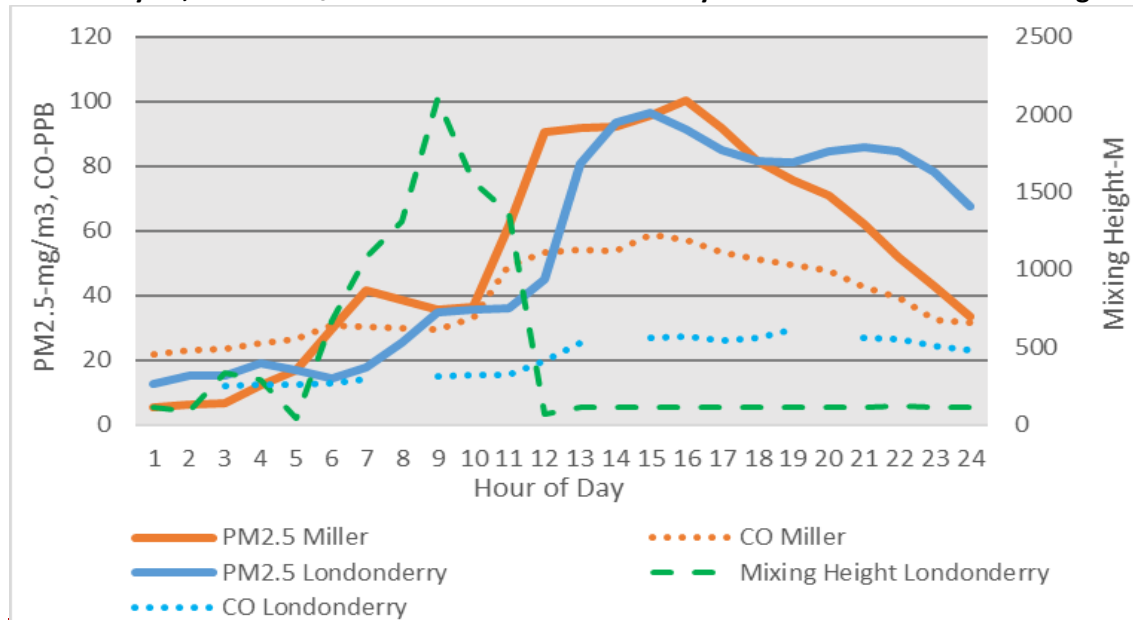
The column configuration on the VOC systems is comprised of a plot and BP-1 column. The plot column is designed to detect the lighter molecular weight, non-polar compounds, while the BP-1 detects the heavier molecular weight compounds. The C2-C6 range includes compounds from ethane to isoprene and C6-C12 captures hexane through undecane. The lighter molecular weight compounds are seen more prevalently in the PM_{2.5} smoke events than the heavier compounds.

Figure 5.44: July 20, 2021 VOC Carbon Ranges compared to PM_{2.5} Values for Londonderry and Miller



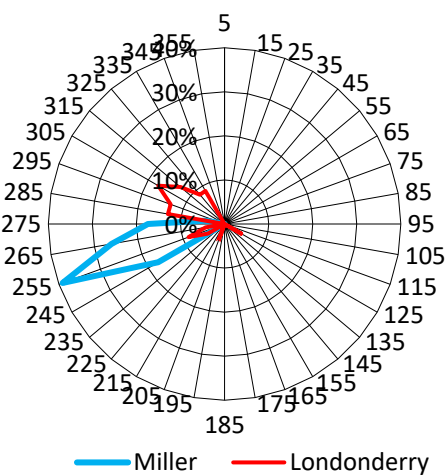
Conditions for the wildfire smoke event on July 26th are similar to the one on the 20th, though PM_{2.5} rose more quickly during the late morning on the 26th as seen in **Figure 5.45** below.

Figure 5.45: July 26, 2021 PM_{2.5} Concentrations at Londonderry and Miller with CO and Mixing Height



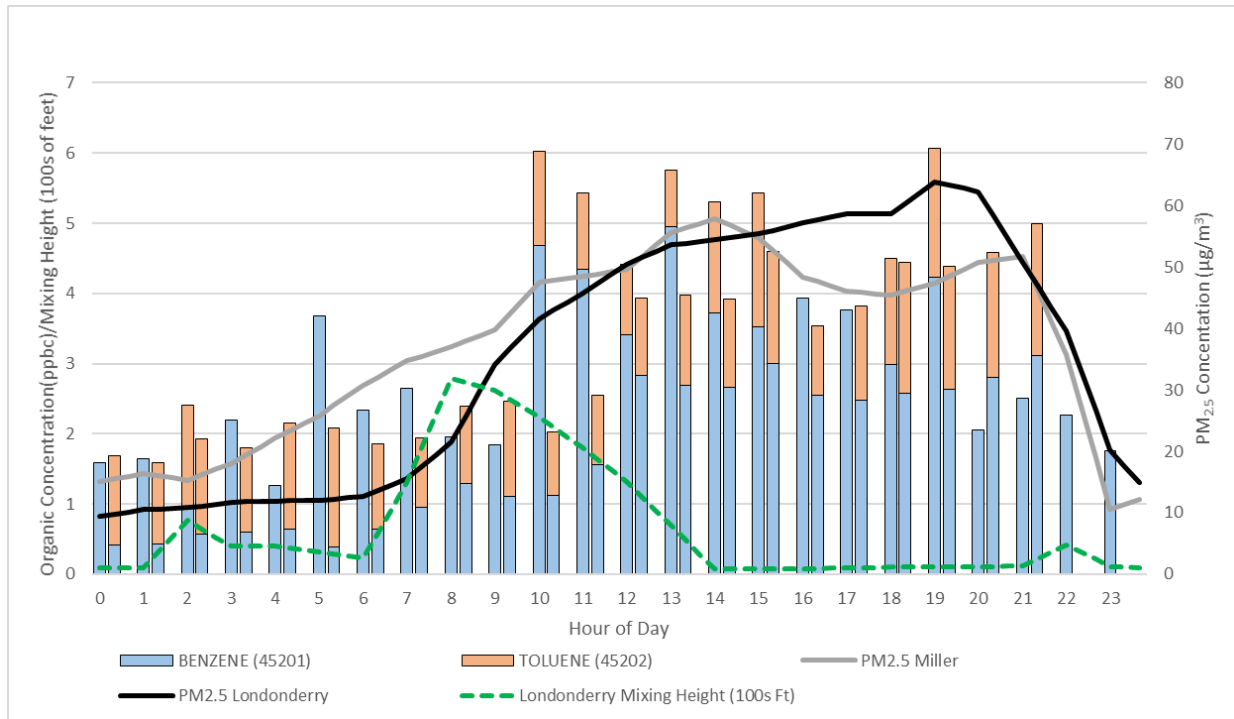
Again, winds were predominantly from the northwest at Londonderry but the west-southwest at Miller on July 26th (**Figure 5.46**). Wind speeds did not exceed 6 mph at Londonderry and at Miller they reached slightly higher, around 8 mph, but fell throughout the course of the day.

Figure 5.46: July 26, 2021 Wind Direction Frequency for Londonderry and Miller



Higher concentrations of benzene and toluene were seen during the July 26th event at Miller, whereas they were higher at Londonderry during the event on the 20th (**Figure 5.47**). Again, the mixing height dropped around the time that concentrations of PM_{2.5} surged.

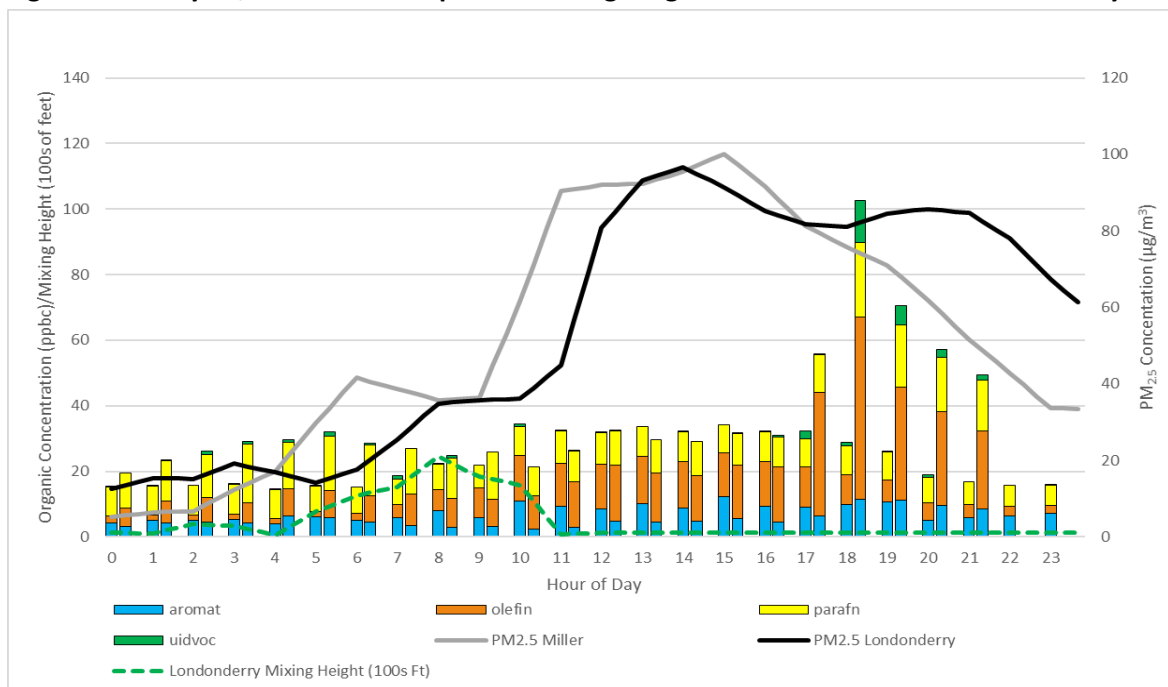
Figure 5.47: July 26, 2021 Benzene and Toluene Concentrations with Mixing Height and PM_{2.5} Values for Londonderry and Miller



**Benzene/toluene stack Miller Left, Londonderry Right*

Again, biogenic olefins dominated the VOC profile at Londonderry (Figure 5.48). The same is true at Miller, however the aromatics make up a larger percentage of the total VOCs at this high elevation site.

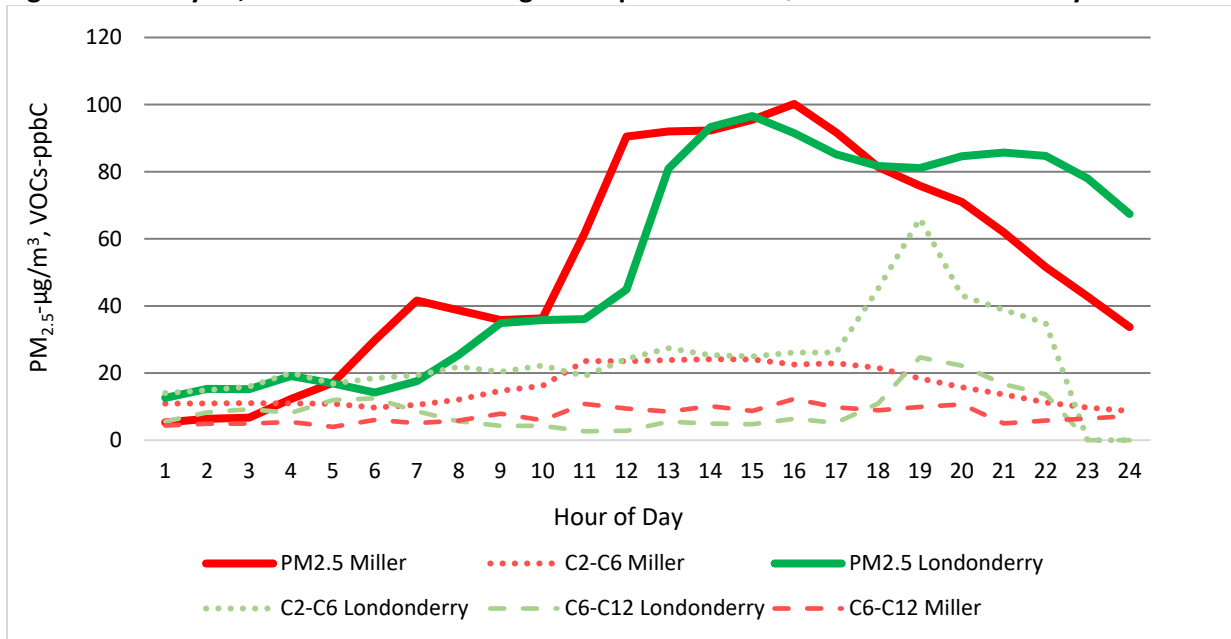
Figure 5.48: July 26, 2021 VOC Groups with Mixing Height and PM_{2.5} Values for Londonderry and Miller



**Benzene/toluene stack Miller Left, Londonderry Right*

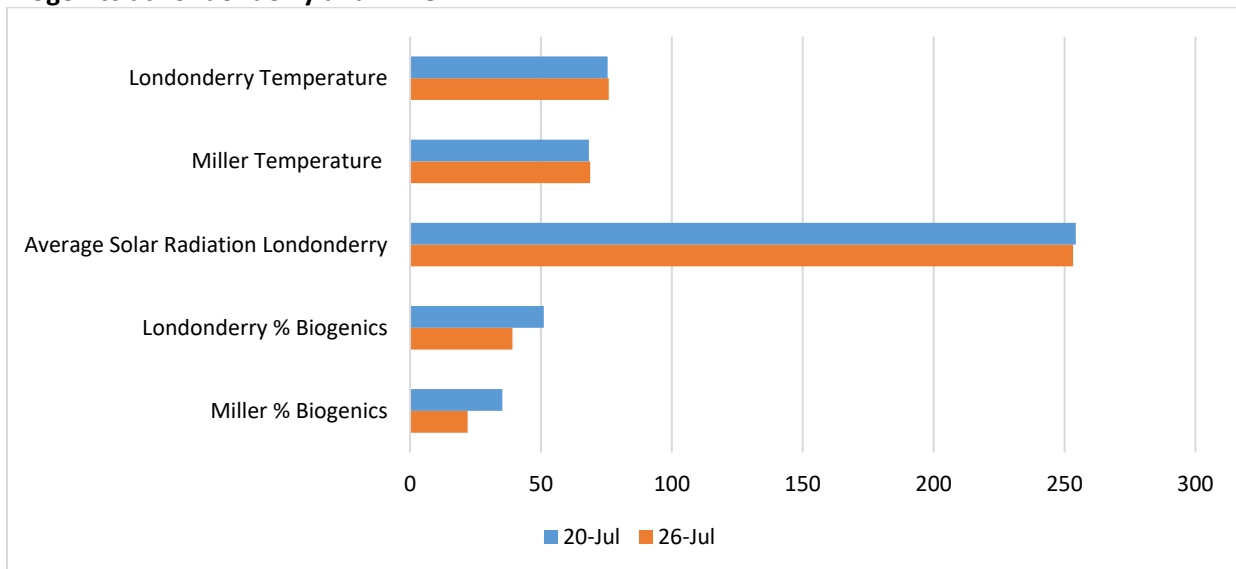
As seen in **Figure 5.49**, compounds in the C2-C6 range also made up the majority of VOCs in the woodsmoke event on July 26th.

Figure 5.49: July 26, 2021 VOC Carbon Ranges compared to PM_{2.5} Values for Londonderry and Miller



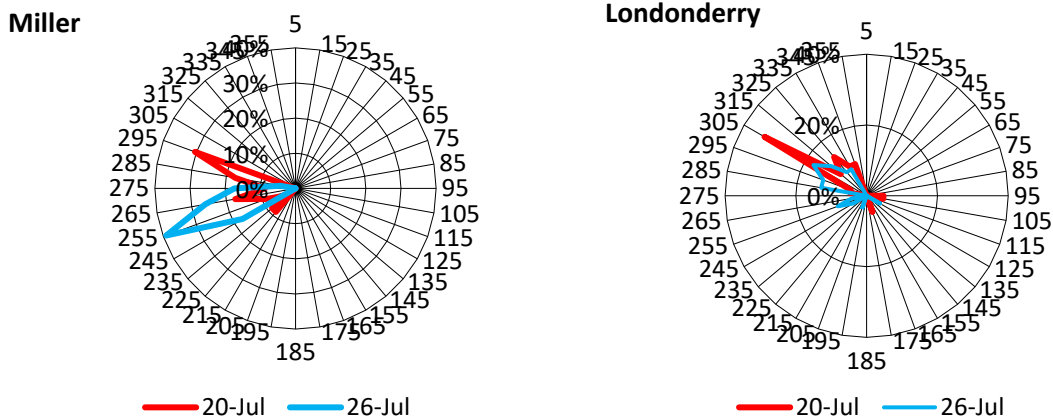
Meteorological conditions during the two events are compared in **Figure 5.50** as well as the total percent of biogenic compounds compared to the total VOCs. As mentioned, the addition of α - and β -pinene at Londonderry adds to the higher percent, but isoprene alone at Miller makes up 39% and 21% of the VOC totals during the events at that site. Temperature and solar radiation averages are nearly identical during the two dates.

Figure 5.50: July 20 and 26, 2021 Average Temperature (deg F), Solar Radiation (W/m²) and Percent Biogenics at Londonderry and Miller



As shown in **Figure 5.51**, wind directions were plotted for each site and date. Wind directions at Londonderry were consistent for both events coming from the northwest. On July 20th winds were coming predominantly from the west-northwest at Miller and then west-southwest on July 26th.

Figure 5.51: July 20 and 26, 2021 Wind Direction Charts for Miller and Londonderry



VOCs generally ran a little lower at the higher elevation Miller location during the wildfire events, but overall, the event appears to be well mixed below 4000 feet. The mixture of VOCs during the event at Miller also appears to be slightly more aged which is probably less diluted from closer proximity of fresh emissions more commonly found at lower elevations.

6. CARBONYL ANALYSIS

Carbonyl compounds are largely products of incomplete combustion from motor vehicles, industrial chemical plants and other emission sources. They are produced by the oxidation of hydrocarbons and formed by photochemical reactions with ozone and its precursors. Chronic exposure to certain carbonyl compounds can cause cardiovascular disease and are linked to increased cancer rates; therefore, they are monitored by EPA under the PAMS and National Air Toxics Assessment Programs.

The method employed by the NHDES PAMS program for carbonyl measurement is EPA Method TO-11A. Samples are collected on 2,4-dinitrophenylhydrazine (DNPH) cartridges and shipped to a subcontractor lab, Eastern Research Group, for analysis via high performance liquid chromatography.

As part of implementing the 2015 ozone NAAQS rule, NHDES resumed routine sampling for carbonyl compounds beginning in 2019 at the Londonderry site. During the months of June, July, and August, carbonyl samples are collected on a one in three-day basis corresponding with the national filter-based particulate monitoring schedule. Three 8-hour samples of carbonyls are collected from 4:00 AM to noon, noon to 8:00 PM, and 8:00 PM to 4:00 AM, during eastern daylight savings time. This schedule was determined to be most appropriate for the PAMS program to be able to capture data from the morning and afternoon commutes.

Data capture was excellent for the 2021 season, as seen in **Figure 6.1** below. There was one voided sample on August 2nd, which is the reason for the lower carbonyl concentrations reported for that day. In general, days with higher carbonyl concentrations correlate well with elevated maximum 8-hour ozone for that day, and solar radiation data also closely resembles ozone trends. A noticeable decrease in carbonyl concentrations starts to occur in late June towards the end of July. Low solar radiation and ozone is seen on some of these dates; however, it does not explain the low carbonyls seen between June 24 and July 24.

Figure 6.1: Total 24-Hour Reportable Carbonyl Concentrations with 8-Hour Ozone Max and Average Solar Radiation at Londonderry PAMS in 2021

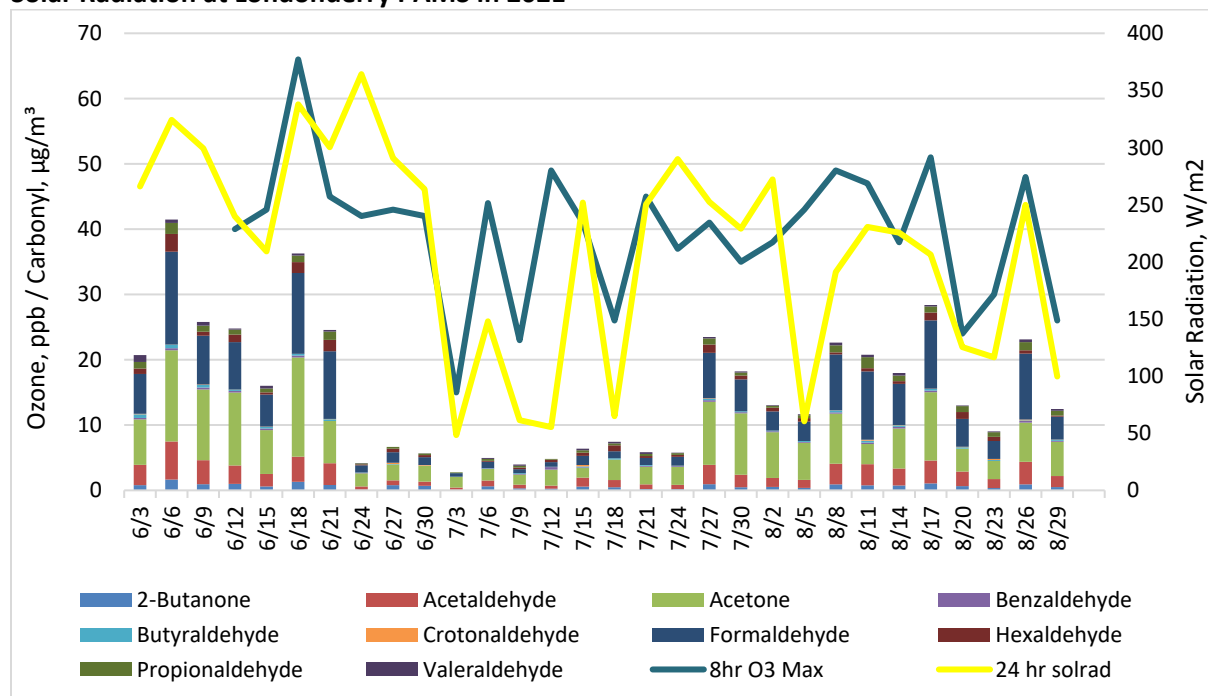
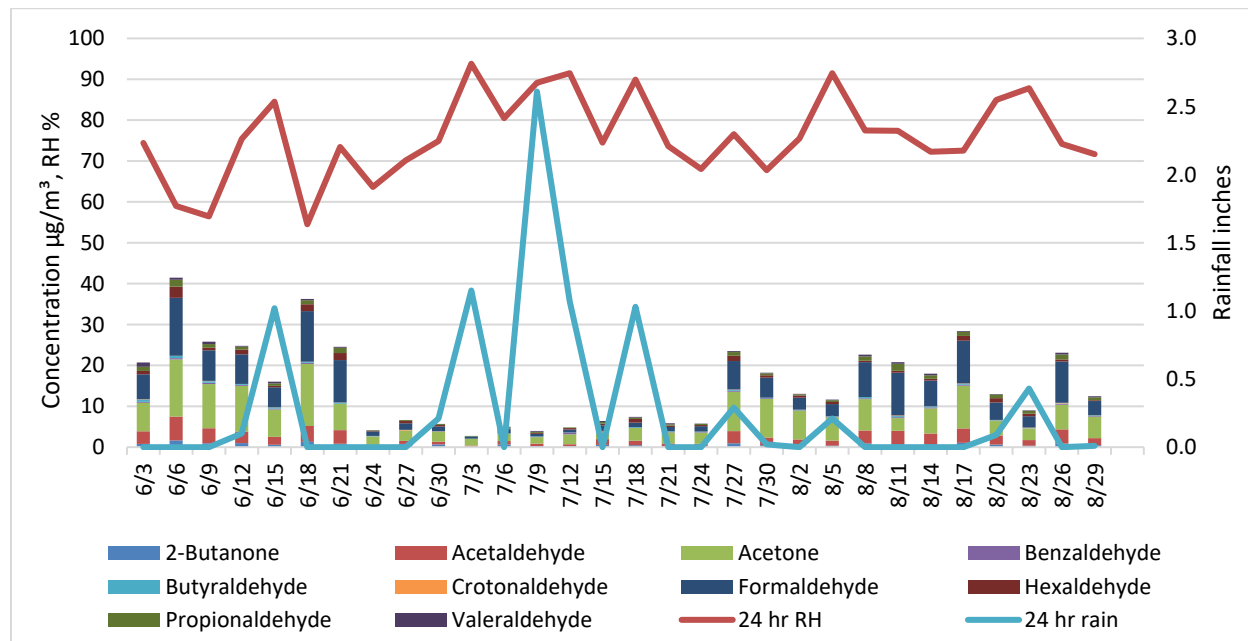


Figure 6.2 explores more of the potential impacts on data during this time. Despite the influx of western wildfire smoke impacting the state most notably on July 20th and 26th (see section 5.5), the carbonyl concentrations do not show evidence of this high PM_{2.5} concentration event during the sampling dates associated with these dates.

Rainfall is known to be an effective removal mechanism of carbonyl compounds, however, not all the sampling events that took place during June 24 and July 24 saw rainfall. Some correlation can also be made when looking at days with higher and lower relative humidity. This connection is suspected to be from high humidity that can cause collection issues in the cartridges and possibly interfering with the sampler's ozone denuder efficiency. In this case, there does not appear to be any pattern that suggest that this could have interfered with the data collection. It is hypothesized that that a flow control issue in the sampler (not activating ports or controlling flow properly) was not readily obvious in the recorded data. This appears to have been an issue with other states during the 2021 PAMS season as well.

Figure 6.2: Total 24-Hour Reportable Carbonyl Concentrations with daily Rainfall and Average Relative Humidity at Londonderry PAMS in 2021



To further illustrate the variance with the carbonyl data during this time frame, the Londonderry data was compared to the closest PAMS site with reportable carbonyl data in Lynn, Massachusetts (Figure 6.3). The two sites track very closely for formaldehyde (used as an example, but similar for all carbonyl compounds) except for the dates in question. Lynn is closer to downtown Boston and well within the metropolitan Boston area, thus it is not surprising that formaldehyde concentrations in Lynn are more frequently slightly higher than those measured at Londonderry. The correlation is very similar, however there is a magnitude of difference in concentration with the Londonderry data, indicating a potential flow issue. No errors or errant sampling flow totals were reported on the sampler during this time.

Figure 6.3: June-August, 2021 Total Reportable Formaldehyde Concentrations at Lynn, MA and Londonderry, NH

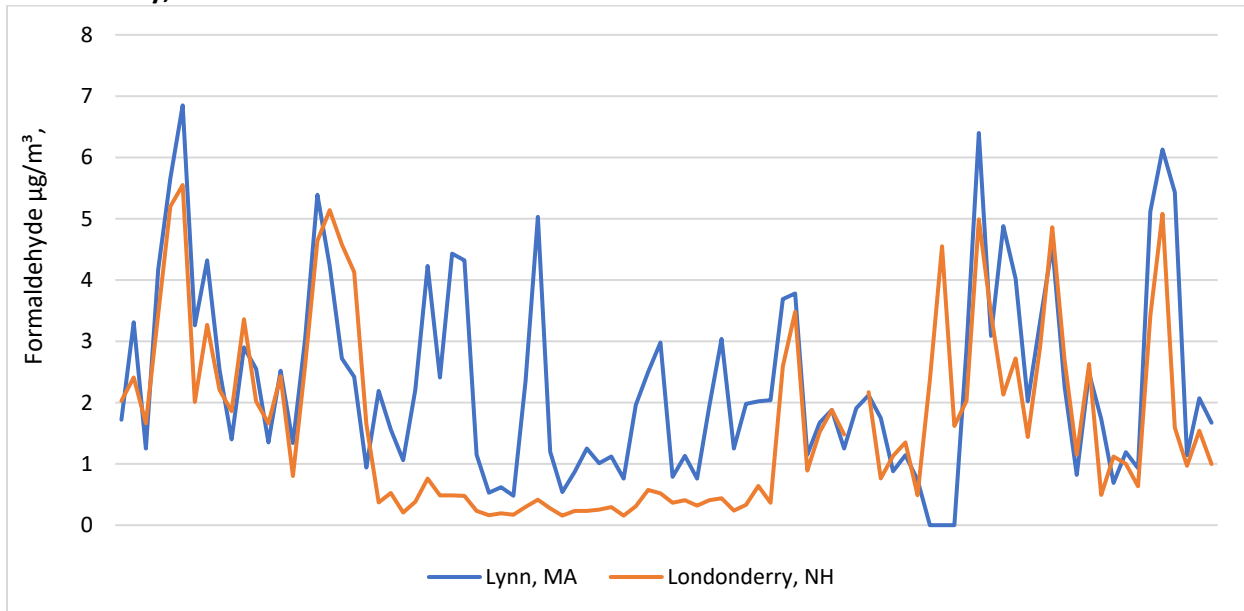


Figure 6.4 shows only the PAMS program required carbonyl compounds which make up most of the total concentrations. Acetone and formaldehyde are most frequently found in higher concentrations than Acetaldehyde. Benzaldehyde is usually found in much lower concentrations at Londonderry.

Figure 6.4: Total 24-Hour Required Carbonyl Concentrations at Londonderry PAMS in 2021

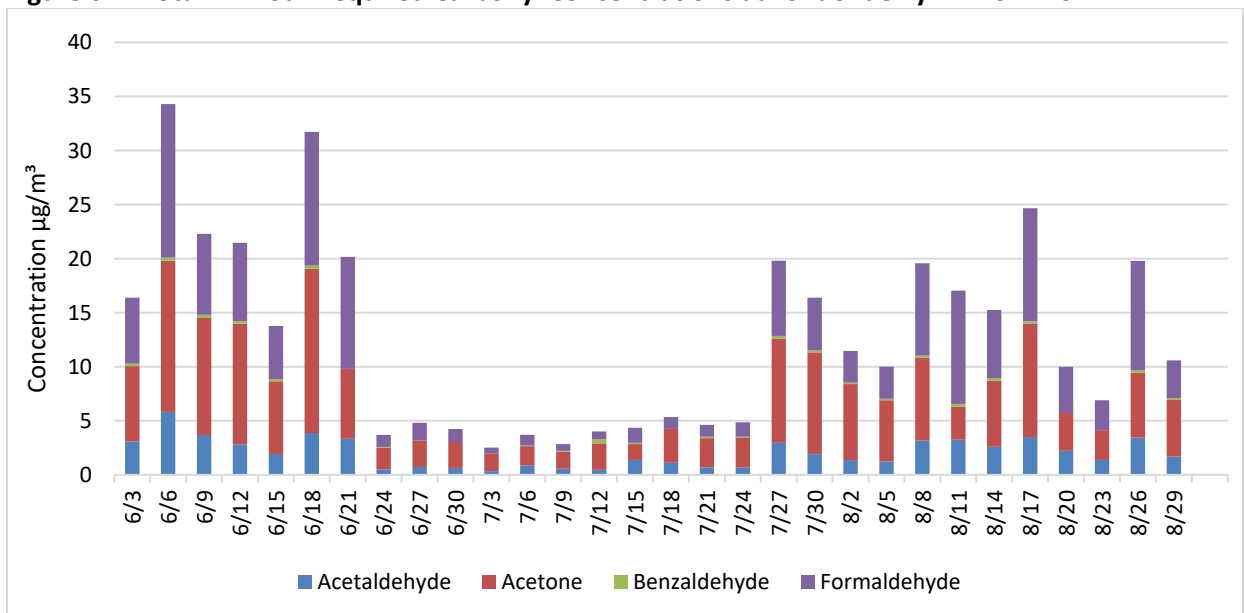


Figure 6.5 shows very little variation in the 8-hour averages for each carbonyl compound apart from formaldehyde. One might have expected a larger range of concentrations when looking at the 4:00 AM and 12:00 PM averages, however, the measurements were steady throughout all sampling periods. The variation seen with Formaldehyde indicates it may be emitted more later in the day or come from more distinct sources.

Figure 6.5: 8-Hour Average Carbonyls by Time of Day at Londonderry PAMS in 2021

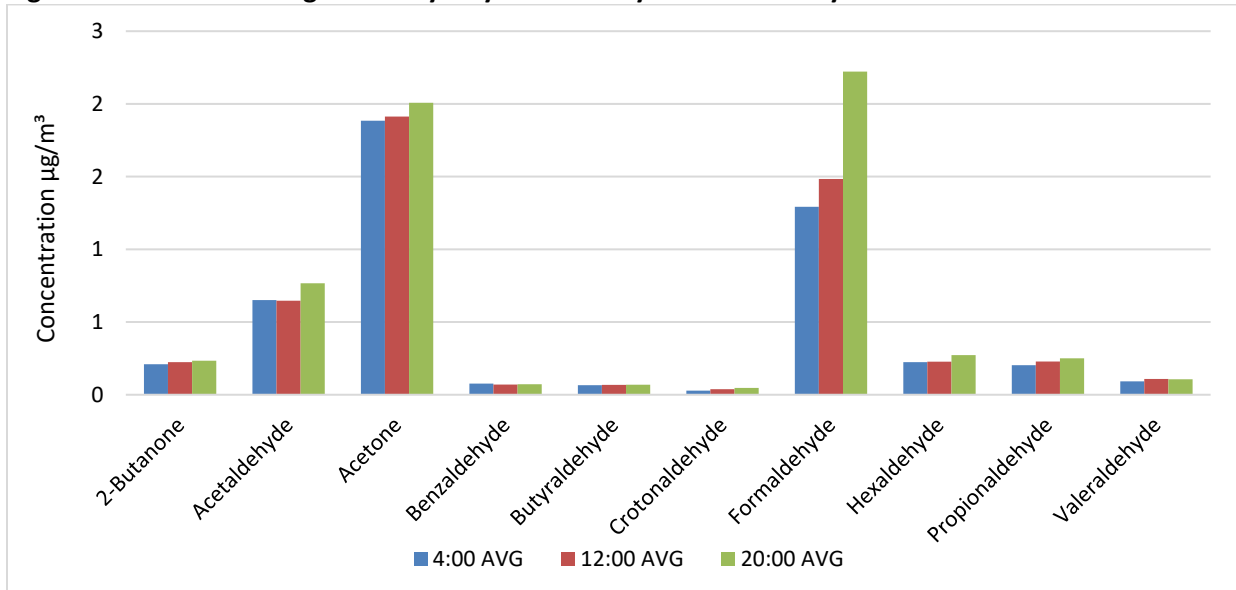


Figure 6.6 and Figure 6.7 compare carbonyl data for the past three years at Londonderry (covering the period since carbonyl sampling was added to the PAMS requirements). Carbonyl compounds are a valuable motor vehicle tracer, and it is obvious in both the compound averages and the carbonyl totals that there were significantly lower concentrations of carbonyls monitored in 2021 and 2020 demonstrating the potential decline of motor vehicle usage during the COVID-19 pandemic, but also due to the data anomaly described above.

Figure 6.6: Carbonyl Compound Averages by Year - Londonderry PAMS

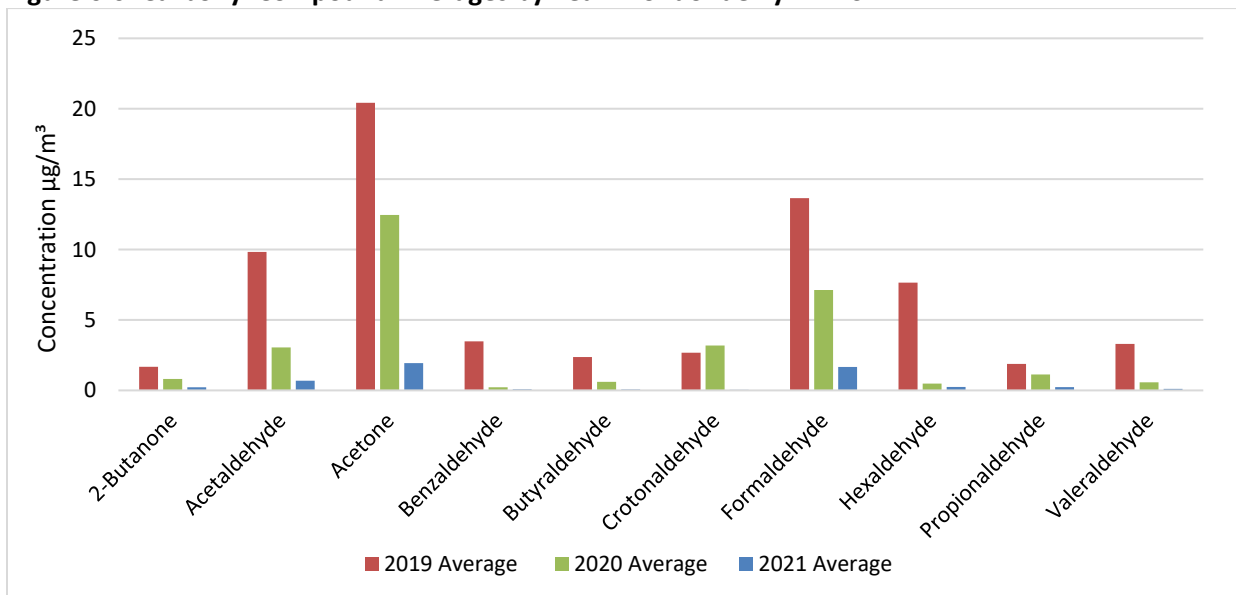
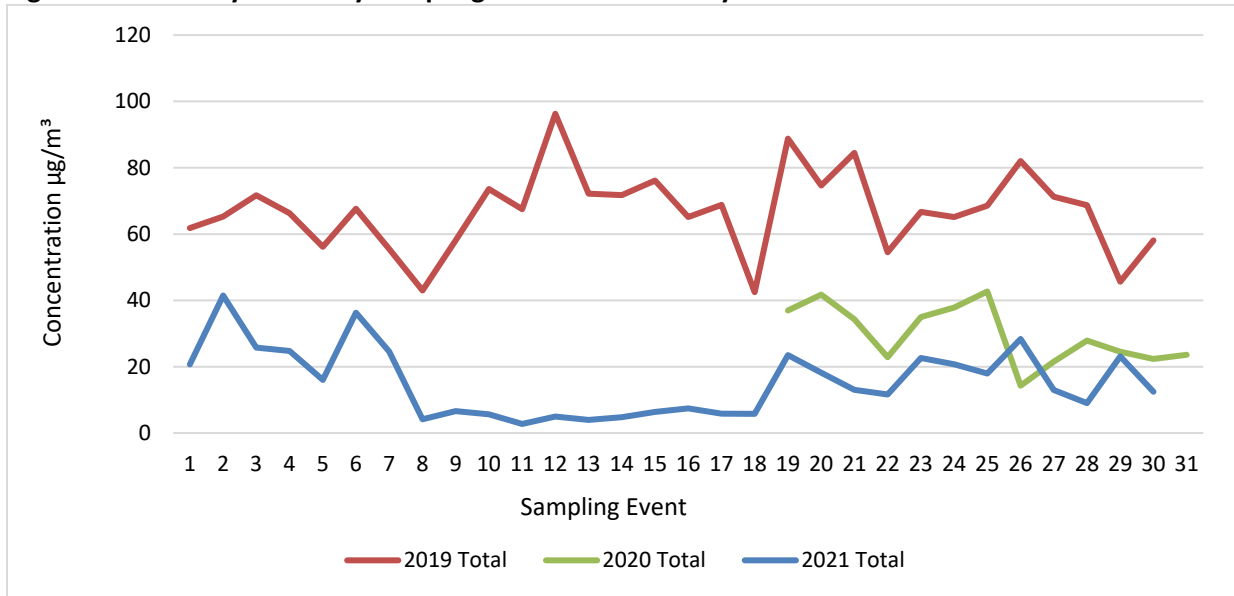


Figure 6.7 also demonstrates the lower concentrations seen, especially during July. August data more closely correlates with 2020 values.

Figure 6.7: Carbonyl Totals by Sampling Event- Londonderry PAMS



7. PAMS SEASON OZONE – 2021

The weather during the 2021 PAMS season, as observed by the National Weather Service in Concord, New Hampshire, featured very warm and dry weather in June, followed by a record wet and cool July. August and September rounded out the summer with a combination of warm and wet weather. The weather pattern in June started with temperatures averaging 3.7 degrees F above normal and with a rain deficit of 2.48 inches. Temperatures in July dropped considerably when averages were below normal by 2.2 degrees F. July also turned out to be the wettest on record with total rainfall of 13.04 inches, 9.42 inches above normal, bringing an end to drought conditions. Conditions normalized heading into August and September with rainfall amounts around average at -0.27 and + 0.83 inches, respectively. Temperatures rebounded in August and were above normal by 3.1 degrees F and 1.8 degrees above normal in September. These conditions contributed to 2021 being the third warmest year on record with a precipitation excess of 2.07 inches.

7.1 Ozone Attainment and NAAQS Exceedances at New Hampshire PAMS Sites

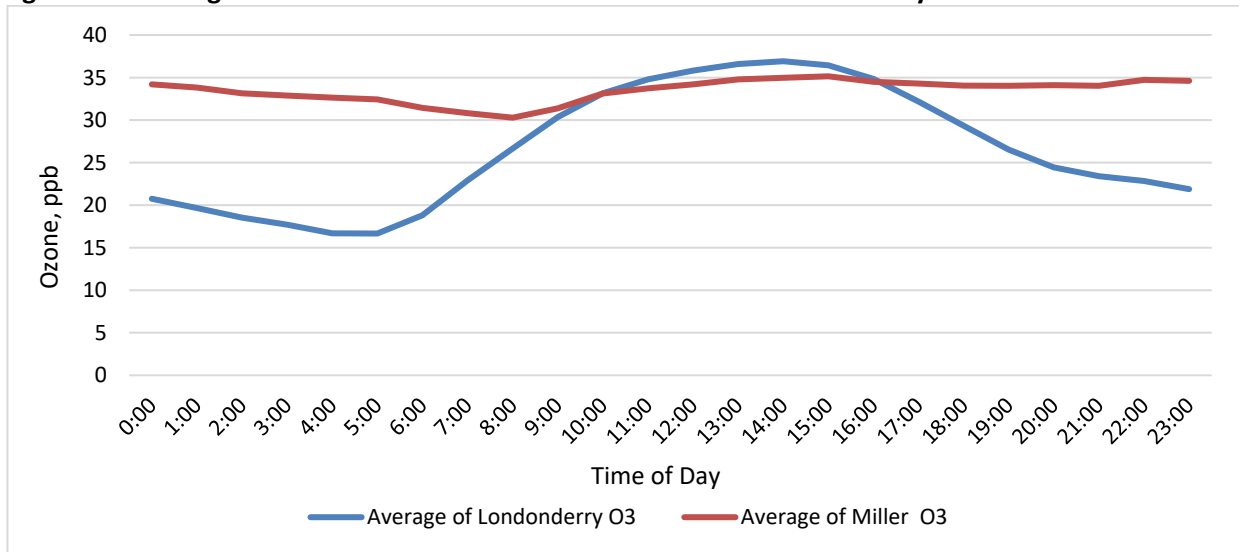
In total, New Hampshire saw four ozone exceedances of the NAAQS in 2021, however these did not occur at the New Hampshire PAMS sites. An exceedance of the 8-hour ozone standard occurs when an 8-hour averaged value during a day is greater than 0.070 ppm (70 ppb). Recording an exceedance of the ozone standard does not necessarily mean that a violation of the standard has occurred. A violation of the 8-hour standard occurs if the three-year average of the annual fourth highest daily maximum 8-hour values at a specific site is greater than 0.070 ppm. The last time a violation of the NAAQS occurred in New Hampshire was in 2010, representing the 2008-2010 design value period. Comparatively, the maximum 8-hour average ozone reading at the two New Hampshire PAMS sites for the 2021 season were 0.066 ppm at Londonderry on June 18th and 0.065 ppm at Miller on June 6th. The ozone analyzer malfunctioned on June 6th in Londonderry, so unfortunately there is no data for what could have been a higher ozone day at that site.

7.2 Ozone Monitoring Summary for the New Hampshire PAMS Sites

2021 ozone concentrations at Londonderry (located at a lower elevation and in a more urban setting compared to Miller) displayed a typical summertime diurnal pattern, related to solar radiation and temperatures increasing during the day. The effect is aided by ozone forming emissions that are released at higher rates during daylight hours, such as from vehicles during traffic, commercial activity, and power generation. Unless there is a strong ozone transport weather pattern, ozone concentrations in New Hampshire tend to drop later in the day as the sun starts to set and the daily emissions subside.

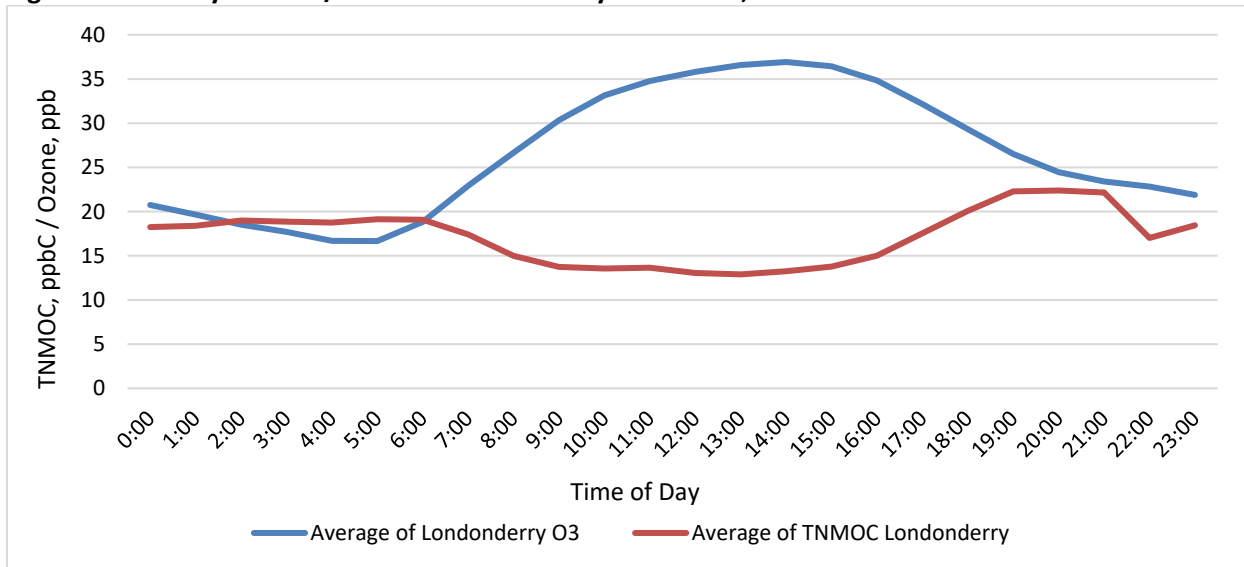
Conversely, due to the lack of emission sources at higher elevations, much of the ozone pollution at higher elevation sites is transported by winds from greater distances including from other states. The results from the higher elevation site at Miller (**Figure 7.1**) show ozone concentrations change little throughout the day and concentrations tend to average higher overall compared to Londonderry. Despite being only 25 miles apart, there is an elevation difference of nearly 2,000 feet.

Figure 7.1: Average Seasonal Diurnal Ozone Concentrations for Londonderry and Miller in 2021



TNMOC and ozone show a symbiotic relationship at Londonderry (**Figure 7.2**). At ground level, early morning traffic increases the emissions of NO_x and VOCs; as morning traffic dies down, their emissions begin to react, forming NO₂. Then as sunlight intensifies over the mid-day hours, the NO₂ is broken down and the byproducts form ozone. Once the sun starts to set and the ultraviolet energy subsides, the production of ozone also subsides and any leftover emissions remaining in the atmosphere are consumed by several different reactions.

Figure 7.2: Hourly TNMOC/Ozone at Londonderry PAMS Site, 2021



The mountaintop ozone measured at Miller is normally formed further away and transported into the area with the wind. Ozone concentrations at higher elevations are less influenced by vertical mixing of locally produced emissions (**Figure 7.3**) than experienced at lower locations like Londonderry. Air flow patterns are more stable at the higher monitoring location. This is especially apparent at night when there is a lack of ozone destroying mechanisms at higher elevations, and as a result, ozone concentrations remain higher at Miller than experienced during the same period at Londonderry. Overall, the higher elevation location is significantly more affected by transport from distant emission sources.

Figure 7.3: Hourly TNMOC/Ozone at Miller, 2021

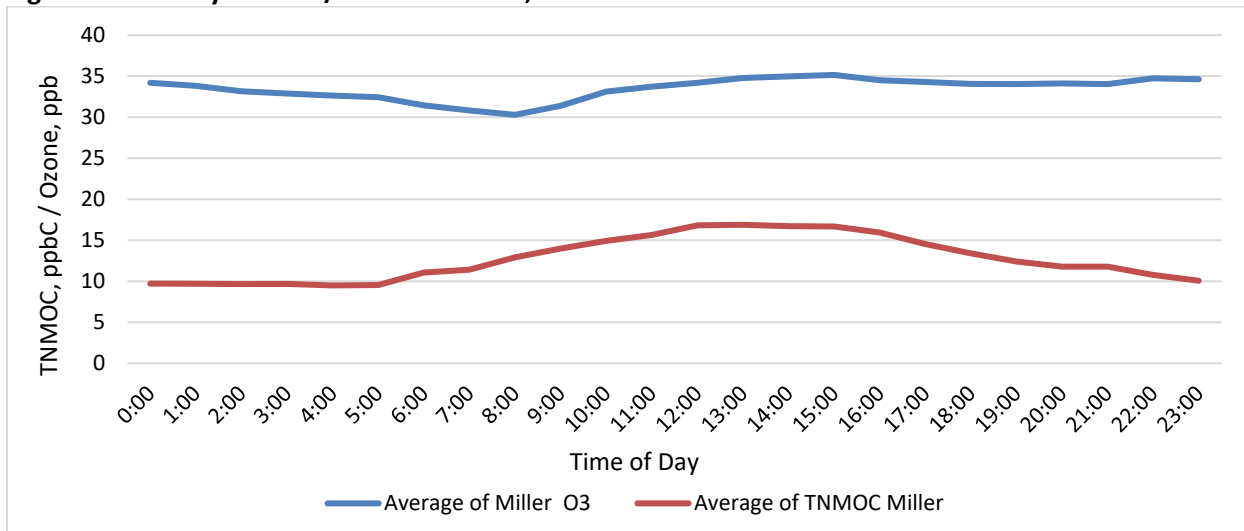
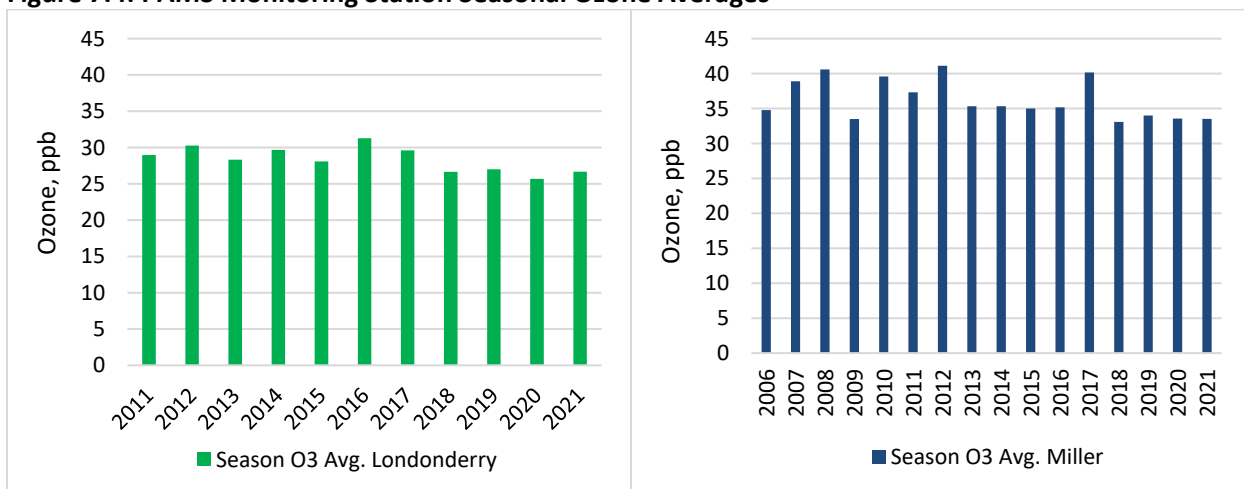


Figure 7.4 depicts average ozone concentration trends during the 3-month PAMS season at both New Hampshire sites. Although PAMS monitoring only began at Londonderry in 2015, ozone monitoring has taken place there since its inception in 2011 and 3-month average ozone concentrations there have been quite stable. Average ozone concentrations at Miller have been mostly steady since 2006, and more notably since 2013, except for 2017 when the seasonal average jumped by about 5 ppb. Overall, both sites have been consistent over the last four years.

Figure 7.4: PAMS Monitoring Station Seasonal Ozone Averages



Tables 7.1 and 7.2 present average monthly ozone concentrations and maximum monthly concentrations for both New Hampshire PAMS sites for 2021. The Londonderry site measured one-hour ozone of 70 ppb or above (the current 2015 8-hour NAAQS) on three occasions during 2021, all on June 18th and Miller measured two hours at or above 70 ppb on June 6th and June 18th.

Table 7.1: 2021 Average and Maximum Monthly Ozone Concentrations

A. Londonderry

Month	1-Hour Ozone, ppb	
	Average	Maximum
June	33	82
July	25	54
August	27	57
September	24	58

B. Miller

Month	1-Hour Ozone, ppb	
	Average	Maximum
June	38	71
July	30	60
August	35	63
September	32	62

Table 7.2: 2021 1-Hour Ozone Measurements Greater Than 70 ppb at Londonderry and Miller

A. Londonderry

Date	Time	Ozone, ppb
06/18/21	20:00	75
06/18/21	21:00	82
06/18/21	22:00	76

B. Miller

Date	Time	Ozone, ppb
06/06/21	11:00	70
06/18/21	21:00	71

On June 18th, the hourly ozone concentrations at both Londonderry and Miller steadily increased from 5:00 AM until 9 PM and then decreased thereafter (**Figure 7.5**). Measured VOCs rose in the afternoon at Miller, correlating to the increase in ozone that day. The Markes/Agilent system was down during this elevated ozone event, so there is no VOC data available at Londonderry on June 18th. Warm weather characterized this period: the temperature that day topped 86°F at Londonderry and 75° at Miller. Wind speeds picked up at the time of the increased ozone and the wind direction was predominately from the south and southwest, suggesting that ozone may have had some degree of transport from the Boston/New York City region helping to drive the higher concentrations (**Figure 7.6**).

Figure 7.5: Hourly Ozone, PAMS and Meteorological Conditions at Londonderry and Miller on June 18, 2021

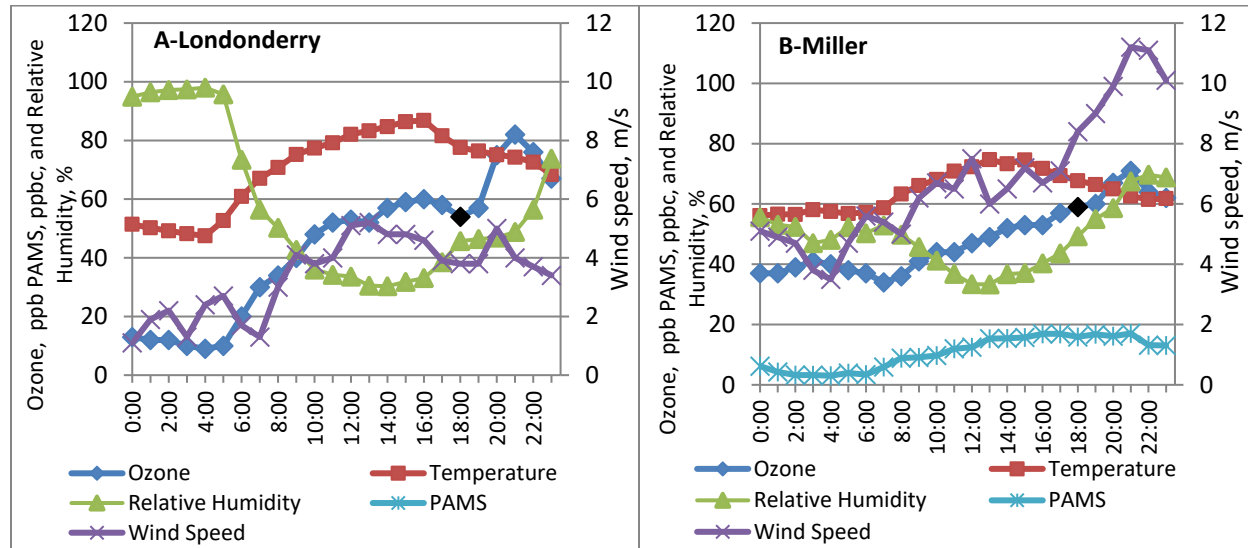
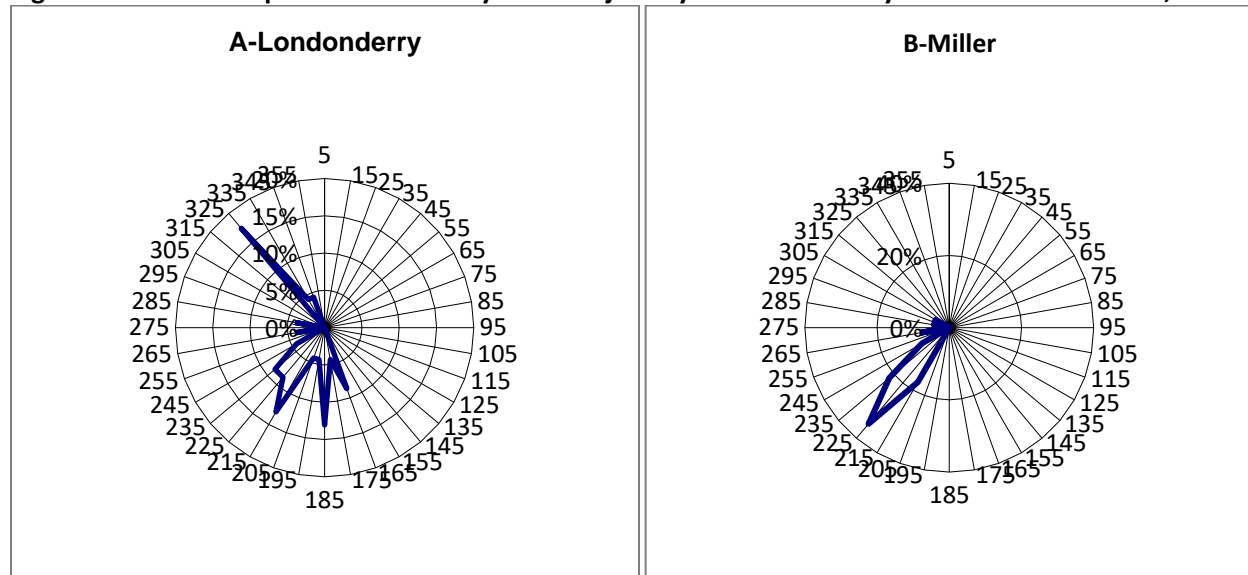


Figure 7.6: Wind Frequencies and 3-Day Back-Trajectory for Londonderry and Miller on June 18, 2021



8. MIXING HEIGHT

As part of the new PAMS program requirements, the measurement of mixing height was added at PAMS sites throughout the country. NHDES, being an early adopter, was able to purchase and install a Viasala CL51 ceilometer for the Londonderry location two years prior to the 2021 requirements. The ceilometer employs a pulsed diode laser (LIDAR) technology where powerful laser pulses are sent out in a vertical direction. The reflection of light caused by clouds, precipitation or other obstruction is analyzed and used to determine cloud heights as well as mixing layer height (MLH).

NHDES participates in using the Unified Ceilometer Network collaboration with the University of Maryland, Baltimore County (UMBC), the EPA, the National Aeronautics and Space Administration and National Atmospheric and Oceanic Administration, to provide a comprehensive assessment related to future policy decisions and key questions on the influence of gasses and aerosols in air quality atmospheric composition and climate. The EPA requirement for state and local air quality agencies to measure hourly MLH at the national PAMS, will be the first concerted effort to use the ceilometer aerosol profiles for the determination of MLH in the Planetary Boundary Layer. The primary purpose for the hourly MLH under PAMS was driven by the state's State Implementation Plan modeling data needs. See [real time MLH data at the Londonderry PAMS site](#).

The following data was retrieved by NHDES but has not been validated or entered into AQS; it is currently being used for forecasting and preliminary purposes only and is presented here in preliminary form. UMBC will work to develop a tool for ceilometer data validation and reporting to AQS. This tool is anticipated to be ready in June 2022.

While the ceilometer provides a vast array of data, the PAMS program is primarily interested in measurements for MLH. It is this information that will be used to define the height of vertical mixing of air. Pollutants emitted or transported below this altitude tend to stay trapped near the ground, while air above it tends to not mix with the air below. This information is especially important during periods of air stagnation, which can occur during ozone events in the summer, or wood smoke events during colder months. In these cases, polluted air below the mixing layer does not readily disperse or dilute with cleaner air that might be above the MLH. Conversely, sometimes the cleaner air is below the MLH, and more polluted air is being transported above the MLH. In this second case, the polluted air would not be able to mix downward to the ground, except for maybe at higher elevation locations like mountain tops. It is not unusual for higher ozone concentrations to be measured at the higher elevation monitors in New Hampshire, such as Miller and Mt. Washington Summit, than measured at nearby lower elevations. This is especially common during overnight hours where the mixing layer is more stable and often closer to sea level.

Figure 8.1 demonstrates the 2021 PAMS season average diurnal relationship among select parameters during the PAMS season. MLH shows a similar diurnal pattern to ozone, temperature, and solar radiation, but not TNMOC. Mixing heights are usually the highest during daytime periods, which are characterized by strong solar heating and the lowest during the night.

Figure 8.1: Londonderry PAMS Season Averages of Ozone, Temperature, Solar Radiation, TNMOC and Mixing Layer Height 2021

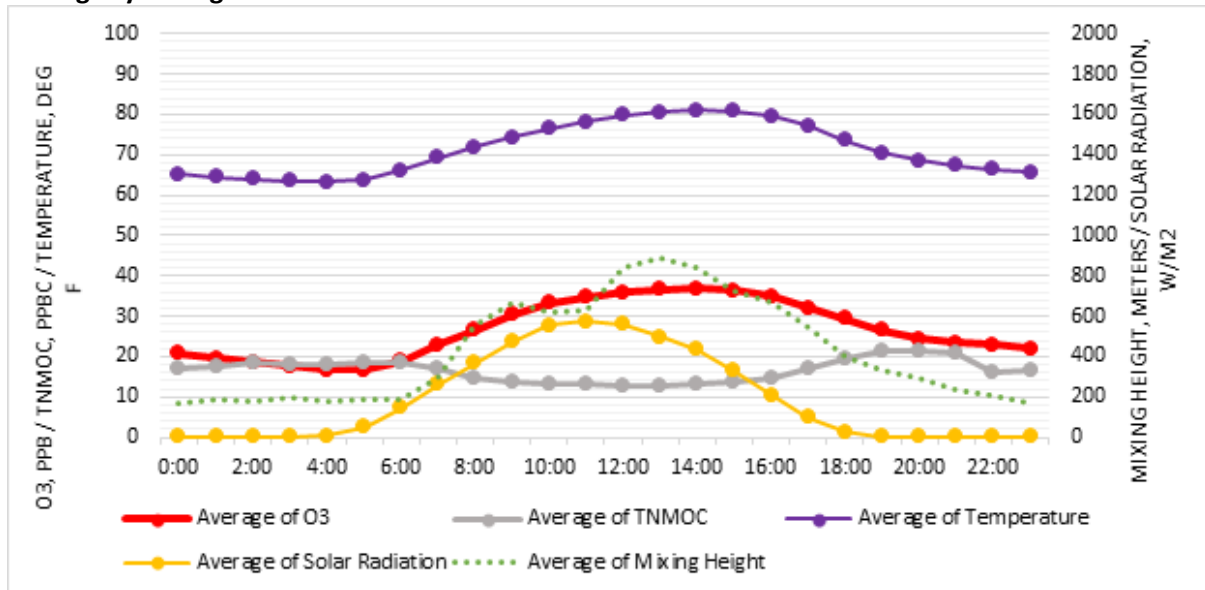
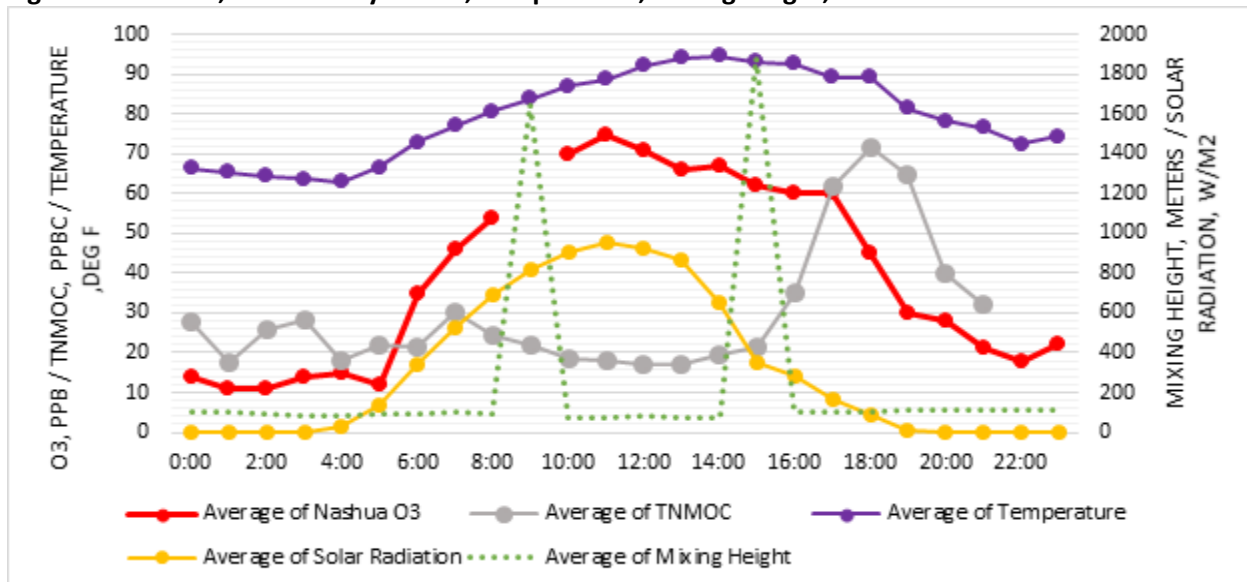


Figure 8.2 looks at June 6th, a day in 2021 where hourly ozone reached values above the 70 ppb threshold in southern New Hampshire. It is important to note that Figure 8.2 displays hourly ozone values for the Nashua, New Hampshire monitoring location due to the lack of Londonderry ozone data for that day. However, the Nashua monitoring station is close enough to Londonderry and has a strong enough ozone correlation with Londonderry to be a representative surrogate. Ozone concentrations start off very low during the early morning and begin to rise rapidly by 6:00 AM reaching a high of 75 ppb by 11:00 AM. The MLH for most of the day hovered around 100 meters except for two hours where it spiked up to 1,650 and 1,850 meters. The MLH remained extremely low throughout this 24-hour period and its lowest at 11:00 AM coincided with the ozone maximum. TNMOC concentrations never climbed very high during the early morning hours which suggest a disconnect between local emissions and the higher ozone concentrations. The sudden jumps in mixing height are probably the result of breaks in the clouds.

Figure 8.2: June 5, 2021 Hourly Ozone, Temperature, Mixing Height, and TNMOC



Note: Nashua, New Hampshire ozone monitor data is used due to lack of Londonderry ozone data for June 18th, 2021

The next two figures take a closer look at MLH and fine particulate matter (PM_{2.5}). **Figure 8.3** displays average hourly PM_{2.5} concentrations and MLH during the 2021 PAMS season while **Figure 8.4** displays hourly PM_{2.5} concentrations, MLH, and other parameters for a wildfire event. Average PM_{2.5} concentrations during the PAMS season (**Figure 8.3**) averaged around 8 µg/m³ and the MLH ranged from 165 meters to just under 900 meters. On July 26th, 2021, smoke from western wildfires contributed to elevated levels of PM_{2.5} (**Figure 8.4**). The early morning hours show that the mixing layer height increased to 2,000 meters but dropped significantly down to 70 meters by 11:00 AM. PM_{2.5} concentrations remained low during the early morning period but increased rapidly as the MLH dropped, trapping the particles from the transported wildfire smoke near the ground. MLH information is a great tool to have to better understand and aid in forecasting higher PM_{2.5} concentrations especially during wildfire smoke events.

Figure 8.3: 2021 PAMS Season Averages of PM_{2.5} and Mixing Height at Londonderry

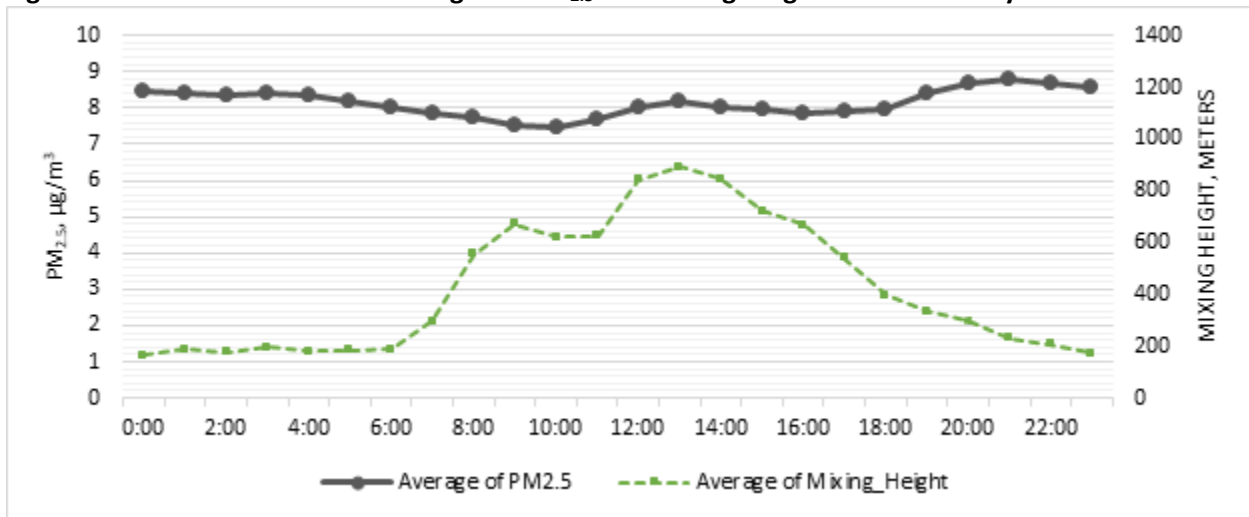
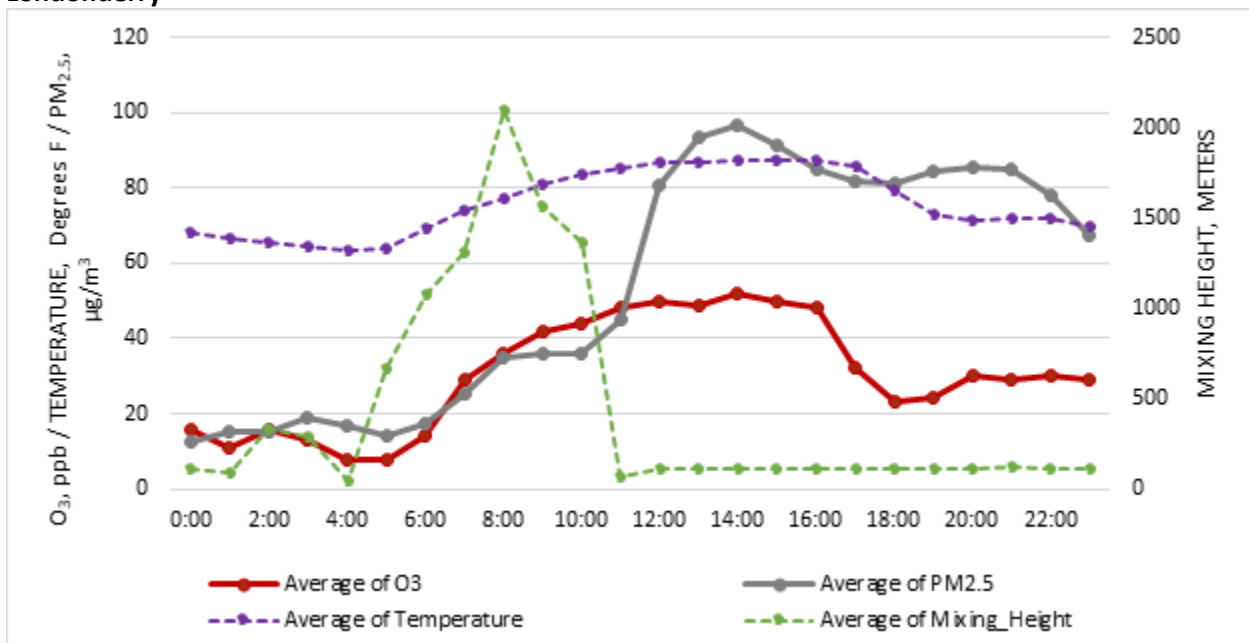


Figure 8.4: July 26, 2021 Wildfire Event - Hourly PM_{2.5}, Ozone, Temperature and Mixing Height at Londonderry



The next set of scatter plots show the relationship between MLH recorded at Londonderry with various other parameters for the period of June 1, 2021, through September 30, 2021. **Figure 8.5 (a-e)** presents relationships between MLH and wind speed, ambient temperature, solar radiation, measured ozone and TNMOC. The data and findings include:

- a. Small tendency for lower wind speeds to have a lower MLH.
- b. Warmer temperatures have a slightly higher MLH.
- c. Solar radiation tends to be stronger with a higher MLH, which probably tracks with fewer clouds.
- d. Higher ozone concentrations typically occur with a higher MLH, which could be related to mixing from distant emission sources.
- e. Lower MLHs better trap locally produced TNMOCs.

There is a heavy influence shown on the charts from mixing heights measured at and below 150 meters, making it difficult to parse out genuine trends. **Figure 8.5 (f)** shows that 65% of all hours with recorded mixing heights are at or below 150 meters (492 feet) before tailing-off to a much lower frequency. The highest mixing height recorded was 3,980 meters (13,058 feet). Because of this, calculated correlations with use of the full range of mixing heights are considered poor.

Accounting for the influence of the high frequency, low MLH can be accomplished by tracking the average value of a parameter at various MLHs. This is shown by dotted red lines in **Figure 8.6 (a-e)**. Low MLHs generally track with low wind speed, low and high temperatures, low solar insolation, and perhaps most importantly, low ozone concentrations. Ozone tends to peak in the mid-range of mixing heights with few high ozone concentrations with low and high mixing heights. On the other hand, higher TNMOC concentrations tend to occur under lower MLHs, likely due to trapping of these pollutants. Higher MLHs track with tailing off temperatures, solar radiation, TNMOC and ozone, but there is lower confidence in trends at higher MLHs due to low frequencies.

Figure 8.5: Mixing Height Scatter Plots with Various Parameters at Londonderry

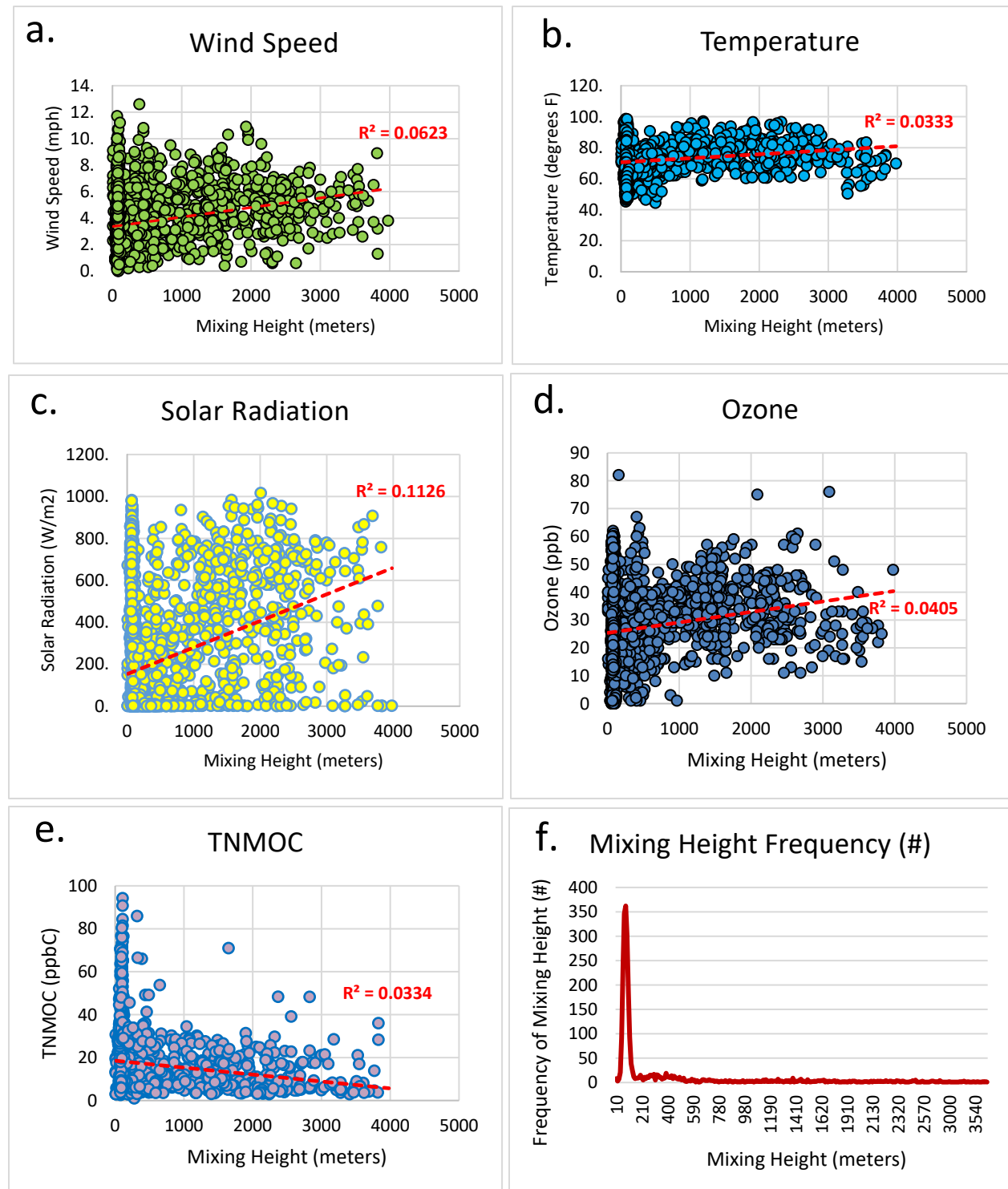
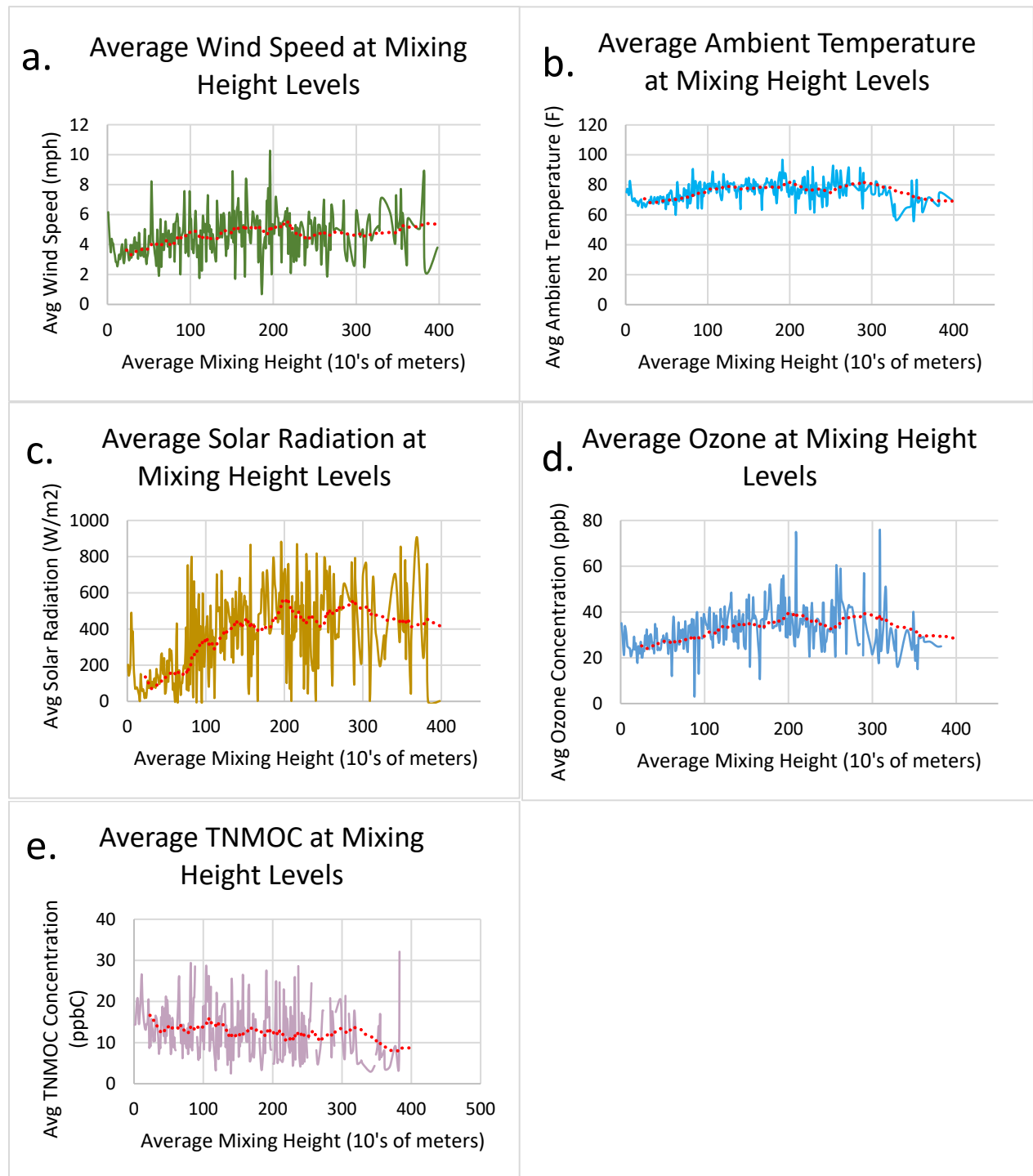
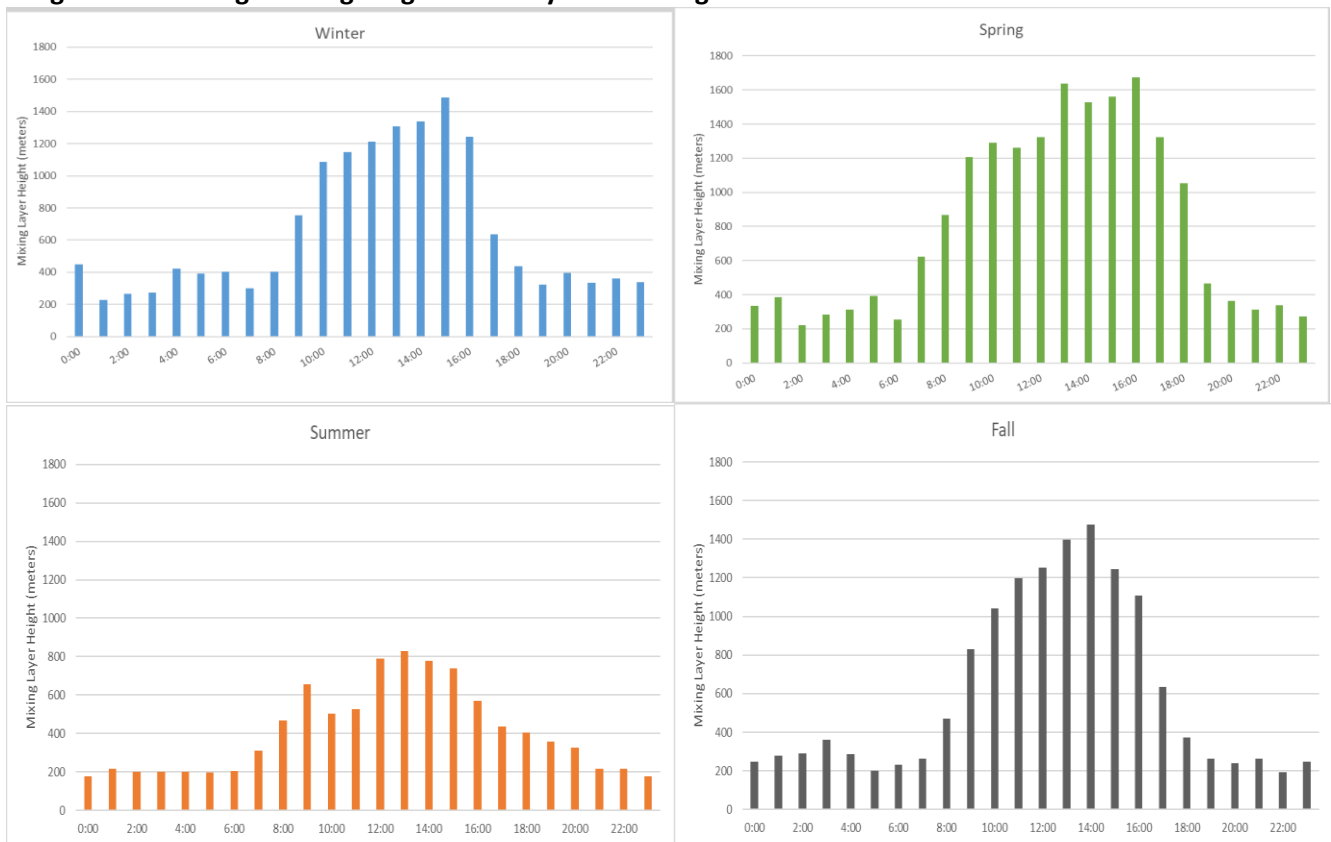


Figure 8.6 Average of Various Parameters by Mixing Height at Londonderry



As previously discussed, cooler air tends to result in a lower MLH, however many factors can affect the depth of the MLH. 2021 MLH data is categorized by meteorological season shown in **Figure 8.7**. Though the PAMS season only runs June through September, the ceilometer is collecting data year-round and can aid in forecasting for PM events due to inversions and wood smoke distribution. Winter, spring, and fall show some of the highest averages for MLH while summer averages remain fairly low. Though this is not what would typically be expected, New Hampshire experienced a very rainy summer season and precipitation can influence MLH height data.

Figure 8.7: Average Mixing Height Levels by Meteorological Season



9. CONCLUSION

NHDES had a successful year of PAMS VOC data collection at both sites in 2021. Instrumentation at the sites experienced some degree of down time and there were issues with getting quality Kori traps for the GC. This was an issue experienced by other states as well and resulted in qualifying many of the heavy molecular weight compounds during the season at Londonderry. The matter was discussed on the multi-state, plus EPA, PAMS required site workgroup calls, and it appears the providing vendor has now changed its protocols to prevent this from happening in the future.

2021 was the first official year that the new PAMS regulations were fully implemented by all states, however, NHDES volunteered to be an early adopter of the new technology by implementing all the regulatory changes during the 2018 and 2019 PAMS seasons. NHDES installed a True NO₂ monitor and new instrumentation for VOC monitoring, adding carbonyl sampling, and measured mixing height data at the Londonderry PAMS site. Unfortunately, the NO samplers at Londonderry (and Miller) suffered from technical malfunctions, so there is no data for the 2021 season for that parameter.

Meteorological conditions for the 2021 PAMS season were characterized by fluctuating temperatures and rainfall. Parts of the summer weather in New Hampshire were warm and dry, while July was exceptionally rainy and cool. In addition, PM events were widespread across the region during parts of July due to wildfires that burned uncontrollably in the Western US and Canada. This had a profound effect on air quality resulting in multiple exceedances of the PM_{2.5} NAAQS on two occasions at each of the PAMS locations.

Average VOC levels at both sites were similar in 2021 compared to 2020, though they did trend slightly higher at Miller and slightly lower at Londonderry. The COVID-19 pandemic carried over to 2021, although many of the restrictions from 2020 were not continued throughout 2021. Schools were back in session and travel seemed more consistent with previous years, though for some, telework has become the new normal.

Ozone average concentrations at the two New Hampshire PAMS locations did not experience any drastic reductions, and the ozone standard was exceeded on three occasions in 2021. Biogenic compounds still made up a large percentage of total PAMS concentrations in 2021. Isoprene was the top contributor at both sites and α -pinene was also in the top 10 at Londonderry while BTEX and HAP compounds, associated with transportation emissions, were similar to 2020 at both sites, minus the increased benzene seen at Miller discussed previously in this report.

Carbonyl concentrations measured in Londonderry seemed to experience some sampling or analytical errors in July, though nothing was definitive as the sampler did not report any flow or leak failures and the ozone denuder passed its efficiency test at the end of the season. Complications with this method are frequent topics of conversation for the entire PAMS network; the subcontract lab plans to communicate errors with the data more effectively prior to the end of PAMS season.

For 2022, the purchase and installation of the Markes Agilent system at Miller will provide additional insight and compare better to the Londonderry location especially with the ability to capture the additional biogenic compounds; α - and β -pinene. The impacts of climate change will also continue to affect our weather and natural events that could influence trends with PAMS data capture in the future.

APPENDIX A: 2021 VOC MDL's FOR MILLER AND LONDONDERRY PAMS

COMPOUND	LONDONDERRY MDL	MILLER MDL
43202 Ethane	0.291	0.096
43203 Ethylene	0.161	0.148
43204 Propane	0.397	0.324
43205 Propylene	0.386	0.121
43214 Isobutane	0.349	0.273
43212 n-Butane	0.463	0.495
43206 Acetylene	0.253	0.057
43216 Trans-2-Butene	0.312	0.217
43280 1-Butene	0.449	0.430
43217 Cis-2-butene	0.344	0.410
43242 Cyclopentane	0.284	0.207
43221 Isopentane	0.344	0.369
43220 n-Pentane	0.284	0.238
43218 1,3-Butadiene	0.317	0.188
43226 Trans-2-Pentene	0.407	0.259
43224 1-Pentene	0.439	0.195
43227 Cis-2-Pentene	0.462	0.332
43244 2,2-Dimethylbutane	0.317	0.485
43284 2,3-dimethylbutane	0.339	0.439
43285 2-Methylpentane	0.194	0.347
43230 3-Methylpentane	0.403	0.324
43243 Isoprene	0.370	0.354
43231 Hexane	0.401	0.495
43262 Methylcyclopentane	0.247	0.241
43247 2,4-Dimethylpentane	0.321	0.298
45201 Benzene	0.398	0.327
43248 Cyclohexane	0.474	0.497
43263 2-Methylhexane	0.391	0.377
43291 2,3-Dimethylpentane	0.481	0.840
43249 3-Methylhexane	0.330	0.463
43250 2,2,4-Trimethylpentane	0.169	0.355
43232 Heptane	0.288	0.357
43261 Methylcyclohexane	0.346	0.432
43252 2,3,4-Trimethylpentane	0.416	0.213
45202 Toluene	0.302	0.322
43960 2-Methylheptane	0.171	0.135
43253 3-Methylheptane	0.246	0.254
43233 Octane	0.383	0.210
45203 Ethylbenzene	0.332	0.258
45109 M/P-xylene	0.437	0.274
45220 Styrene	0.218	0.211
45204 O-xylene	0.226	0.112
43235 Nonane	0.493	0.184
45210 Isopropylbenzene	0.420	0.392
43256 AlphaPinene	0.346	NA
45209 n-Propylbenzene	0.254	0.240
45212 m-Ethyltoluene	0.455	0.546
45213 p-Ethyltoluene	0.177	0.479
45207 1,3,5-Trimethylbenzene	0.306	0.662
45211 O-ethyltoluene	0.272	0.139
45208 1,2,4-Trimethylbenzene	0.388	0.535
43238 Decane	0.338	0.393
45225 1,2,3-Trimethylbenzene	0.305	0.460
43257 BetaPinene	0.133	NA
45218 1,3-Diethylbenzene (M)	0.345	0.466
45219 1,4-Diethylbenzene(P)	0.348	0.354
43954 Undecane	0.374	0.508