

NEW HAMPSHIRE DEPARTMENT OF
ENVIRONMENTAL SERVICES
2018 PAMS SUMMARY

Photochemical Assessment Monitoring Station (PAMS)



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**NEW HAMPSHIRE DEPARTMENT OF
ENVIRONMENTAL SERVICES
2018 PAMS SUMMARY**

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1. ACRONYMS USED IN THIS REPORT

AAL	Ambient Air Limits, a health based air limit
AIRS	Aerometric Information Retrieval System, repository for air pollution information
ACGIH	American Conference of Governmental Industrial Hygienists
AQS	Air Quality System
BTEX	Benzene, Toluene, Ethylbenzene, and Xylene (inherent to gasoline)
CBSA	Core Based Statistical Area
CO	Carbon monoxide
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
HFC	Hydrofluorocarbon
HCFC	Hydrochlorofluorocarbon
HYSPLIT	Hybrid Single-Particle Lagrangian Integrated Trajectory
MDL	Minimum Detection Limit
NAAQS	National Ambient Air Quality Standard, health-based ambient air standard
NCORE	National Core, an air monitoring network
NHDES	New Hampshire Department of Environmental Services
NIST	National Institute of Standards & Technology
OSHA	Occupational Safety and Health Administration
O ₃	Ozone, a chemically reactive air pollutant
PAMS	Photochemical Assessment Monitoring Station
ppb	parts per billion, a measure of concentration
ppbc	parts per billion times carbon, a measure of concentration
QAPP	Quality Assurance Project Plan
QA/QC	Quality Assurance/Quality Control
SOAP	Secondary Organic Aerosol Precursors
TAD	Technical Assistance Document, Issued by EPA
TLV	Threshold Limit Value
TNMOC	Total Non-Methane Organic Compounds
UTC	Coordinated universal time, a worldwide time reference
UV	Ultra violet (radiation), a type of light from the sun
UVRAD	Ultra violet radiation, a type of light from the sun
VOCs	Volatile organic compounds

2. INTRODUCTION

In 2018, monitoring for the Photochemical Assessment Monitoring Stations (PAMS) was completed for the fourth summer season at the Moose Hill School (MHS) site in Londonderry, New Hampshire, and the 13th at Miller State Park (MSP) atop Pack Monadnock in Peterborough, New Hampshire. The combination of the two sites provides a unique high-low look (elevation 345 ft. vs. 2290 ft.) at ozone precursors in New Hampshire. PAMS monitoring locations have changed through the years but the current locations in Londonderry and Peterborough 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, oxides of nitrogen, ozone and meteorology at different elevations. The locations of these stations in the state are shown in Figure 2-1. 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) Air Monitoring Program.

The 2015 revision of the ozone National Ambient Air Quality Standard (NAAQS) changed the criteria for required PAMS sites across the country effective in 2019.¹ NHDES elected to implement the mandated changes at the Londonderry location in 2018, while continuing the monitoring in Peterborough under the Enhanced Monitoring Plan for the Ozone Transport Region. The Londonderry equipment was upgraded to meet the new requirements in 2018. The new 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 that removes moisture from sampled air much more effectively than the Nafion dryer used at Miller State Park. The Markes KORI dryer not only allows the passage of certain compounds (notably, alpha- and beta-pinene) to enter the gas chromatogram 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 increased, as expected. New Hampshire will continue PAMS monitoring at the Peterborough site using the current PerkinElmer VOC system.

The original objectives of the PAMS program were to help verify ozone precursor emission inventories, identify their trends and distribution, and to 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. Current PAMS monitoring is 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 over 20 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 standard has been revised many times, most recently in September of 2015 when the standard was lowered from 0.75 ppb to 0.70 ppb [\[80 FR 65292\]](#). Included in the revision of the standard were changes to the monitoring requirements in 40 CFR part 58, Appendix D Section 5, "Network Design for Photochemical Assessment Monitoring Station (PAMS) and Enhanced Ozone Monitoring."

¹ The EPA has proposed revising the start date to June 1, 2021 [\[84 FR 25221\]](#). Comment period ended July 1, 2019.

Under the updated requirements, NCORE sites in a Core Based Statistical Area (CBSA) with a population of 1,000,000 or more will require PAMS monitoring regardless of ozone attainment status in order to provide spacial coverage to meet national model evaluation needs. This change is not effective until June 1, 2019; however, NHDES took proactive measures to accommodate the new regulations concerning the relocation of the PAMS site from Nashua to Londonderry in 2014. Also, effective in 2019 is a revision of the VOC list and the addition of both mixing height and carbonyl sampling. Carbonyl sampling will be required at the Londonderry site on a one and three-day basis with three, eight-hour samples from June through August. New technologies have been developed that will improve data quality and further our knowledge base on the topic.

Ozone in New Hampshire has improved significantly in recent years. However, the area in which the PAMS stations are located is a chemically complicated air region, and ozone nonattainment areas exist near the New Hampshire border (the Boston-Manchester-Portsmouth (Southeastern) New Hampshire maintenance area that includes portions of three counties in the southern portion of the state, and the Boston-Lawrence-Worcester (Eastern) Massachusetts nonattainment area – both related to the 1997 ozone standard, Figure 2-2).

Figure 2-1: Map of PAMS stations in New Hampshire

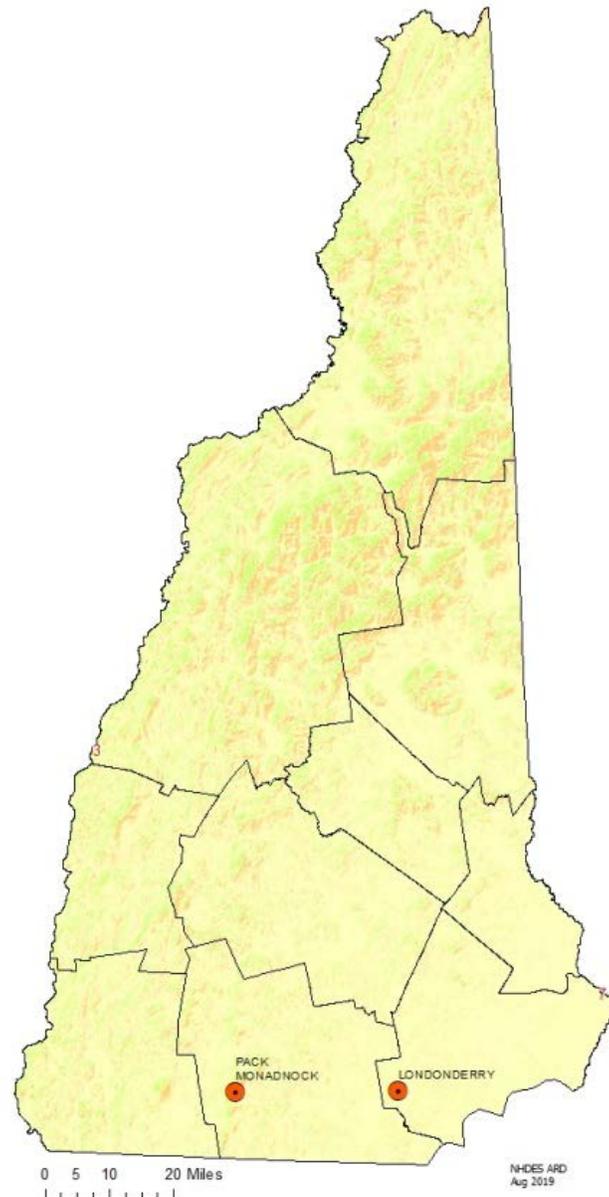


Figure 2-2: Nonattainment/Maintenance Areas in or near New Hampshire²

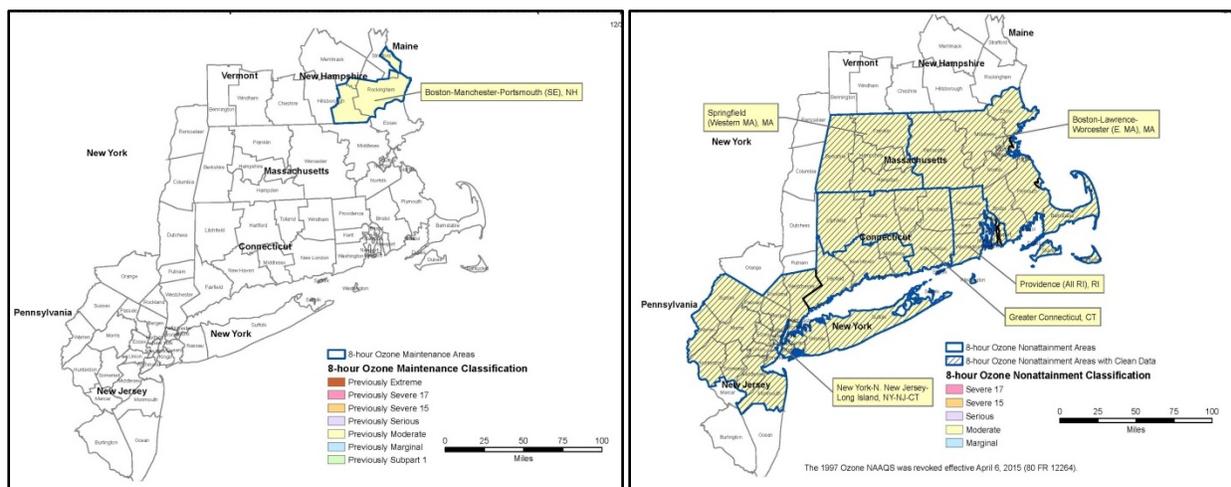


Table 2-1 lists the current PAMS VOC target compounds along with the chemical species' Air Quality System (AQS) codes. The PAMS program entails collection of data in accordance with 40 CFR 58 Appendix D, Part 5. This report summarizes that data and examines VOC concentration patterns, meteorological conditions, and a comparison of ozone values with PAMS compounds associated with New Hampshire's 2018 PAMS program data collection.

Table 2-1: List of PAMS organic compounds and their AIRS codes

VOC	AQS	VOC	AQS	VOC	AQS	VOC	AQS
Ethane	43202	Ethylene	43203	Propane	43204	Propylene	43205
Isobutane	43214	1-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 Moose Hill School site

² <https://www.epa.gov/green-book/green-book-8-hour-ozone-1997-area-information-naags> (As of December 31, 2018)

3. DATA VALIDATION

Data validation is necessary to identify data with errors, biases and physically unrealistic values before they are used for identification of exceedances, for analyses or for modeling. Data validation for the 2018 data was conducted in accordance with the NHDES PAMS Quality Assurance Project Plan (QAPP).³ Values that fail to meet the acceptance criteria are flagged in this report. Based on that evaluation, data for the following compounds and dates has been flagged. Where this data is referenced in the report, it is also flagged.

Table 3-1: 2018 Data Failing QC Parameters

Site	VOC Compound(s)	Date(s)
Londonderry (Moose Hill School)	3-methylhexane	June 1-30
	Styrene	
	n-propylbenzene	July 1-31
	2,2,4 trimethylpentane	
	Styrene	
n-propylbenzene	July 1-13	
	1,2,4 trimethylbenzene	July 29-31
	3-methylhexane	August 1-31
	Styrene	
	1,2,4 trimethyl-benzene	
	3-methylhexane	September 1-30
	1,2,4 trimethylbenzene	
Peterborough (Miller State Park)	Propylene	August 1-17

4. QUALITY CONTROL

NHDES performs PAMS monitoring in accordance with the Environmental Protection Agency’s (EPA) PAMS Technical Assistance Document (TAD). Quality control procedures are documented in the QAPP, which ensures certain quality control processes are in place to maintain high quality PAMS data. With new regulations effective in 2019, new QA/QC procedures are being developed and will include a Performance Evaluation study as well as increased calibration certification frequency and use of a second source standard.

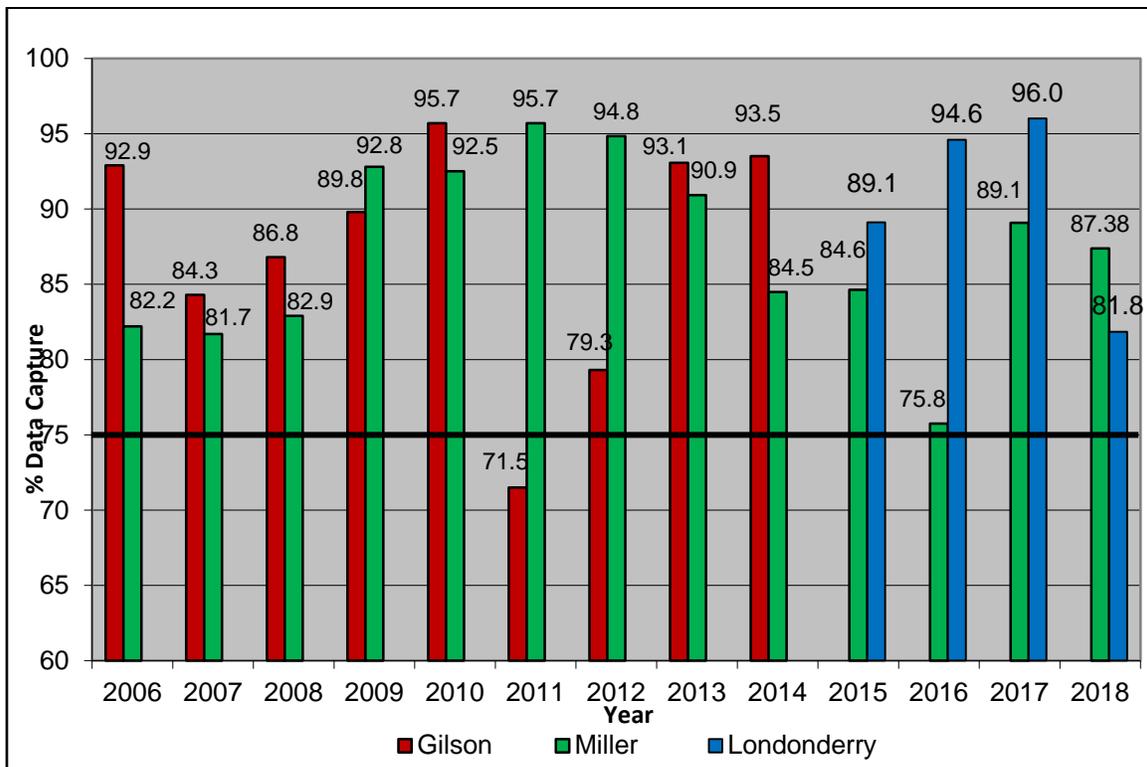
5. DATA COMPLETENESS

Data capture rates met the EPA acceptance criteria of 75% at both sites for 2018 (black line in Figure 5-1). Data collection rates at the Londonderry site were impacted by the learning curve associated with the new equipment and software and an electrical storm that knocked out power to the site for several days. Over 200 hours of data collection were missed at Moose Hill School, including missing one or more days in all four months of the monitoring season. The Miller State Park, operating with the same equipment several years, fared somewhat better, although a computer malfunction in August resulted

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

in the loss of almost seven days' worth of hourly data (161 hours). Still, the capture rate at both sites is above the 75% acceptance criteria.

Figure 5-1: Data Capture Rates 2006-2018



*Reduced data capture rates at Gilson Rd. in 2011 and 2012 are largely due to instrument errors that led to significant down time. NHDES holds a maintenance contract with the instrument manufacturer; however, these problems were difficult to troubleshoot and required lengthy and costly repairs. The ongoing situation with the thermal desorber was rectified in 2013 and it ran smoothly thereafter.

The Miller State Park data was also examined to determine how frequently the target VOCs were measured above the method detection limit (MDL), illustrated by Figures 5-2. Only species that were measured at or above the MDL by 10% are shown. For Miller State Park, these coincide roughly with the ten most abundant species detected.

Method detection limits were not calculated for Moose Hill School. Given the challenges associated with installing the new equipment and software, and time associated to ensure its proper operation, there was little time available before the start of the monitoring season to perform the analyses needed to determine method detection limits. This information will be provided in the 2019 PAMS report. To provide a comparable chart to Figure 5-3 for Moose Hill School, an arbitrary 0.5 parts per billion (ppb) detection limit was used. A great many more compounds were captured above 10% in this scenario, although nine of ten of the highest concentration compounds at this site are represented in those most frequently measured above 0.5 ppb (Figure 5-2).

Figure 5-2: VOCs Captured at or above the MDL at Miller State Park

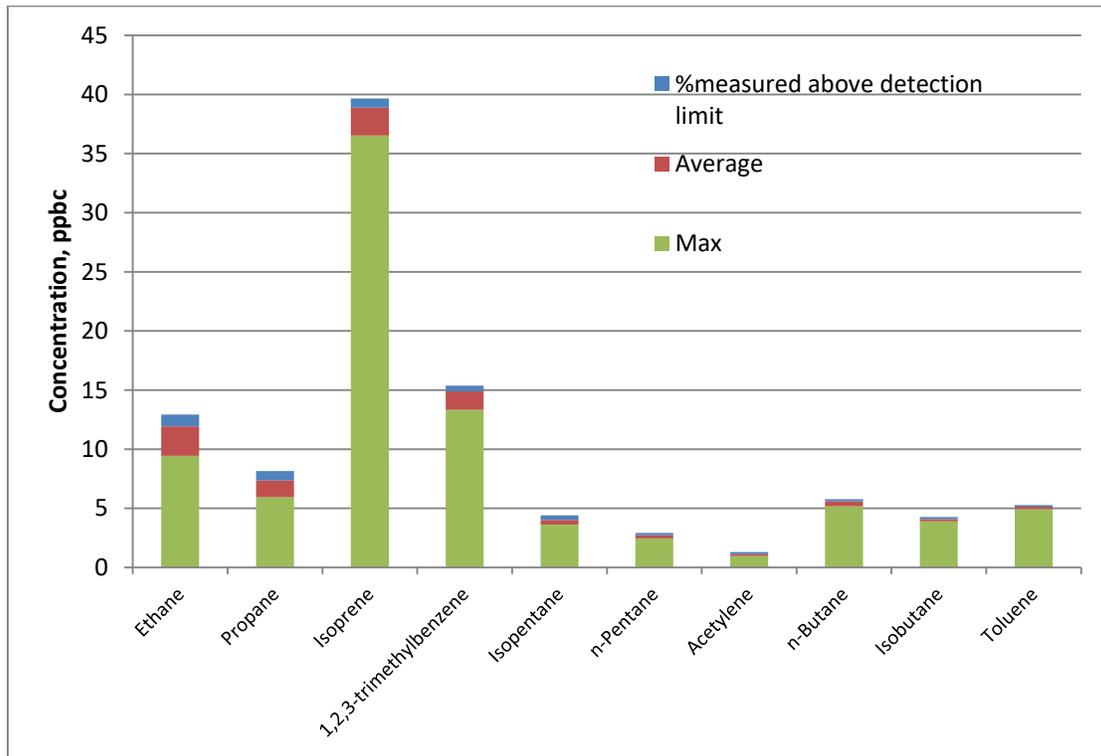
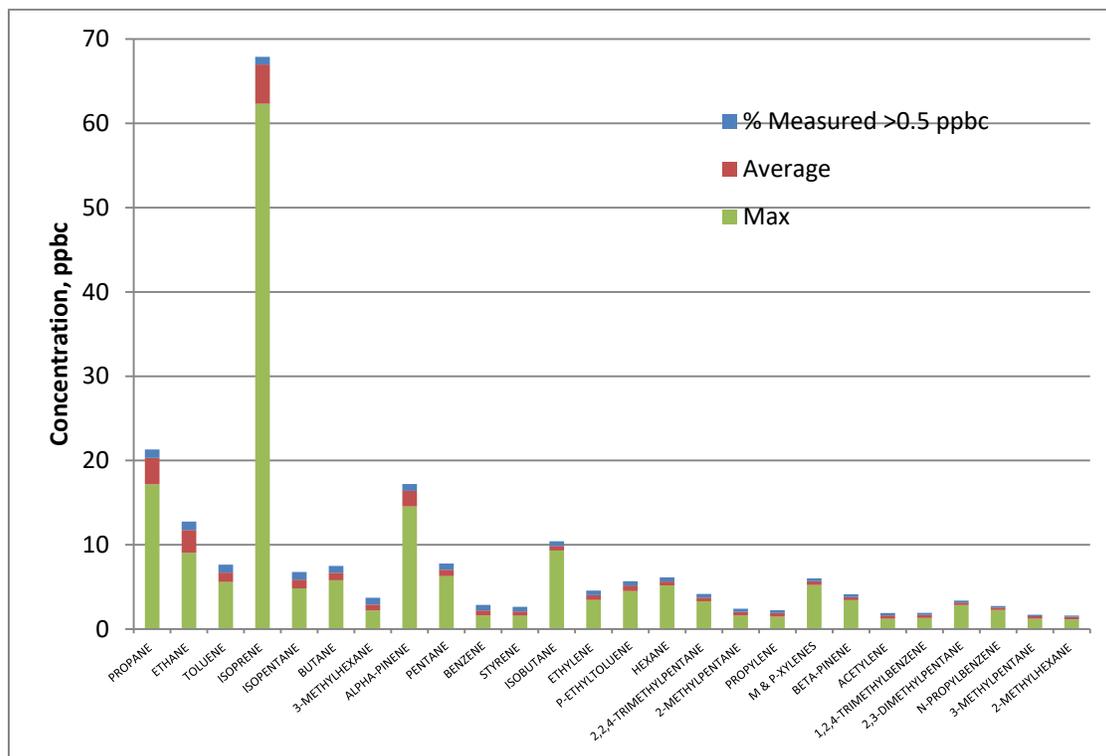


Figure 5-3: VOCs Captured at or above 0.5 ppbc – Moose Hill School

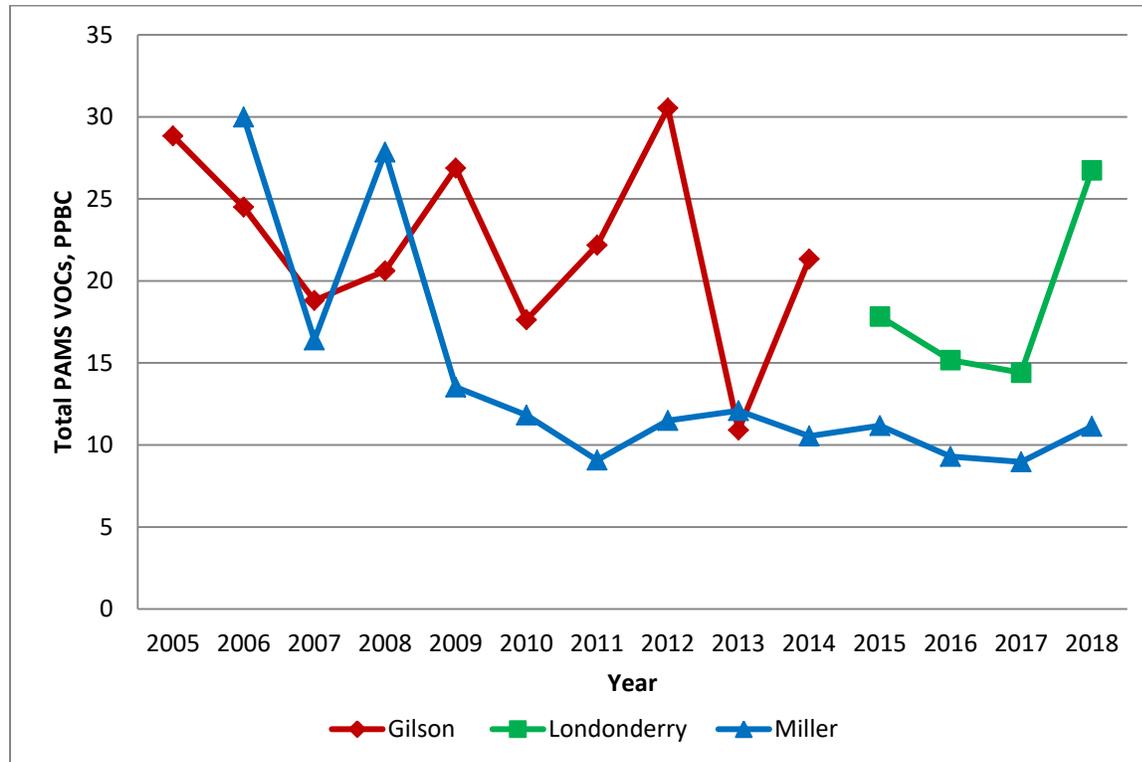


6. DATA ANALYSIS

6.1 PAMS Compounds and Major Species

Figure 6-1 represents the seasonal average PAMS compound concentrations at the Gilson Road, Miller State Park and Moose Hill School sites since 2005. Although PAMS sampling discontinued at Gilson Road in Nashua in 2013, the data is retained in some of the trending charts for the purpose of comparison.

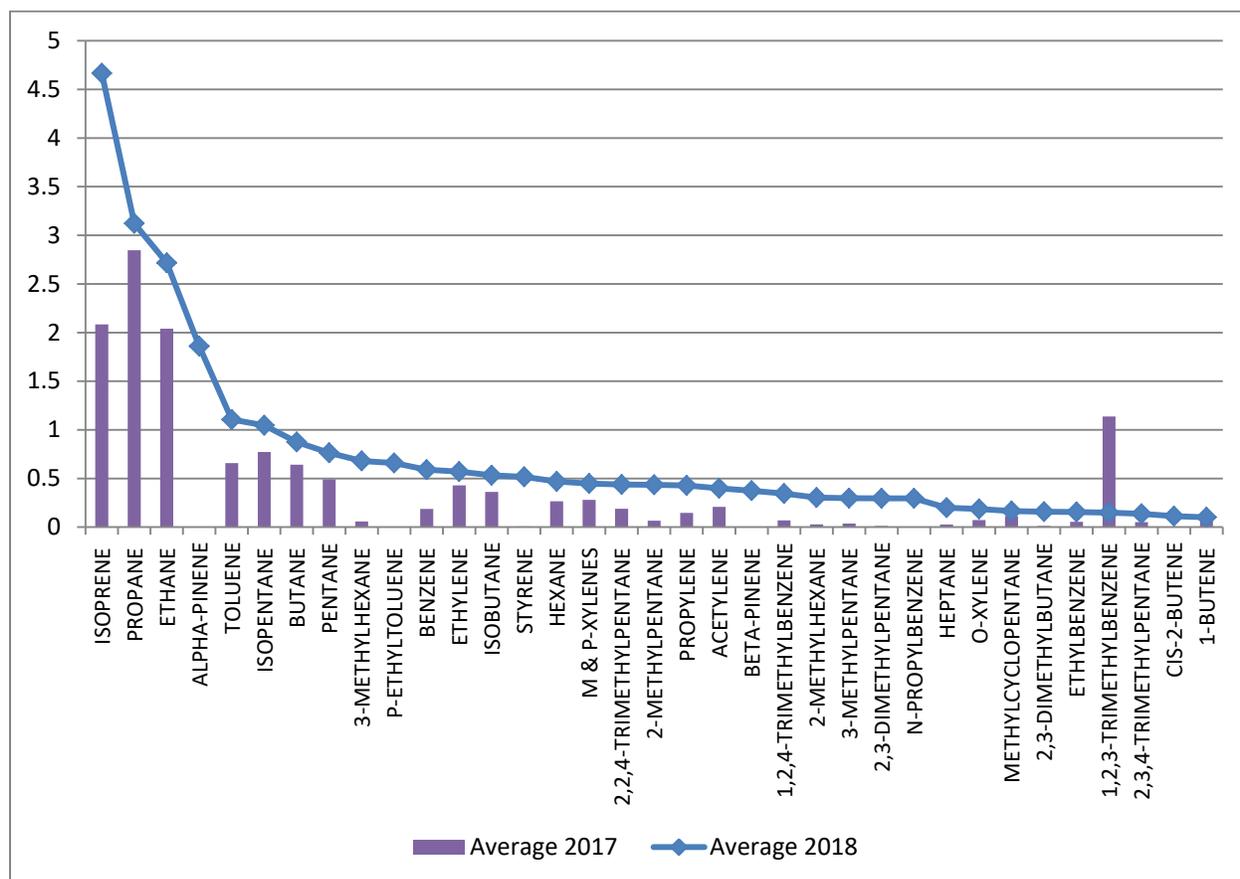
Figure 6-1: Seasonal Average PAMS Compound Trends New Hampshire PAMS Sites 2005-2018⁴



Concentrations of PAMS target compounds were variable at the Gilson Road site in the first ten years of monitoring. At the current PAMS sites, they have in general trended downward since 2015 until last year. At Miller State Park, a slight increase in PAMS compounds was seen in 2018. A dramatic increase is seen in the seasonal average at Moose Hill School – a 90% increase for both total nonmethane hydrocarbons (TNMHCs) and PAMS compounds. This is demonstrated by comparing the 2017 v. 2018 for the top 35 compounds at Moose Hill School (Figure 6-2). This increase is likely attributable to the change in equipment described in section 2, but potential other factors will be examined later in this report, along with trends in ozone and summer weather patterns. As shown in Figure 6-2, 1,2,3 trimethylbenzene is the only compound that measured higher in 2017 v. 2018.

⁴ 2008 Miller data are biased high due to the installation of new instrumentation and contamination of high molecular weight compounds; 2009 Gilson Road 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.

Figure 6-2: Comparison of 2017 v. 2018 for top 35 compounds at Moose Hill School



Tables 6-1 summarizes the 10 most abundant PAMS volatile organic compounds measure at each site. The lists of compounds are somewhat consistent at both sites – exceptions are highlighted in green. At Miller State Park, the most abundant compounds were similar to what was measured in 2017 with the exception of pentane, which replaced 1-butene in the top ten (Figure 6-3). Alpha-pinene was abundant at Moose Hill School in 2018 – this compound was not on the measured in 2017 because the existing equipment was not able to capture it. The profile of abundant compounds changed quite a bit here as a result of the new monitoring equipment, where 1,2,3 trimethylbenzene, m-ethyltoluene, and ethylene were replaced in the top ten by alpha-pinene, 3-methylhexane, and p-ethyltoluene (Figure 6-4).

Looking at the 10 most abundant compounds at Miller State Park over the last several years (Figure 6-3), the top five have been consistent, and the differences in the remainder have been minimal. The change is more dramatic at the Moose Hill School site for 2018, for the reasons previously noted (Figure 6-4).

Table 6-1: Top 10 Most Abundant Compounds New Hampshire PAMS Sites 2018*

Miller State Park	Seasonal Daily Average Concentration (ppbc)	Seasonal Daily Maximum Concentration (ppbc)
ETHANE (43202)	2.49	9.44
ISOPRENE (43243)	2.36	36.5
1,2,3-TRIMETHYLBENZENE (45225)	1.56	13.3
PROPANE (43204)	1.42	5.94
P-ETHYLTOLUENE (45213)	0.81	6.40
BUTANE (43212)	0.41	5.18
ISOPENTANE (43221)	0.39	3.63
PENTANE (43220)	0.27	2.46
ETHYLENE (43203)	0.23	1.21
TOLUENE (45202)	0.20	4.94
Moose Hill School	Seasonal Daily Average Concentration (ppbc)	Maximum Hourly Concentration (ppbc)
ISOPRENE (43243)	4.73	62.3
PROPANE (43204)	3.17	17.2
ETHANE (43202)	2.74	9.04
ALPHA PINENE (43256)	2.11	14.6
TOLUENE (45202)	1.11	5.59
ISOPENTANE (43221)	1.05	4.83
BUTANE (43212)	0.88	5.80
PENTANE (43220)	0.77	6.28
P-ETHYLTOLUENE (45213)	0.68	4.51
3-METHYLHEXANE (43249)^	0.68	2.22

* Green highlighted compounds unique to this site

^ Flagged for quality control purposes

Figure 6-3: Ten Most Abundant Species Yearly Averages for Miller State Park PAMS

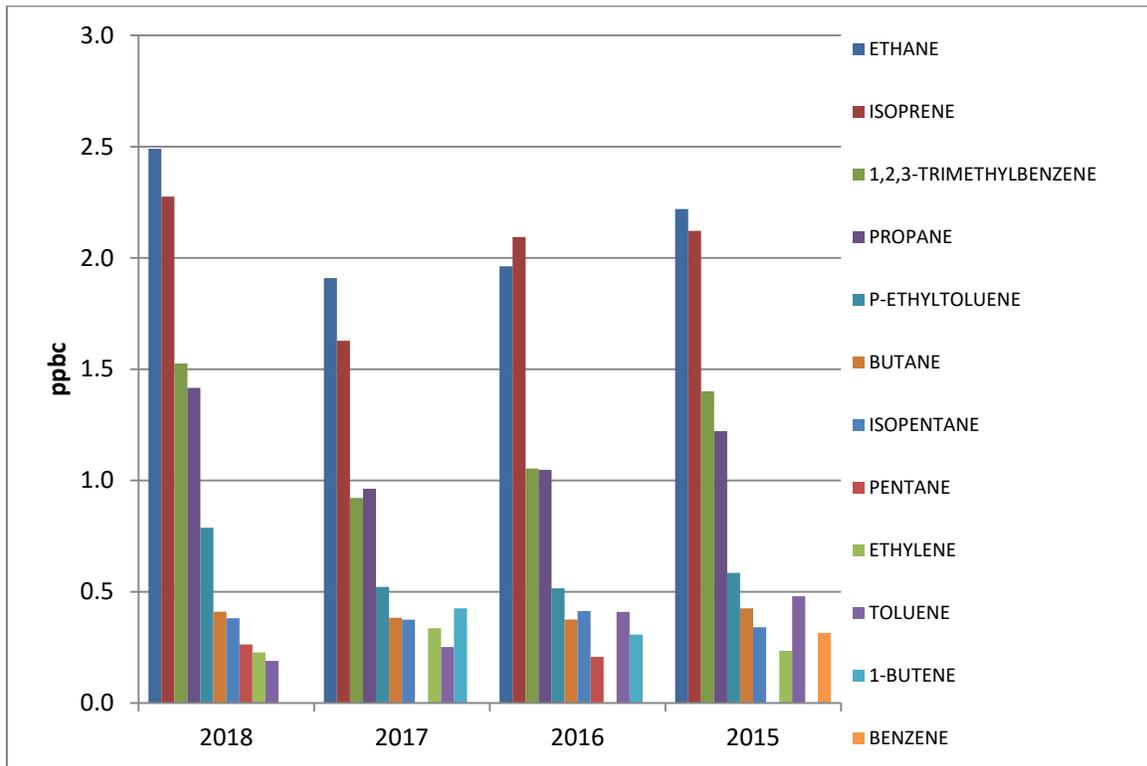
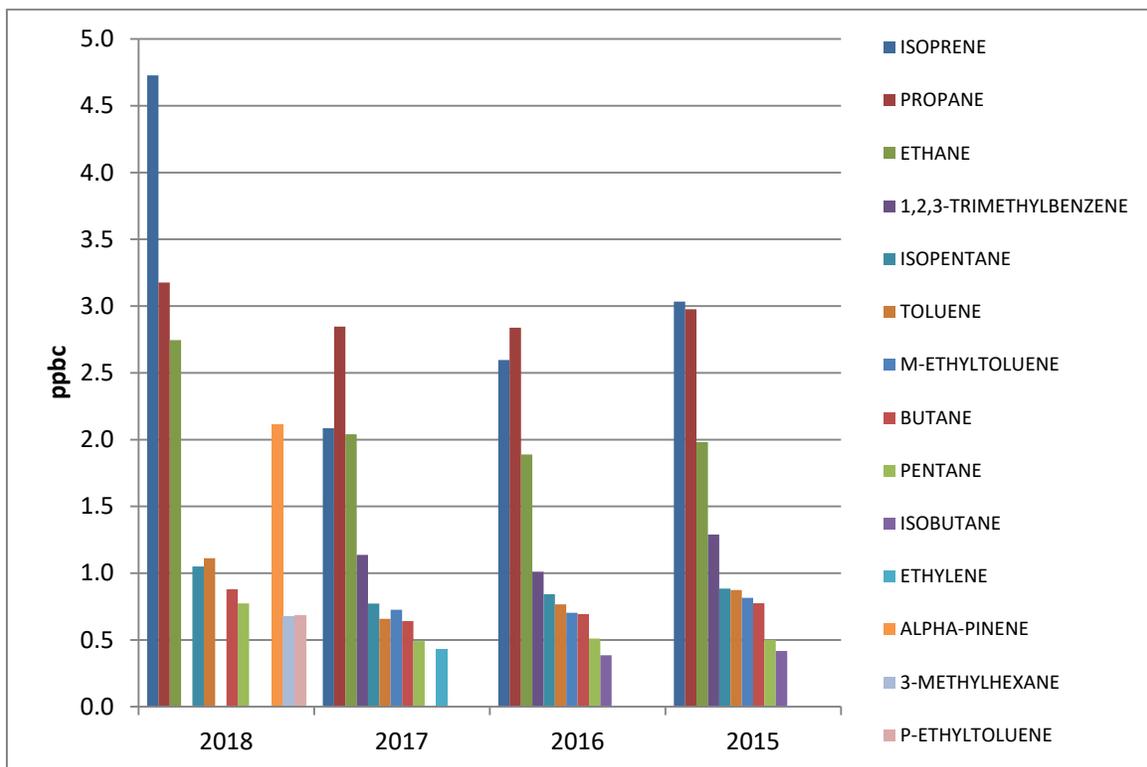
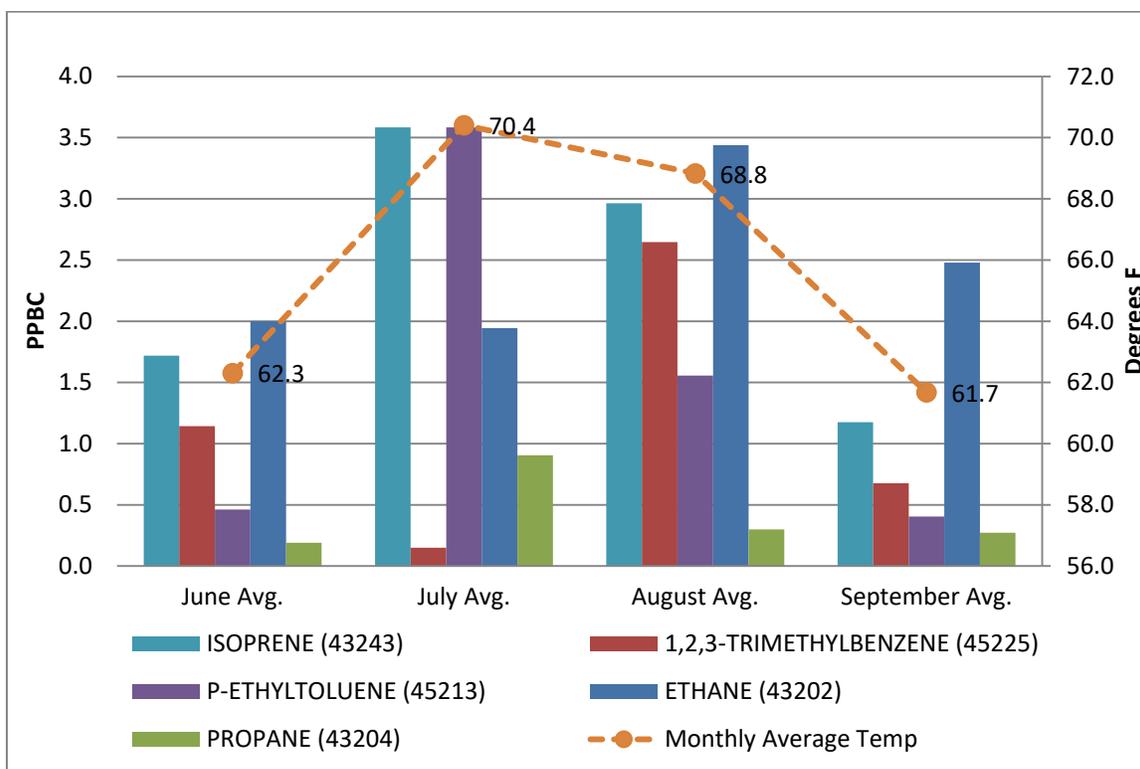


Figure 6-4: Ten Most Abundant Species Yearly Averages at Moose Hill School PAMS



The highest concentrations of the five most abundant species in 2018 at Miller State Park, shown in Figure 6-5, generally occur in July and August, coinciding with the highest average temperature.

Figure 6-5: Five Most Abundant Species Monthly Averages - Miller State Park 2018



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. Isoprene production is highest in the warmest months - product shows a strong positive correlation with light and temperature. As shown in Figures 6-5 and 6-6, isoprene production was highest during the warmest month at both sites. This compound measured higher at both sites in 2018 v. 2017, 38% higher at Miller State Park and 48% higher at Moose Hill School.

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 from conifers varies seasonally, with emissions increasing as length of daylight and temperature increase.

1,2,3-Trimethylbenzene ($C_6H_3(CH_3)_3$) is an aromatic hydrocarbon that occurs naturally in coal tar and petroleum. It is one of the three isomers of trimethylbenzene (1,2,4 and 1,3,5 trimethylbenzene are also PAMS compounds). It is used in fuel, mixed with other hydrocarbons, to prevent the formation of solid particles that might damage the engine. It may be released into the atmosphere by industry producing or using it. It might also be released during the storage of fuel and refueling of vehicles and it is present in diesel exhaust fumes. The compound measures much lower this year at Miller State Park compared to 2017.

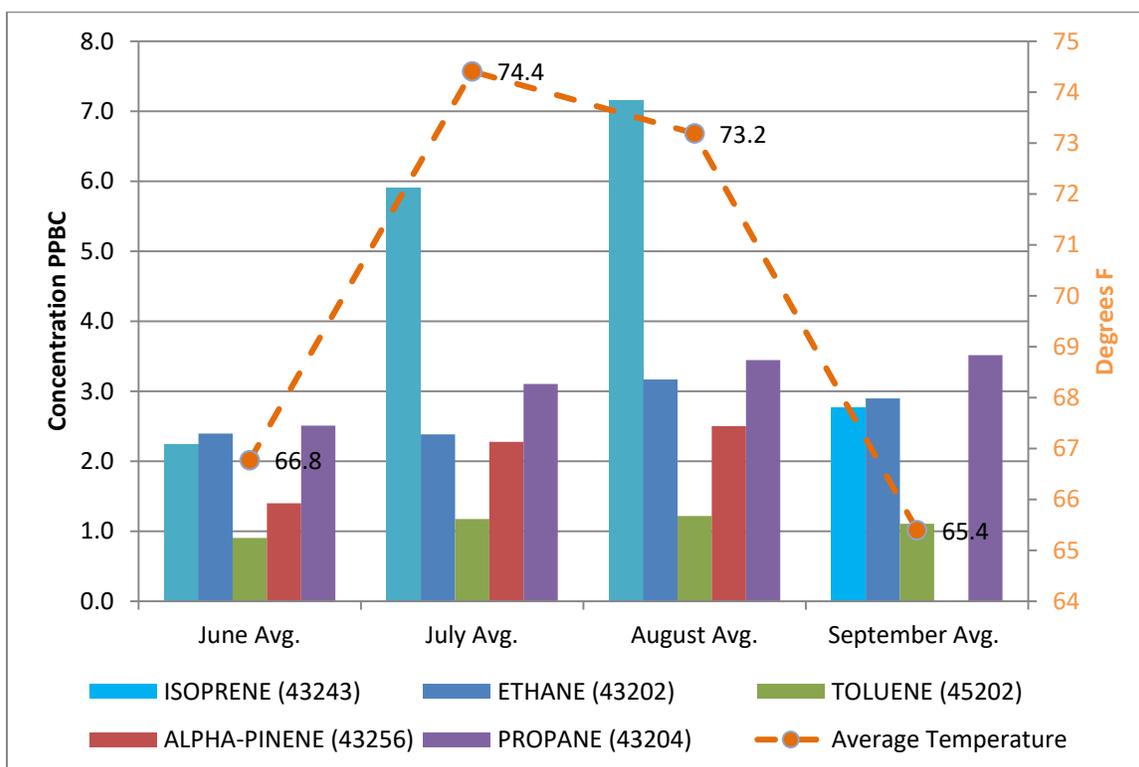
p-Ethyltoluene (C_9H_{12}) is added to fuels to increase performance. Some is also used in the manufacture of a variety of other chemicals, plastics and coatings, in printing materials and inks, in solvents and cleaning products and in pesticides. P-Ethyltoluene in the environment comes from petroleum refineries

and gas stations. It may also be released in vehicle exhaust fumes. Relatively very small amounts of the compounds 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 as well as local level. P-Ethyltoluene measured 38% higher in 2018 (as a monthly average) at Miller State Park compared to 2017.

Ethane (C₂H₆) 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 by-product 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 2 percent of the globe's ethane, or 250,000 tons per year.⁵ This compound measured higher at both sites this year compared to 2017 – 18% higher at Miller State Park and 29% higher at Moose Hill School.

Propane (C₃H₈) is a by-product of natural gas processing and petroleum refining and is commonly used as a fuel. Propane is one of a group of liquefied petroleum gases (LP gases) that also includes butane, propylene, butadiene, butylene, isobutylene, and mixtures thereof. Propane is emitted during combustion processes and has a tendency to accumulate in the atmosphere. Propane measured much lower this year at Miller State Park (-200%) and slightly higher at Moose Hill School (+9%).

Figure 6-6: Five Most Abundant Species Monthly Averages – Moose Hill School 2018



⁵ University of Michigan, "One oil field a key culprit in global ethane gas increase." Science Daily. Science Daily, 26 April 2016. <www.sciencedaily.com/releases/2016/04/160426144918.htm>.

Alpha-pinene, or α -pinene, ($C_{10}H_{16}$) was measured at the Moose Hill School site for the first time in 2018. This compound is found in the oils of many species of coniferous trees, notably pine. New Hampshire is 84% forested, of which 12%, or 566,000 acres are predominantly white and red 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 which partly condense on existing aerosols, thereby generating secondary organic aerosols. Oxidation of α -pinene is an important source of secondary organic aerosol (SOA) in the troposphere and plays a significant role in ozone (O_3) chemistry in rural areas.⁷ SOAP (secondary organic aerosol precursors) are discussed later in this section.

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 such as 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.

6.2 Diurnal and Weekly Variation

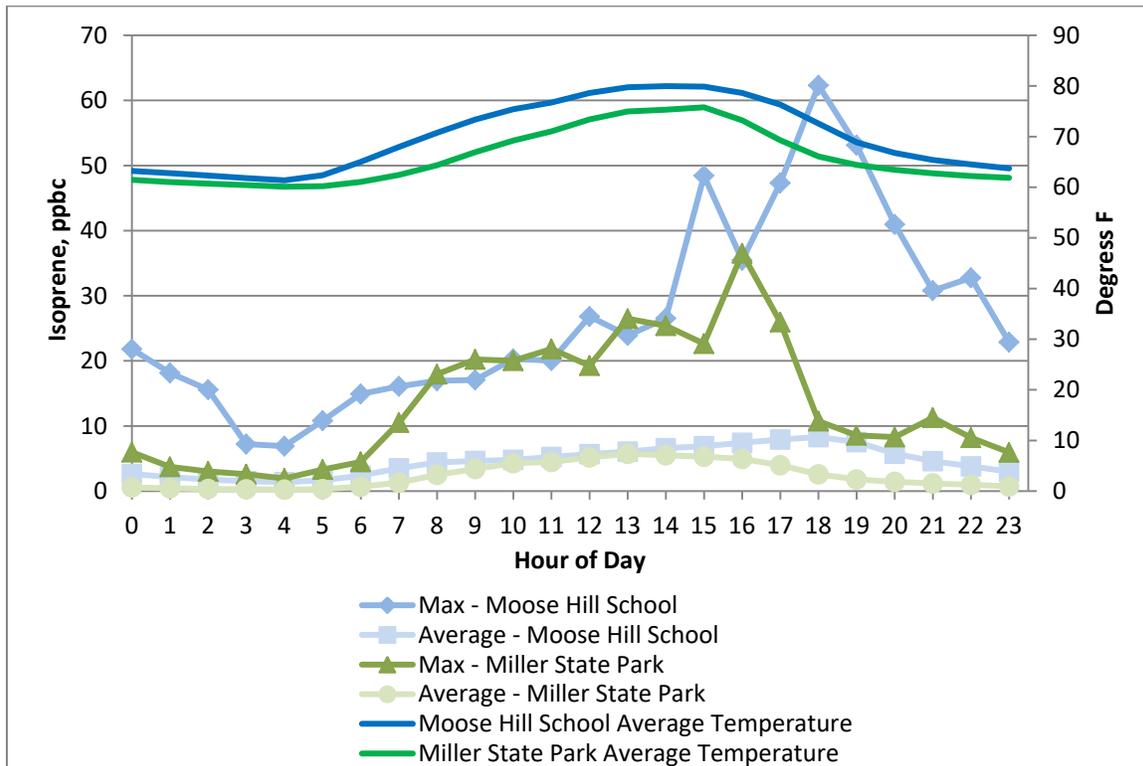
The next series of graphs compare the top 10 compounds at each site with their diurnal patterns and hourly maximum concentrations. These figures compare the high elevation site (Miller State Park) compared to the low elevation site (Moose Hill School) where applicable. In general, the average value (average for the hour for the entire monitoring season) exhibits a weaker diurnal pattern the maximum (maximum value for that hour for the entire monitoring season).

Isoprene is the most abundant species at Moose Hill School and the second most abundant at Miller State Park. The species shows a distinct diurnal pattern (Figure 6-7), with the highest maximum concentration peaking at the former site on August 5 at 6 PM (62.3 parts per billion carbon [ppbc]), and at July 1 at 4 PM (36.5 ppbc) at the latter site. The average concentration is similarly delayed. The peaks do not correspond with highest daily temperatures as expected.

⁶ North East State Foresters Association, "The Economic Importance of New Hampshire's Forest-Based Economy 2013,"

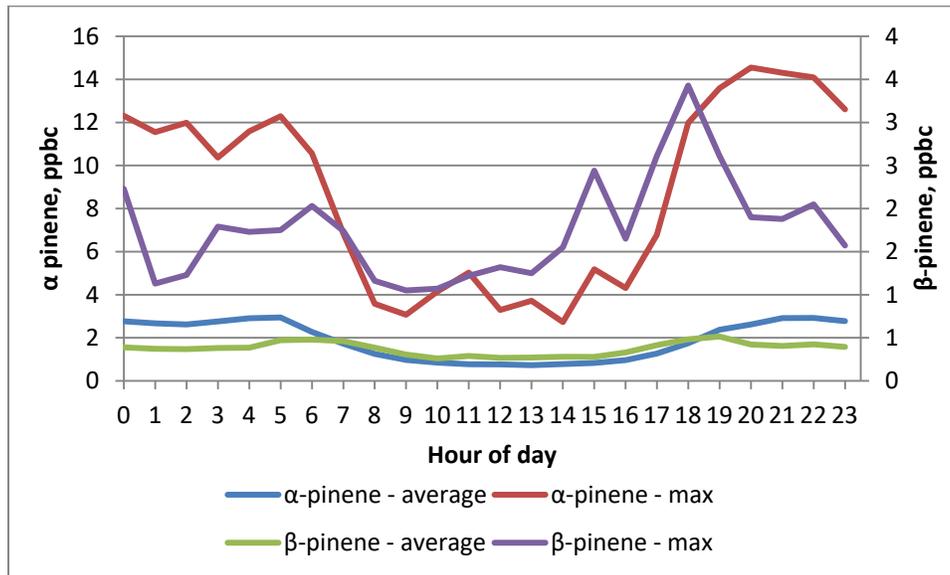
⁷ Pathak, R. K., C. O. Stanier, N. M. Donahue, and S. N. Pandis (2007), Ozonolysis of α -pinene at atmospherically relevant concentrations: Temperature dependence of aerosol mass fractions (yields), *J. Geophys. Res.*, 112, D03201, doi:10.1029/2006JD007436.

Figure 6-7: 2018 Average Diurnal Pattern and Max for Isoprene at both New Hampshire PAMS sites



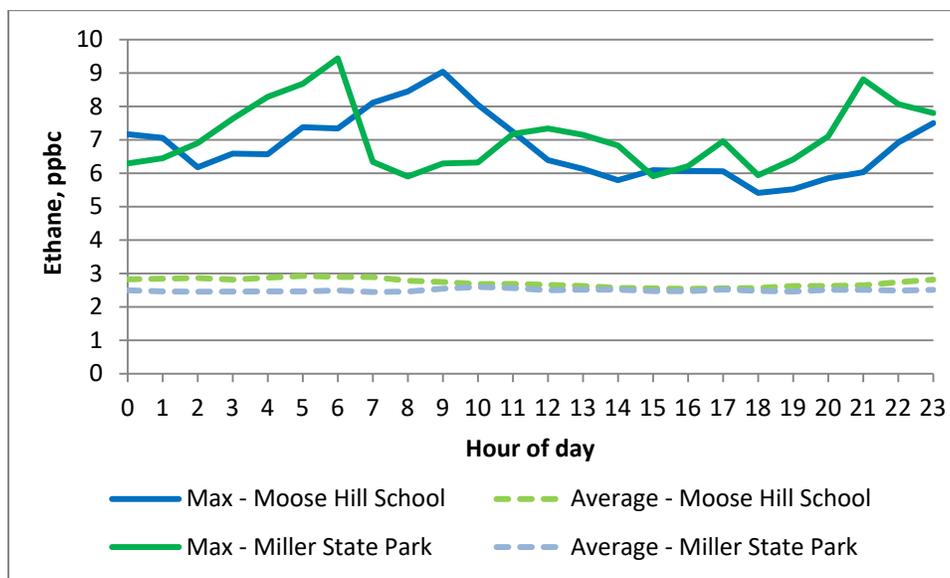
Because new equipment was installed there, alpha (α) and beta (β) pinene were measured for the first time at Moose Hill School in 2018. α -pinene and β -pinene are organic compounds of the terpene class. Like isoprene, they are a biogenic volatile organic compound emitted from plants. As the name suggests, 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 (mainly α -pinene) are emitted in the evening hours and their concentration decreases during the day as they react photochemically.

Figure 6-8: Average and Maximum Diurnal Variation for α - and β -pinene at Moose Hill School



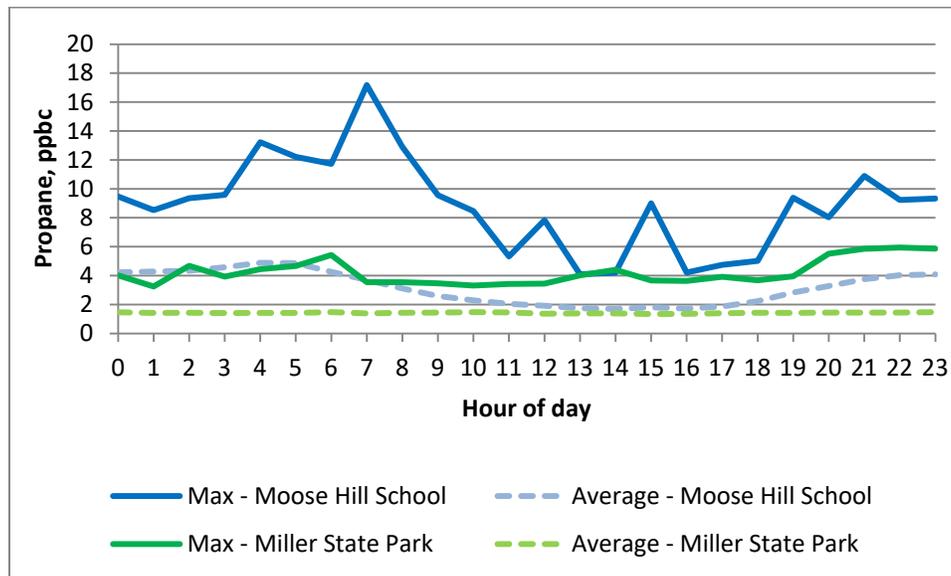
Ethane is the most abundant compound measured at Miller State Park and the third most abundant at Moose Hill School. Average ethane emissions at both sites were consistent in 2018. Interestingly, peaks representing maximum values in the morning occurred on August 28 at both sites – between 7-10 AM at Moose Hill School and 4-6 AM at Miller State Park. Meteorological data indicates that winds were blowing steadily from west to east during that time, in other words, from Miller State Park to Moose Hill School.

Figure 6-9: 2018 Diurnal Pattern for Average and Maximum Hourly Values for Ethane at New Hampshire PAMS sites



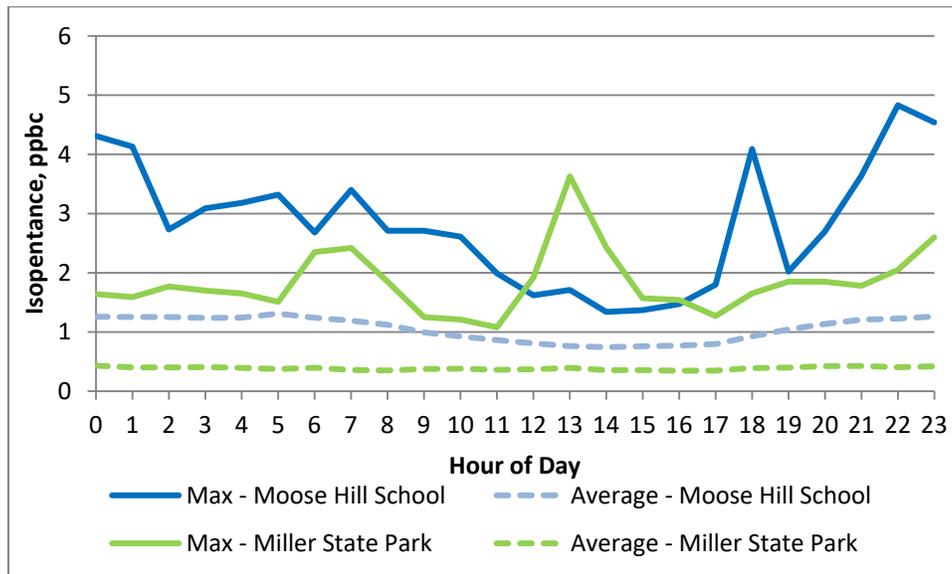
Propane is very persistent in the air in New Hampshire and most emissions come from natural gas leakage and combustion of liquid propane (LP) gas. Propane has a tendency to accumulate in the atmosphere, which seems to occur overnight at lower elevation at Moose Hill and be more evenly distributed throughout the day at higher elevation at Miller. This tendency and may even be seen at higher concentrations during the colder months when PAMS is not running. Propane concentrations are stable at Miller and show a variable, diurnal pattern at Moose Hill School, which is situated in a more urban locale.

Figure 6-10: 2018 Diurnal Pattern for Average and Maximum Hourly Values for Propane at New Hampshire PAMS sites



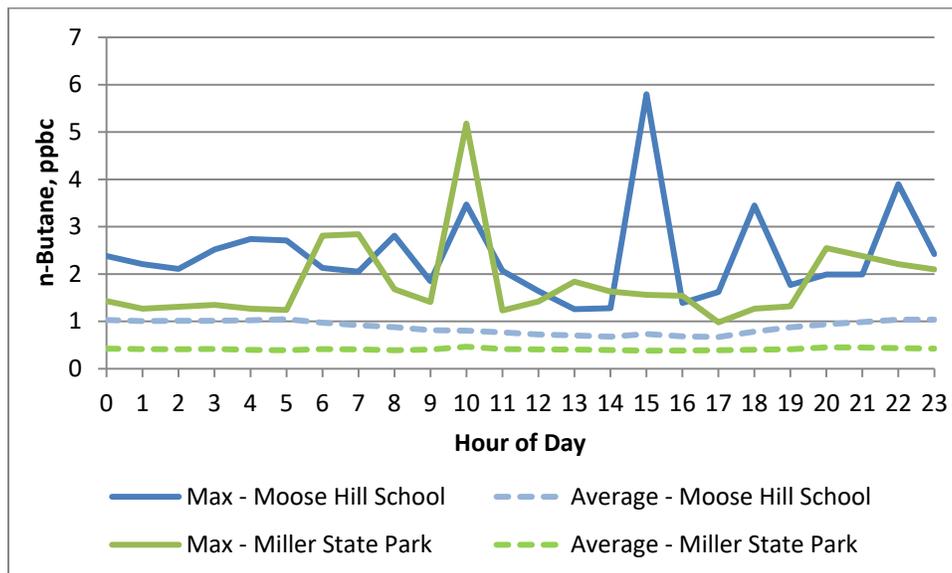
Isopentane is a paraffin and can be a more stable indicator of long-range transport. Miller State Park is showing a more dramatic diurnal pattern than it has in prior years, with a slight increase in the early morning, then peaking around midday. Isopentane at Moose Hill School shows a somewhat reverse pattern from what is seen at Miller, with the nadir occurring midday.

Figure 6-11: 2018 Diurnal Pattern for Average and Maximum Hourly Isopentane Values at New Hampshire PAMS sites



Maximum n-butane concentrations had various peaks throughout the day at both sites but were not necessarily indicative of a daytime pattern, although the concentrations are consistently low in the early morning hours. Average concentrations show no distinct pattern.

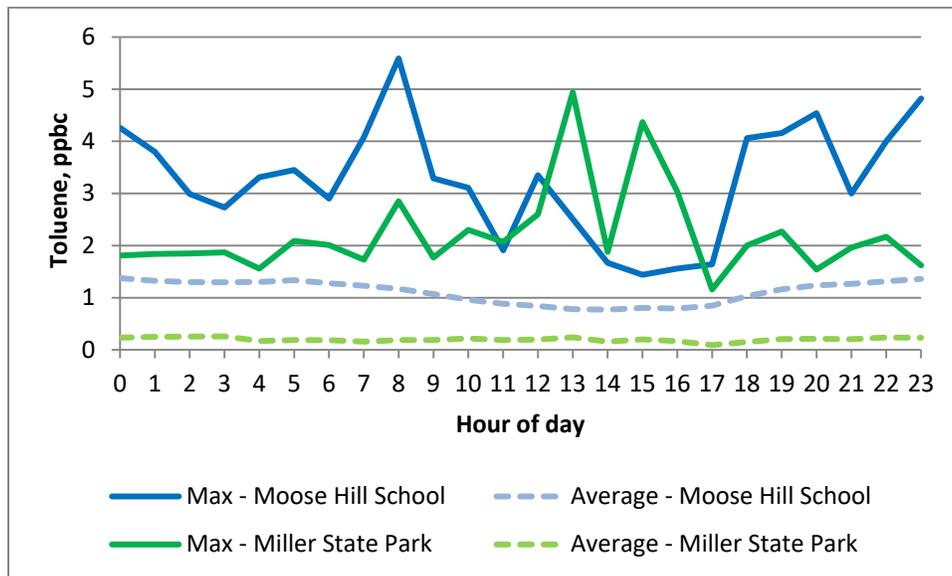
Figure 6-12: 2018 Diurnal Pattern for Average and Maximum Hourly Values for n-Butane at New Hampshire PAMS sites



Toluene is a major indicator of motor vehicle exhaust and is usually from a local influence. There is only slight average variations at Miller while Moose Hill School shows patterns associated with traffic increases building in the early morning and then again in the afternoon and evening. Maximum values occur midday at Miller State Park – this may coincide with park traffic. There is an auto road to the top

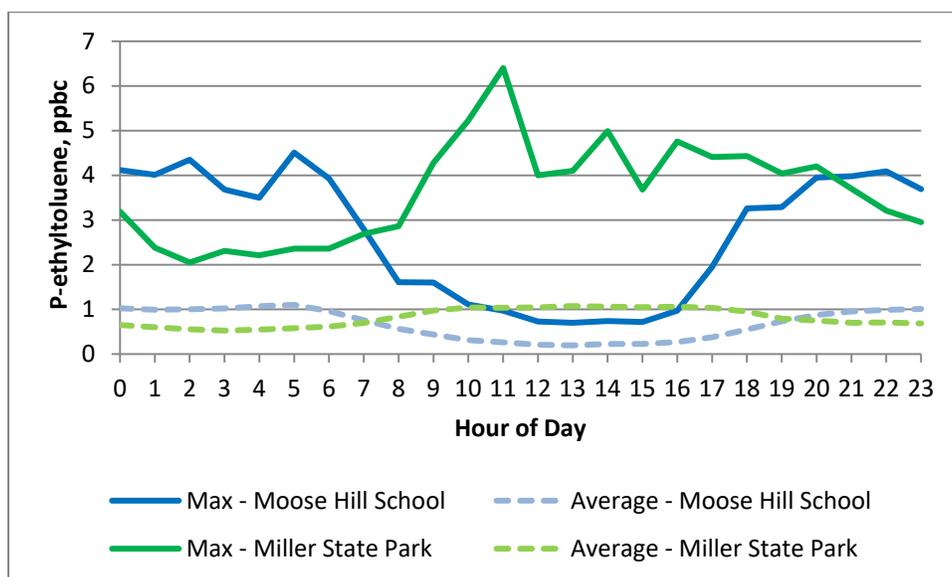
of Pack Monadnock Mountain where the park is located. The New Hampshire Division of Parks and Recreation reports that 35,657 vehicles paid for access to the park in 2018.

Figure 6-13: 2018 Diurnal Pattern for Average and Maximum Hourly Values for Toluene at New Hampshire PAMS sites



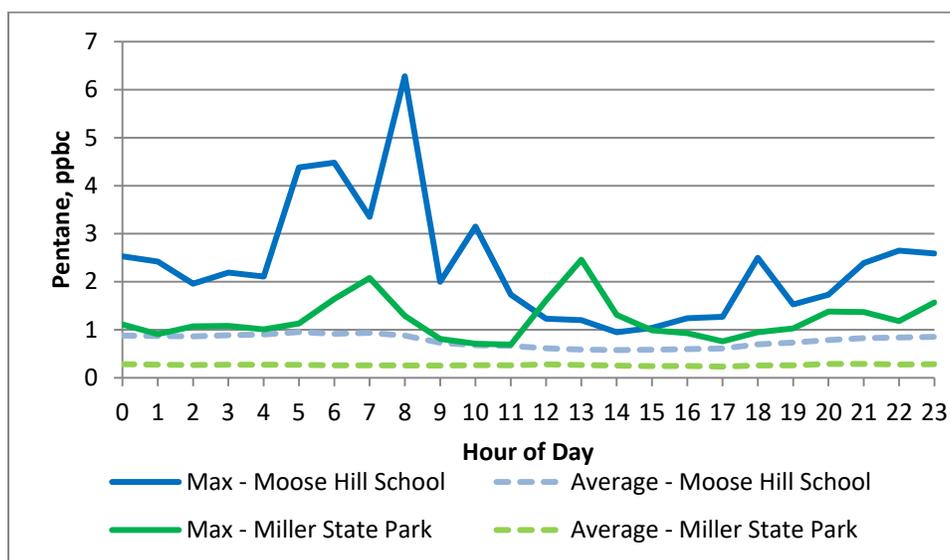
p-Ethyltoluene is a heavy hydrocarbon associated with gas and diesel tailpipe emissions. The diurnal patterns are opposite each other at the two PAMS sites. p-Ethyltoluene maximums peak in the morning and evening at Moose Hill School and midday at Miller State Park— perhaps in response to increased vehicular traffic.

Figure 6-14: 2018 Diurnal Pattern for Average and Maximum Hourly Values for P-Ethyltoluene at New Hampshire PAMS sites



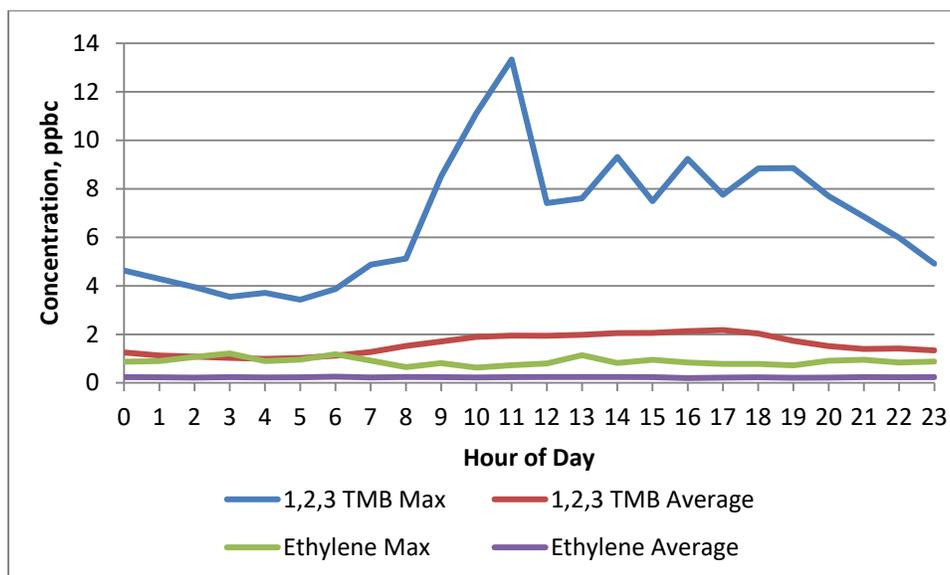
Pentane (C₅H₁₂) is an ingredient of fuel for vehicles. It is also used in the chemical industry as a solvent and in the production of other chemicals. Pentane is used to fill plastic foams, replacing the use of hydrofluorocarbons (HFCs) and hydrochlorofluorocarbons (HCFCs) as they are phased out because of their damaging effects on the ozone layer. In the environment, pentane may come from releases from industry manufacturing or using it during the disposal of products containing it. Pentane is found naturally in natural gas. Like other species described above, pentane maximums coincide with likely increases in vehicular activity.

Figure 6-15: 2018 Diurnal Pattern for Average and Maximum Hourly Values for Pentane at New Hampshire PAMS Sites



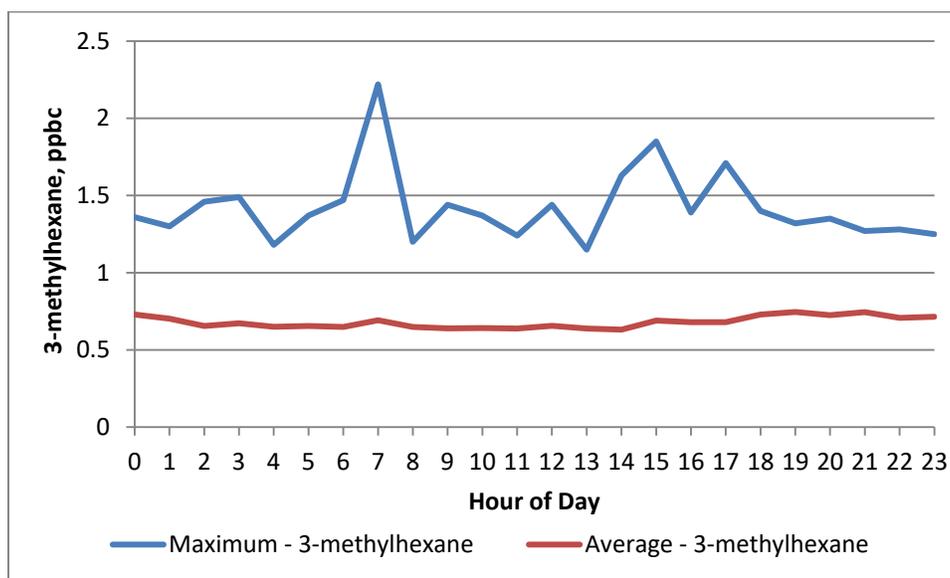
1,2,3-Trimethylbenzene (1,2,3 TMB) and ethylene are two PAMS compounds that were in the top 10 in abundance at Miller State Park but not at Moose Hill School. 1,2,3 TMB is an aromatic hydrocarbon occurring naturally in coal tar and petroleum; it is also used in jet fuel and gasoline as well as an industrial solvent. 1,2,3-TMB has an hourly maximum and diurnal preference from about 9 AM to 8 PM. The maximum values at Miller show this trend as well, but on a smaller scale. Natural sources of ethylene include both natural gas and petroleum and it is released in vehicle exhaust fumes and from waste incineration plants. The majority of ethylene in ambient air comes from mobile sources.

Figure 6-16: 2018 Diurnal Pattern for Average and Maximum Hourly Values for 1,2,3-Trimethylbenzene and Ethylene at Miller State Park



3-methylhexane⁸(C₇H₁₆) was detected as a top 10 most abundant compound (albeit in small quantities) at Moose Hill School in for the first time in 2018. 3-methylhexane is an isomer of heptane that is found in gasoline and is widely used a solvent. Heptanes are also sold as fuel for outdoor stoves. This compound shows a slight diurnal pattern, probably related to vehicle activity.

Figure 6-17: Diurnal Pattern for Average and Maximum Hourly Values for 3-methylhexane⁴ at Moose Hill School



⁸ 3-methylhexane was found in the blanks throughout the season which could explain its increase in 2018. This compound was flagged in the AIRS data.

The data was then examined to determine if there was any variation between weekday and weekend emissions. First, categories of VOCs were analyzed to look for patterns. Total Nonmethane hydrocarbon and PAMS VOCs appear more prevalent on weekends when looking at maximum values at Moose Hill School, which is the opposite of what is occurring at Miller State Park. At both areas, the olefins hydrocarbons are more prominent on weekends. This group includes isoprene and α -pinene, which are examined in more detail below and in section 6.4.5. The next most abundant group is the alkanes, which includes ethane, propane, butane, pentane and Isopentane. This is followed by the aromatics group comprised here of benzene, toluene, and 1,2,3 trimethylbenzene. The latter two groups are higher on weekdays.

When looking at average values, there is little difference between weekdays and weekends at Moose Hill School and only a slight increase in average values on weekdays at Miller State Park. Concentrations overall measure almost 2 times higher at Moose Hill School compared to Miller State Park.

Figure 6-18: Average Weekday v. Average Weekend VOC Trends at Moose Hill School

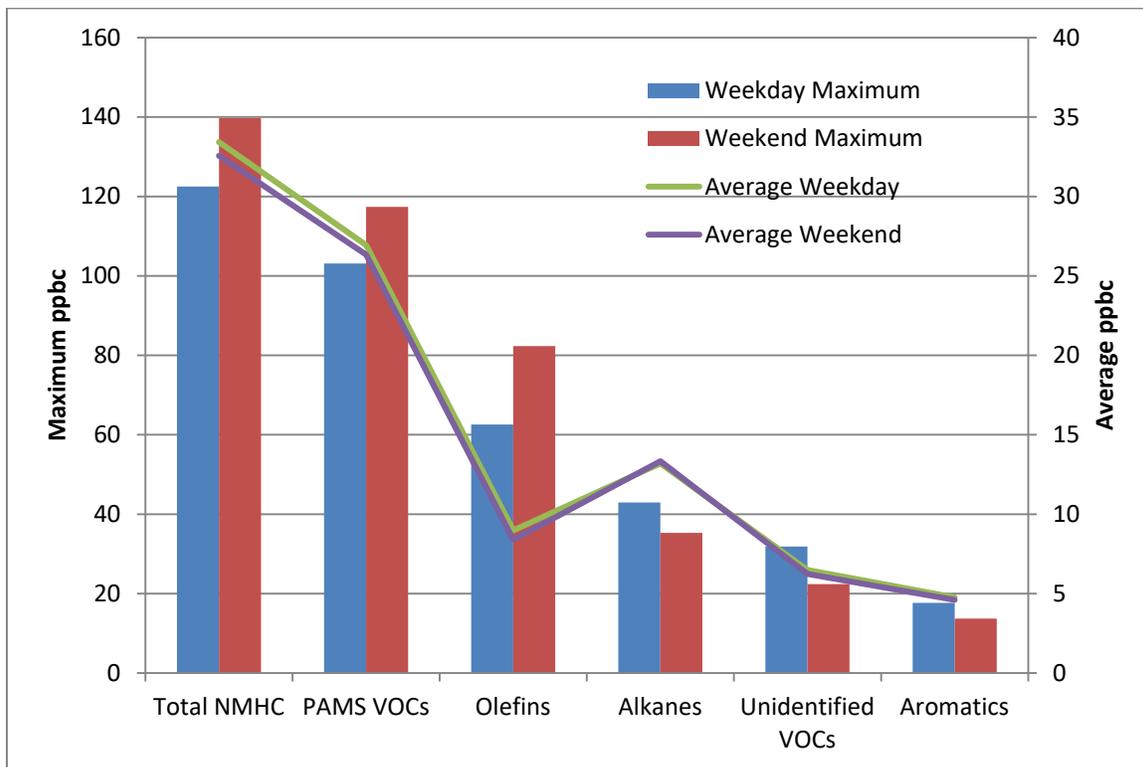
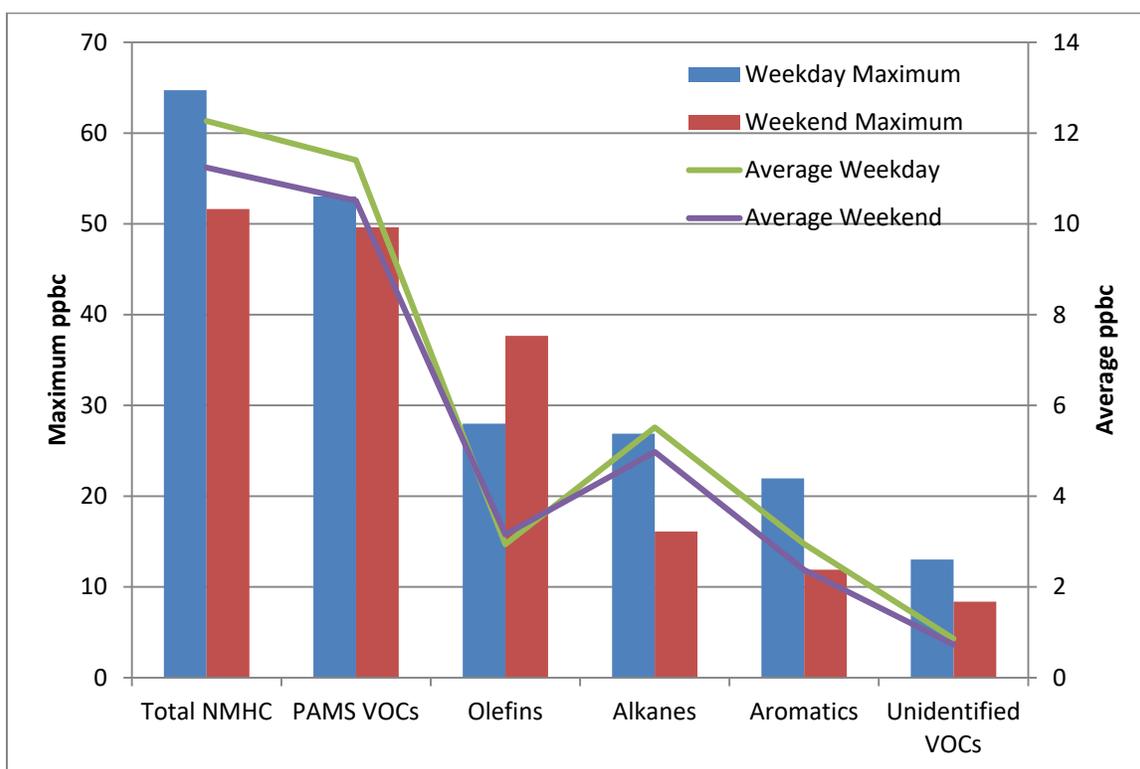


Figure 6-19: Weekday v. Weekends VOC Trends at Miller State Park



6.3 Compound Groups

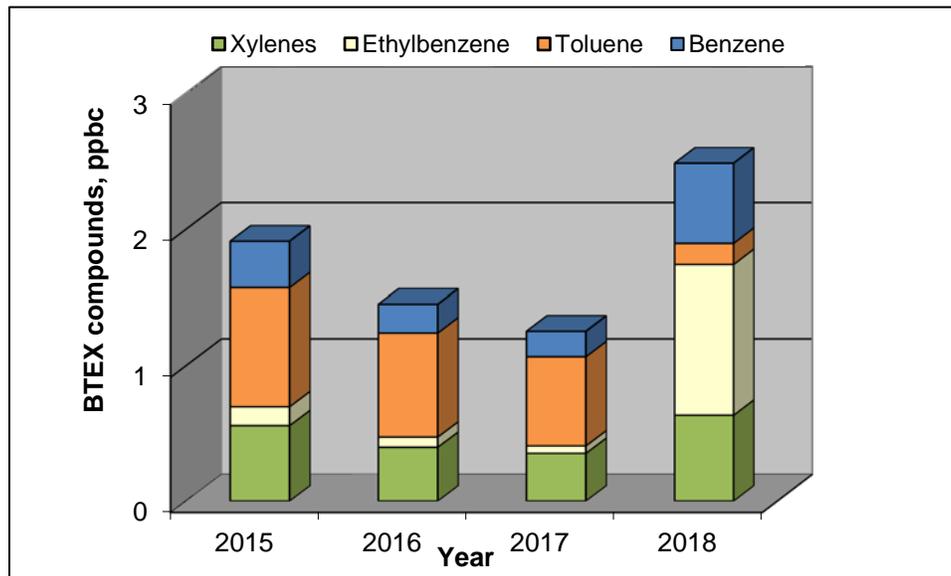
Trending of select compound groups is another useful way to analyze PAMS data. The concept is to group compounds associated with certain types of emission sources to determine how those emissions trend over time and how they appear to affect ozone forming potential.

6.3.1 Gasoline related compounds

One such grouping includes benzene, toluene, ethylbenzene and xylene (BTEX) - organic compounds that are emitted from petroleum derivatives such as gasoline.

As expected, the Moose Hill School location sees higher values for the BTEX compounds due in part to its location in a more urban area. Though still rural, its proximity to heavily traveled roadways, an airport and an industrial park have an influence on compound concentrations. As previously mentioned, new equipment installed at this site in 2018 has resulted in higher measurements of most VOCs. One difference from prior years is the predominance of ethylbenzene among the four BTEX compounds where toluene was more dominant in prior years. This may be a result of the increased sensitivity of the new equipment there. Aromatics measured about 46% higher in 2018 compared to 2017.

Figure 6-20: Yearly Averages of BTEX Compounds Moose Hill School PAMS

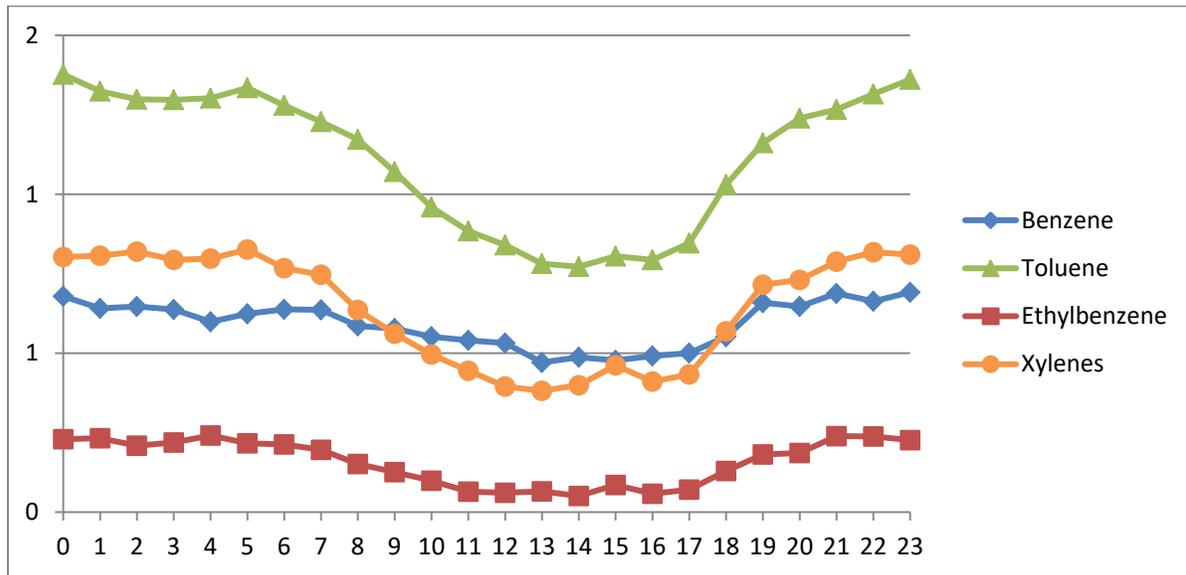


The diurnal pattern of BTEX emissions at Moose Hill School display a typical pattern for reactive, anthropogenic VOCs with emissions generally dominated by automotive-related sources. This pattern is interpreted as follows:

- The morning maximum is associated with high emissions and limited vertical mixing in the lower atmosphere.
- The mid-day minimum is associated with decreased mobile source emissions, increased vertical mixing resulting in a rapid growth of the daytime boundary layer, 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 mixing.⁹

⁹ USEPA, PAMS Data Analysis Results Report, EPA-454/R-96-006, November 1996

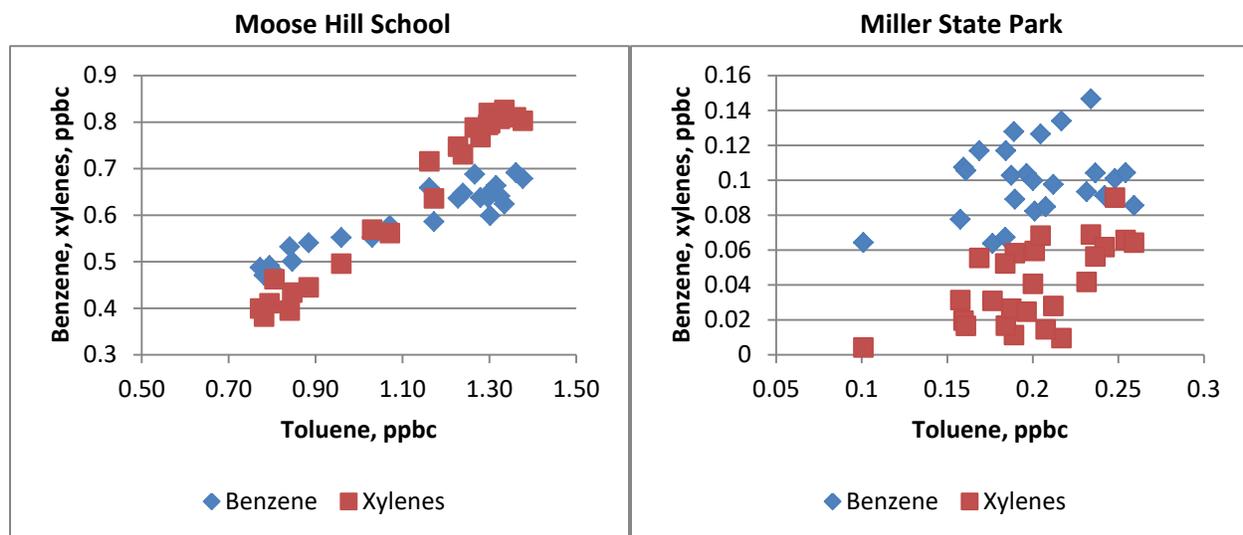
Figure 6-21: Diurnal Hourly Averages for BTEX Compounds at Moose Hill School



Concentration (ppbc) is along Y-axis and Hour of day is indicated along X-axis.

The scatter plot below (Figure 6-22), representing average hourly emissions for the season shows that toluene levels at Moose Hill School were highly correlated with both benzene and xylenes, which is consistent with fresh emissions. The same data plotted for Miller State Park (Figure 6-22) shows less correlation, with a decrease in the xylene/toluene ratio and an increase in the benzene/toluene ratio, indicative of a more aged air mass.

Figure 6-22: Benzene/toluene and xylene/toluene ratios



The Miller State Park site is much more remote and at a higher elevation. As a result, this site measures lower BTEX concentrations than Moose Hill School. Despite year-to-year variability, figure 6-23 shows

BTEX compound concentrations have clearly trended downward since 2006 at this site. The diurnal pattern for these compounds here show a similar pattern to Moose Hill School, though more variable.

Figure 6-23: Yearly Averages of BTEX Compounds Miller State Park

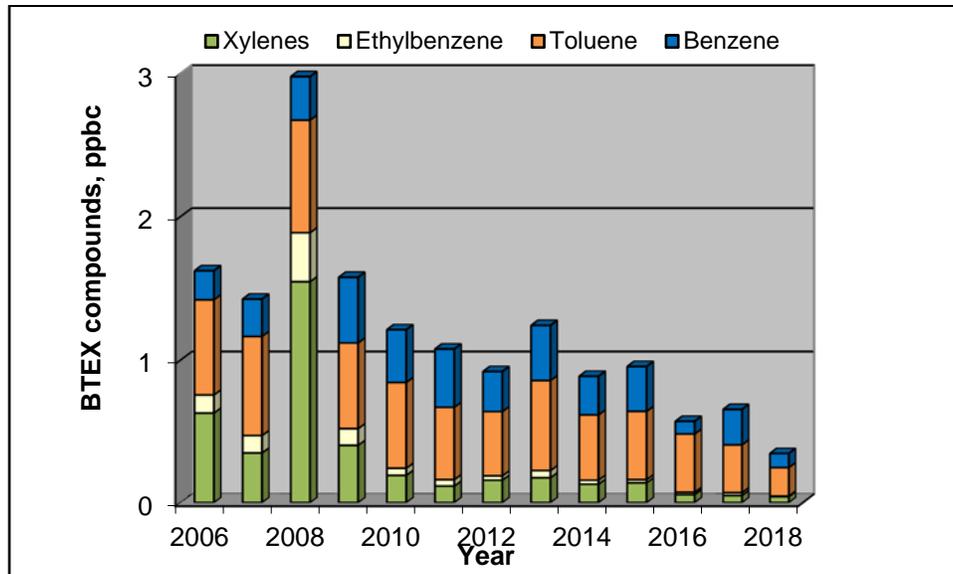
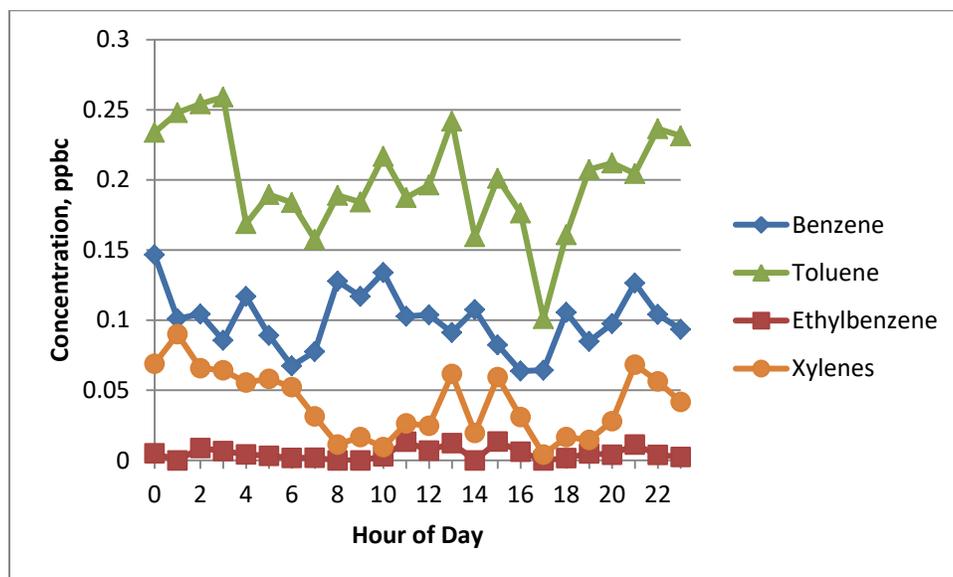


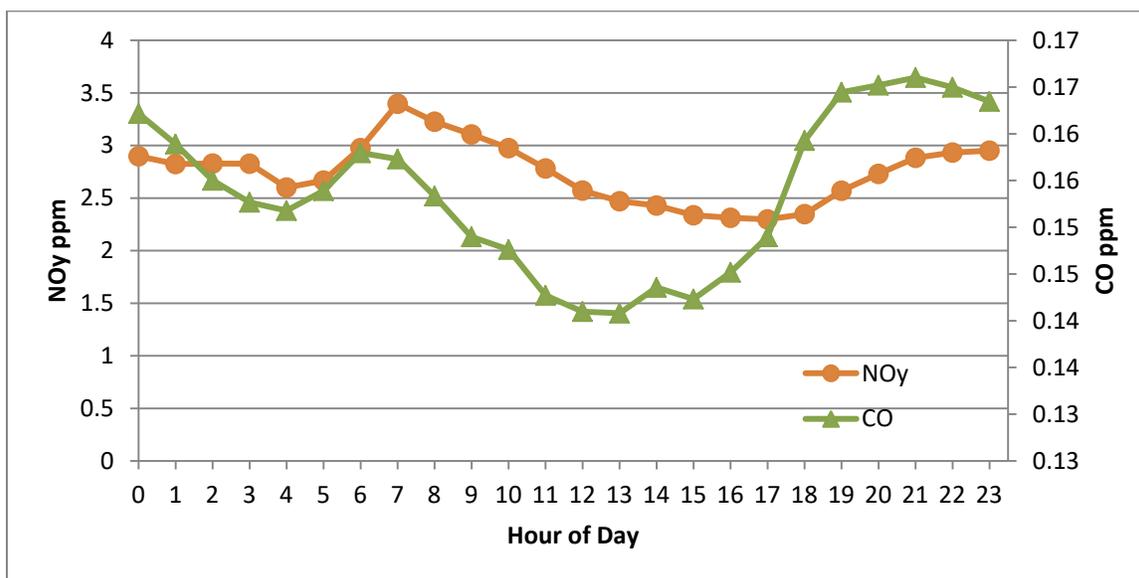
Figure 6-24: Diurnal Hourly Averages for BTEX Compounds at Miller State Park in 2018



6.3.2 Motor Vehicle Tracers

The following figure (6-25) outlines NO_y and CO values at the Londonderry site during the 2018 PAMS season. These compounds are good motor vehicle tracers as seen in Figures 6-25 below where higher concentrations are seen during commuting time. NO_x is oxidized in the hours and days after emission to various organic and inorganic nitrates. NO_y comprise these product species plus unreacted NO_x.

Figure 6-25: Diurnal CO and NO_y Values at Moose Hill School



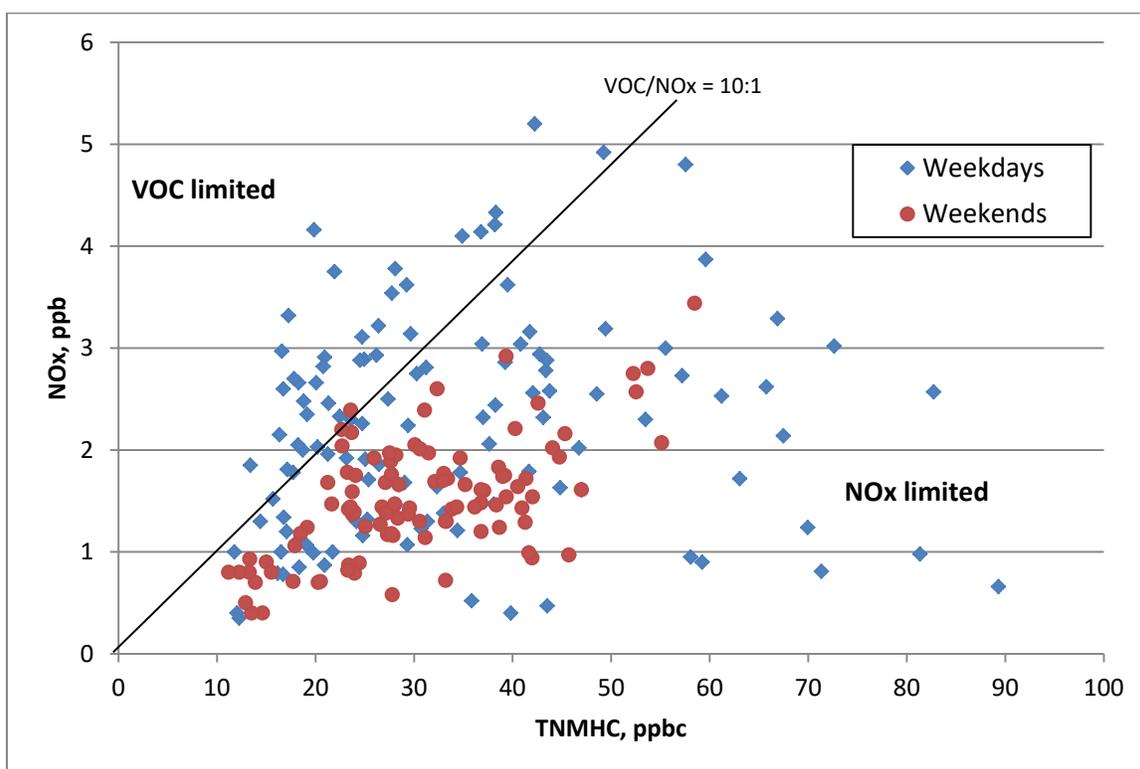
The ratio of total nonmethane hydrocarbons (TNMHC) to oxides of nitrogen (NO_x) is used to understand the relative importance of TNMOC and NO_x precursors to ozone formation. In general, when TNMOC/NO_x is low (well below 10), the atmosphere is considered to be "VOC-limited", which infers that a VOC-based emission control strategy is necessary for ozone reductions. Conversely, when ratios are well above 10, the atmosphere is "NO_x-limited," and NO_x emission controls will be more effective than VOC emission controls in reducing ozone. However, in the actual atmosphere, wide variations in the measured TNMOC/NO_x ratio occur, making interpretation less straightforward. Nevertheless, ratios based on the concentrations of VOC to NO_x are useful for delineating control requirements.

The 6:00 - 9:00 AM TNMOC/NO_x ratios tend to emphasize the importance of motor vehicle exhaust, since this source peaks during the 6:00 - 9:00 AM time period. Other VOC sources such as biogenic hydrocarbons, non-road mobile sources, and evaporative sources of all types, peak at midday or in the afternoon.

Figure 6-26 shows the VOC/NO_x for the hours of 6-9 AM at the Moose Hill site for both weekdays and weekends. The chart shows weekday emissions fairly well distributed, implying that ozone is neither VOC- nor NO_x- limited. This is an indication that fresh emissions likely dominate the local concentrations throughout the day.

Weekend emissions show a clear NO_x limited condition. Stagnation or changes in wind direction have the potential to cause significant buildup of emissions, or transport of aged emissions, at that site. NO_x data is not collected at Miller State Park – therefore, no similar chart is provided for that site.

Figure 6-26: VOC/NOx Ratio for PAMS Season at Moose Hill School, 6:00 – 9:00 AM.

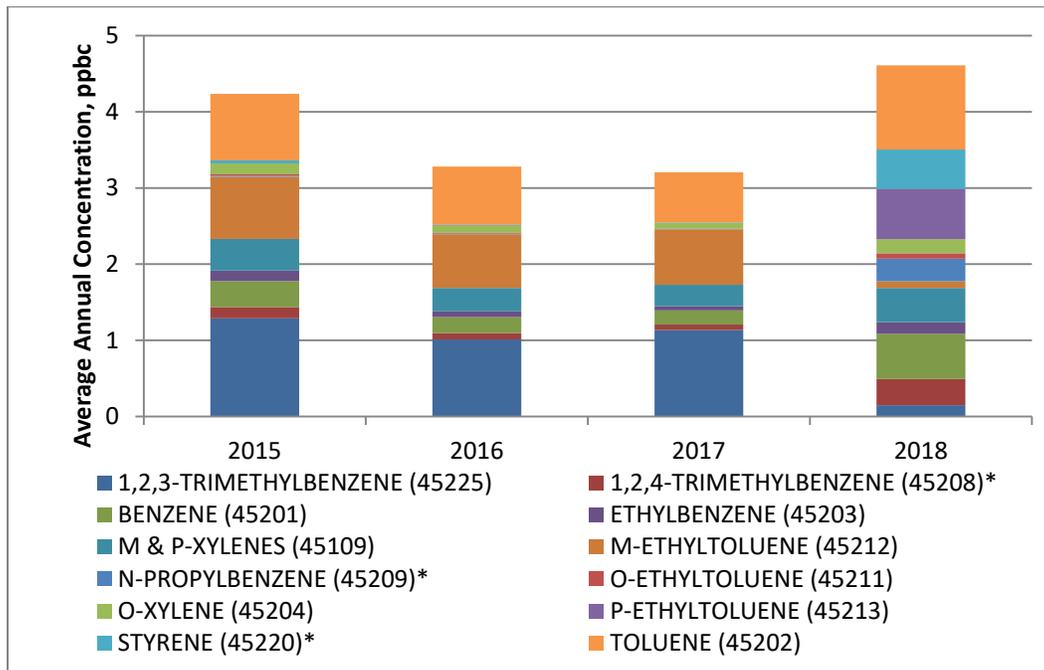


6.3.3 Secondary Organic Aerosol Precursors (SOAP)

Secondary organic aerosol (SOA) is formed from the atmospheric oxidation of gas-phase organic compounds leading to the formation of particulate matter. SOAs are a major component of fine particle pollution (PM_{2.5}), which has been found to cause lung and heart problems and other health effects. Fine particles are also the main 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 precursors. A number of PAMS compounds fall into this precursor category and are examined for their overall trend at the New Hampshire PAMS sites.

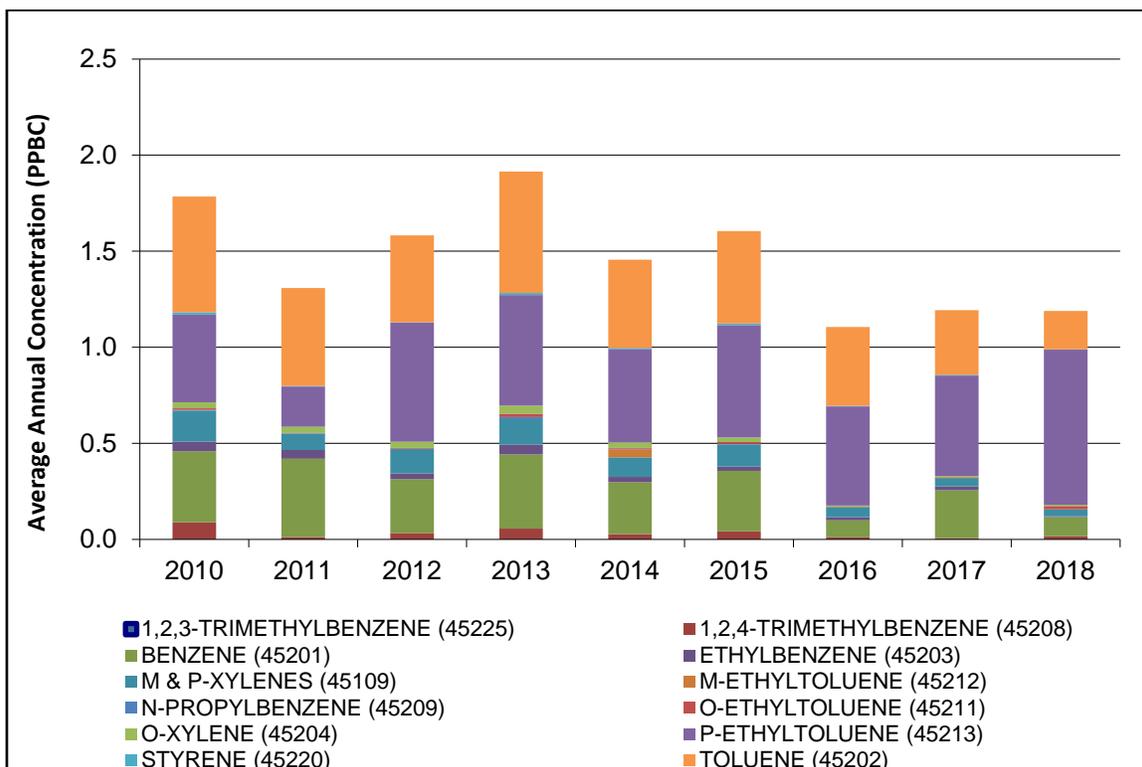
At Moose Hill School (Figure 6-27), average concentration of these precursors combined increased by 44% combined to the prior year, likely a result of the equipment change. Although SOAP compounds at this site are increased significantly, 1,2,3 trimethylbenzene and m-ethyltoluene which measured 80% less than the prior year, 2017. Trends at Miller State Park have been consistent since 2010, although in 2018, 1,2,3 trimethylbenzene is more prevalent, compared to toluene in prior years.

Figure 6-27: Trends of Secondary Organic Aerosol Precursors (SOAP) Compounds, Moose Hill School 2015-2018



* Some of the data for these compounds was flagged in 2018 for quality control purposes.

Figure 6-28: Trends of Secondary Organic Aerosol Precursors (SOAP) Compounds, Miller State Park 2010-2018



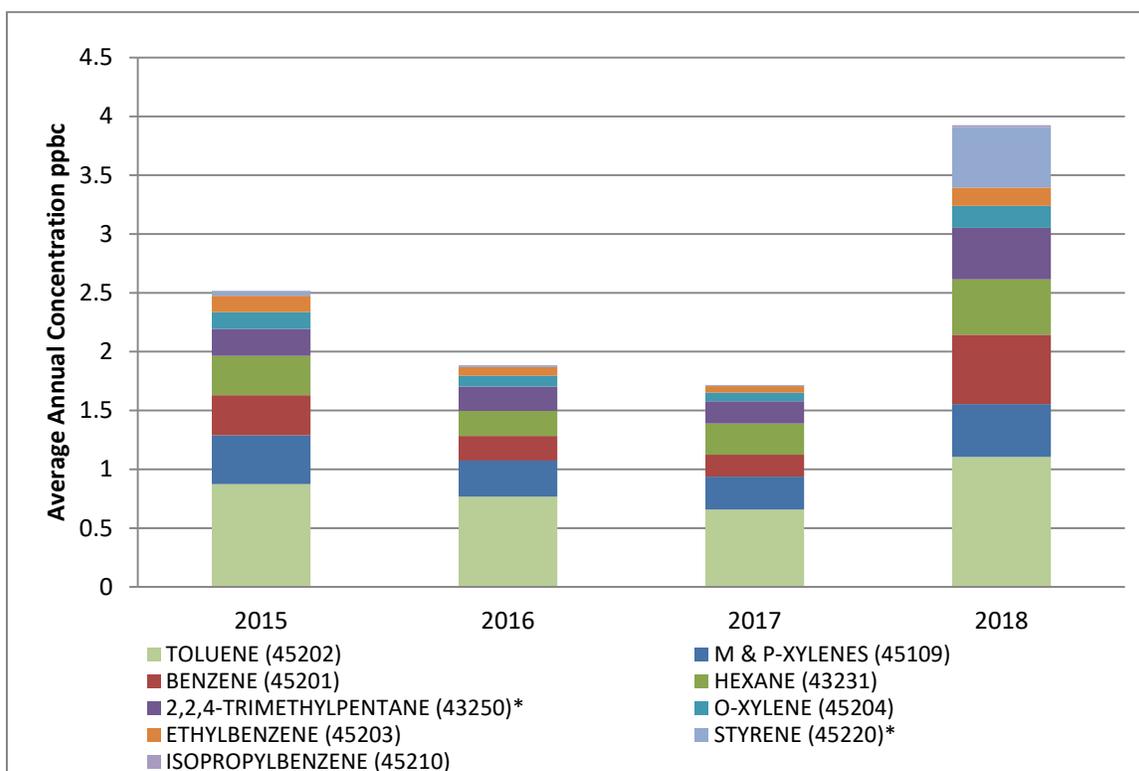
6.4 Other Species

6.4.1 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](#)¹⁰ in this group including substances that are known or suspected to cause cancer or other serious health effects, such as reproductive effects or 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 concentrations in ambient air in New Hampshire. HAP concentrations at Moose Hill School increased dramatically in 2018 (Figure 6-29), for styrene¹¹ in particular, though these increases are thought to be a function of the sensitivity 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.

HAP trends at Miller State Park have remained fairly steady and trending downwards since 2009 (Figure 6-30).

Figure 6-29: Trends of HAP Compounds Moose Hill School 2015-2018

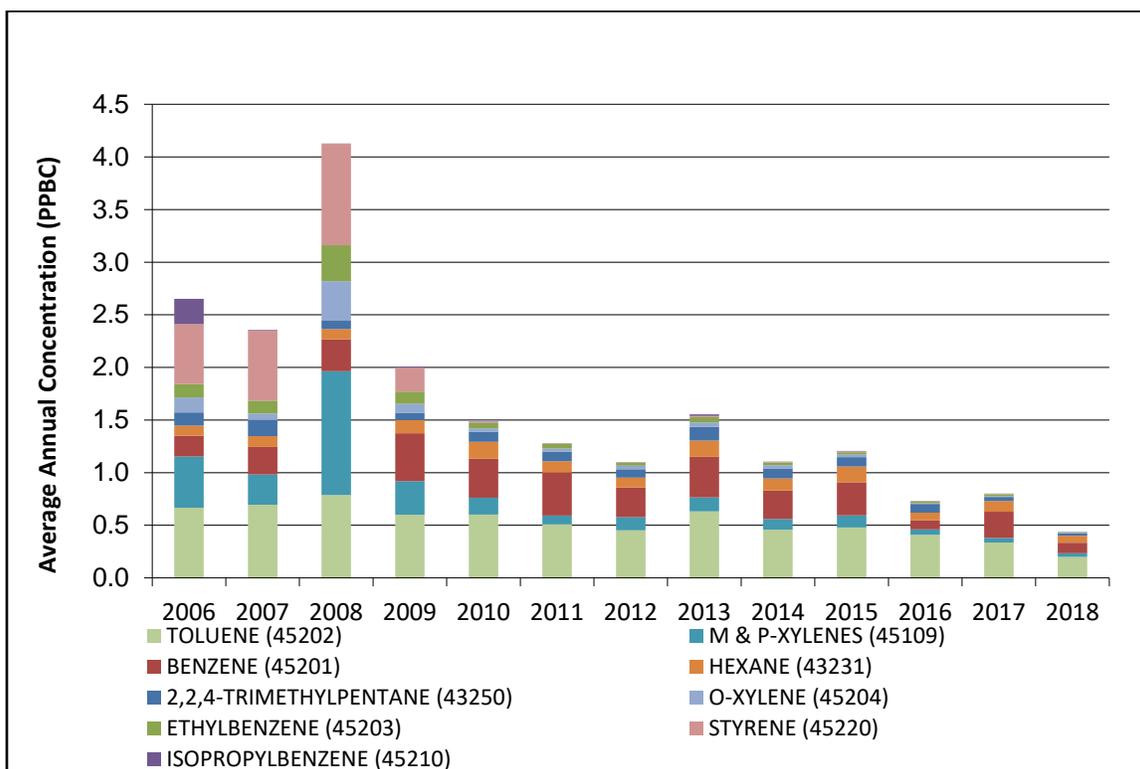


* July data for 2,2,4 trimethylpentane was flagged in 2018 for quality control purposes. Styrene was flagged in June, July and August.

¹⁰ [Hazardous Air Pollutants | US EPA](#)

¹¹ Styrene was found in the blanks, therefore skewed the results high for this compound. It was flagged in the reported AIRS data for this reason.

Figure 6-30: Trends of HAP Compounds Miller State Park 2006-2018



6.4.2 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 (TLV) has been established by the American Conference of Governmental Industrial Hygienists (ACGIH); and (3) those compounds not otherwise included that are regulated by the Occupational Safety and Health Administration (OSHA). 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 6-2 and 6-3 summarize the Ambient Allowable Limits (AAL's) for the relevant PAMS compounds at each site. Measured benzene concentrations at Moose Hill School and Miller State Park are 21% and 19%, respectively, of the AAL. Benzene concentrations measured at these sites was discussed in section 6.3.1. All other PAMS compounds with an assigned AAL have consistently measured less than 1% of their AAL.

Table 6-2: Seasonal 24-hour Values at Moose Hill School for Toxic Species vs. AAL

PAMS Parameter	AAL µg/m ³	Max 24 Hr. Avg. (µg/m ³)				Max as % of AAL	2018 Change
		2015	2016	2017	2018		
PROPYLENE (43205)	35,833	0.37	0.21	0.28	0.85	0.002%	↑
CYCLOPENTANE (43242)	25,595	0.11	0.15	0.07	0.24	0.001%	↑
ISOPENTANE (43221)	36,875	1.17	1.73	1.27	1.90	0.005%	↑
PENTANE (43220)	36,875	0.59	0.73	0.73	1.44	0.004%	↑
2-METHYLPENTANE (43285)	36,875	0.16	0.25	0.13	0.76	0.002%	↑
3-METHYLPENTANE (43230)	36,875	0.16	0.29	0.11	0.60	0.002%	↑
HEXANE (43231)	885	0.44	0.64	0.5	0.97	0.110%	↑
BENZENE (45201)	6	0.53	0.27	0.33	1.28	21.333%	↑
CYCLOHEXANE (43248)	6,000	0.12	0.18	0.1	0.45	0.008%	↑
HEPTANE (43232)	8,249	0.18	0.44	0.11	0.52	0.006%	↑
METHYLCYCLOHEXANE (43261)	23,958	0.12	0.24	0.07	0.37	0.002%	↑
TOLUENE (45202)	5,000	1.11	1.65	1.17	2.06	0.041%	↑
OCTANE (43233)	7,000	0.11	0.15	0.04	0.27	0.004%	↑
ETHYLBENZENE (45203)	1,000	0.18	0.22	0.16	0.45	0.045%	↑
M & P-XYLENES (45109)	1,550	0.51	0.61	0.53	0.94	0.061%	↑
STYRENE (45220)	1,000	0.17	0.07	0.07	*1.01	0.101%	↑
O-XYLENE (45204)	1,550	0.2	0.21	0.21	0.49	0.032%	↑
NONANE (43235)	15,625	0.13	0.11	0.12	0.25	0.002%	↑
1,3,5-TRIMETHYLBENZENE (45207)	619	0.1	0.12	0.07	0.13	0.021%	↑
1,2,4-TRIMETHYLBENZENE (45208)	619	0.21	0.27	0.19	*0.65	0.105%	↑

* Some data flagged for quality control purposes.

All data in micrograms per cubic meter (µg/m³).

Table 6-3: Seasonal 24-hour Values at Miller State Park for Toxic Species vs. AAL

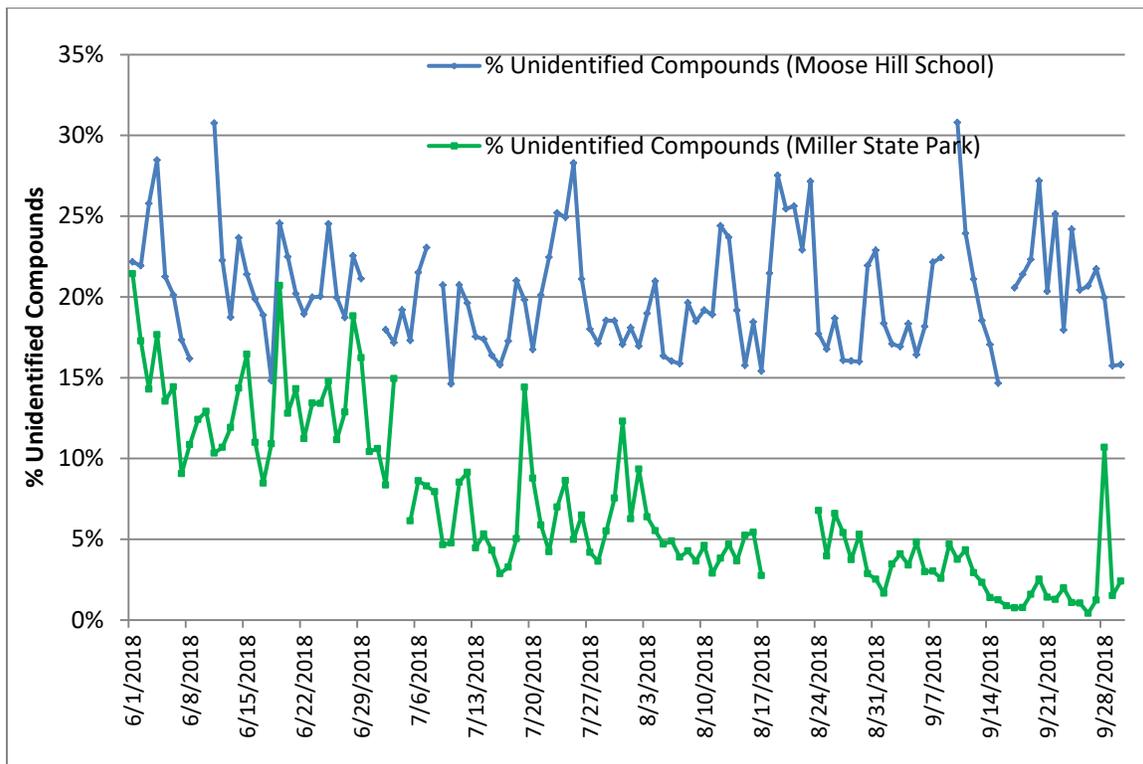
PAMS Parameter	AAL µg/m ³	Max 24 Hour Avg. (µg/m ³)													Max as % of AAL	2018 Change
		2006	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017	2018		
PROPYLENE (43205)	35,833	0.28	0.25	0.46	0.15	0.20	0.59	0.38	0.17	0.16	0.28	0.29	0.23	0.61	0.002%	↑
CYCLOPENTANE (43242)	25,595	0.42	0.53	1.63	0.29	0.09	0.17	0.21	0.13	0.13	0.23	0.11	0.11	0.09	0.000%	↓
ISOPENTANE (43221)	36,875	1.03	1.09	0.70	0.89	0.75	1.84	2.32	0.95	0.73	0.96	0.68	1.34	0.74	0.002%	↓
PENTANE (43220)	36,875	45.41	7.63	0.55	0.45	0.38	0.86	0.76	0.48	0.40	0.51	0.38	0.69	0.55	0.001%	↓
2-METHYLPENTANE (43285)	36,875	0.19	0.27	0.04	0.06	0.04	0.30	0.25	0.06	0.07	0.12	0.07	0.09	0.07	0.000%	↓
3-METHYLPENTANE (43230)	36,875	0.13	0.17	0.01	0.04	0.03	0.21	0.19	0.03	0.02	0.05	0.03	0.02	0.02	0.000%	-
HEXANE (43231)	885	0.21	0.27	0.19	0.32	1.36	1.01	0.48	0.28	0.24	0.40	0.16	0.18	0.29	0.033%	↑
BENZENE (45201)	6	0.31	0.33	0.32	0.41	0.73	1.09	0.45	0.38	0.41	0.64	0.18	0.45	0.32	5.333%	↓
CYCLOHEXANE (43248)	6,000	0.14	0.05	0.02	0.08	0.04	0.48	0.15	0.06	0.04	0.09	0.01	0.06	0.03	0.001%	↓
HEPTANE (43232)	8,249	0.71	0.16	0.15	0.17	0.13	0.79	0.21	0.14	0.11	0.14	0.04	0.04	0.03	0.000%	↓
METHYLCYCLOHEXANE (43261)	23,958	1.23	0.15	0.15	0.11	0.16	0.49	0.14	0.07	0.06	0.10	0.04	0.03	0.02	0.000%	↓
TOLUENE (45202)	5,000	1.00	1.05	1.11	1.01	0.77	2.48	1.36	0.80	0.56	0.67	0.53	0.54	0.54	0.011%	-
OCTANE (43233)	7,000	0.91	0.17	0.27	0.11	0.06	0.40	0.23	0.07	0.04	0.02	0.02	0.02	0.01	0.000%	↓
ETHYLBENZENE (45203)	1,000	0.35	0.20	0.59	0.21	0.15	0.42	0.18	0.13	0.07	0.08	0.05	0.09	0.04	0.004%	↓
M & P-XYLENES (45109)	1,550	1.88	0.37	2.38	0.46	0.23	1.22	0.42	0.42	0.19	0.25	0.13	0.12	0.20	0.013%	↑
STYRENE (45220)	1,000	1.03	1.13	1.80	0.40	0.08	0.18	0.14	0.05	0.18	0.04	0.03	0.02	0.02	0.002%	-
O-XYLENE (45204)	1,550	0.60	0.13	0.67	0.15	0.08	0.45	0.20	0.16	0.08	0.06	0.04	0.04	0.06	0.004%	↑
NONANE (43235)	15,625	8.83	1.33	0.57	0.23	0.08	0.16	0.20	0.36	0.05	0.09	0.06	0.03	0.03	0.000%	-
1,3,5-TRIMETHYLBENZENE (45207)	619	1.75	0.08	0.29	0.13	0.04	0.10	0.12	0.08	0.01	0.09	0.01	0.02	0.04	0.006%	↑
1,2,4-TRIMETHYLBENZENE (45208)	619	3.91	1.34	0.79	0.53	0.14	0.38	0.26	0.08	0.09	0.15	0.04	0.04	0.06	0.010%	↑

All data in micrograms per cubic meter (µg/m³).

Unidentified Compounds

In addition to individual PAMS compounds, unidentified VOCs can be estimated by taking the difference between total PAMS and TNMOC concentrations. Unidentified compounds were higher at the lower elevation site, Moose Hill School, compared to the higher elevation site (20% v. 7%, respectively), calculated using the seasonal hourly average. At its relative urban location, Moose Hill School is exposed to a wider range of organic carbon compounds. The number of unidentified compounds decreased as the season progressed at Miller. In past years, the number of unidentified compounds remained consistent throughout, with the exception of 2015 and 2017 when the opposite was true- unidentified were more numerous at the end of the season. The site log indicates that the cold trap at Miller was changed on June 19. The cold trap in the beginning of the season may have been failing leading to leaching of compounds and contributing to the higher unknowns in the beginning of the season. In addition, the weather pattern changed in August and September and became much wetter. Although this did not seem to affect the compounds at Moose Hill School, more of the VOC's at Miller are from transport. Therefore, the wet weather pattern coupled with a new cold trap may have had more of an influence on an aged air mass. Unidentified compounds are higher on weekends versus weekdays, as shown in Figures 6-18 and 6-19.

Figure 6-31: Daily Percentage of 2018 Unidentified Compounds



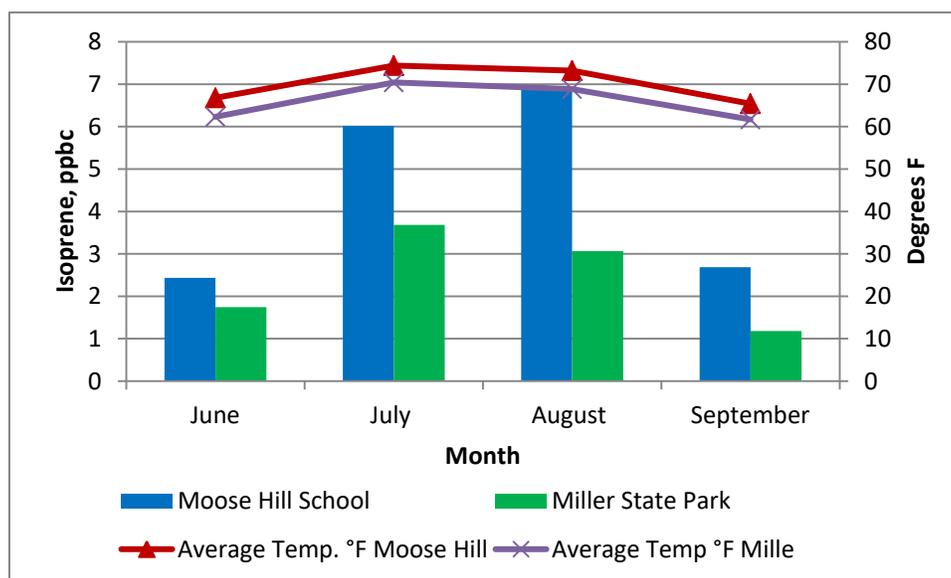
6.4.3 Naturally Emitted VOCs

On a global scale, biogenic emissions dominate the organic carbon budget, with anthropogenic emissions contributing >15%.¹² 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 most conducive to ozone formation.

Isoprene is emitted by many types of vegetation, notably conifers, and emissions are thought to be influenced by factors that affect tree health and growth such as rainfall and temperatures. Isoprene emissions are comparable with natural emissions of methane worldwide, around 500 million tons into the air each year.¹³ The majority of isoprene emissions in the Northeast comes largely from oak trees.

Figure 6-32 shows how Moose Hill School and Miller State Park average monthly isoprene concentrations compare in 2018. Figure 6-33 depicts isoprene concentration trends since 2005. The higher temperatures at Moose Hill School likely contribute to the increase in isoprene concentrations at that site, as isoprene emissions vary with temperature; cool temperatures result in less 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.¹⁴

Figure 6-32: Isoprene Monthly Averages Miller State Park and Moose Hill School 2018



The graph below shows lower isoprene concentrations at three New Hampshire sites since 2006. Cooler, wetter summers were experienced in 2013 and 2014. Average isoprene increased at both PAMS monitoring sites in 2018. The increase is more significant at Moose Hill School, likely due to the change

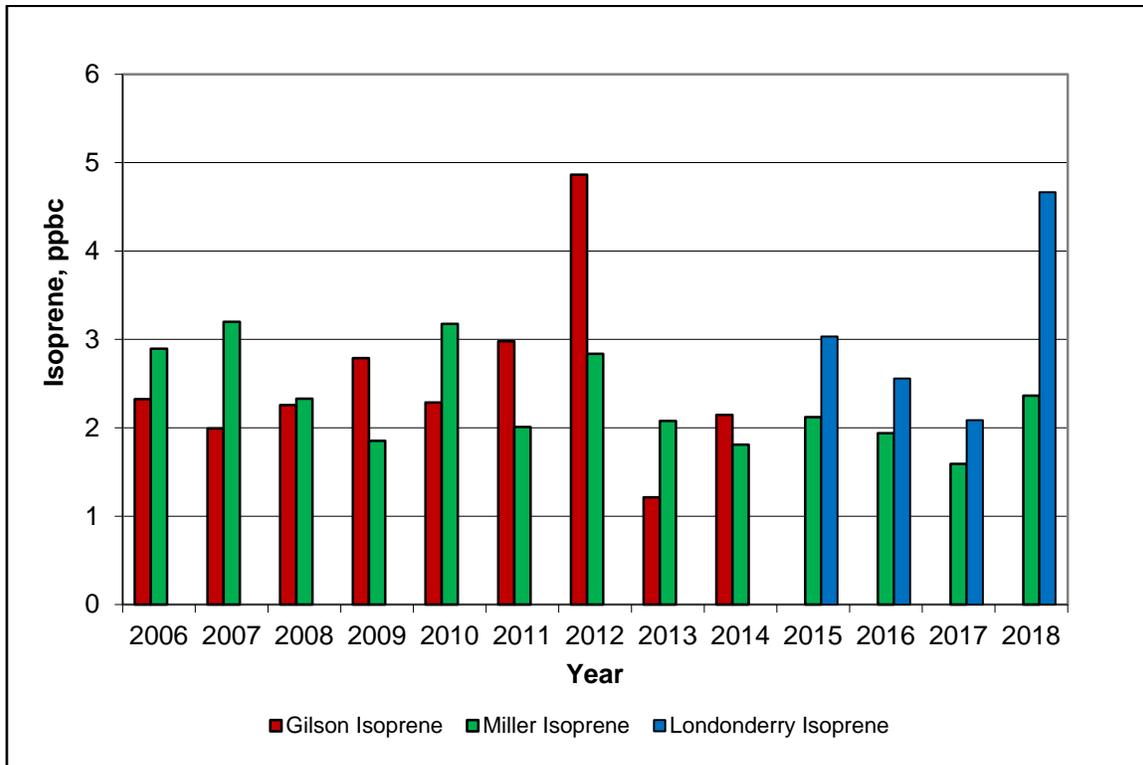
¹² Goldstein, A. H. (2007), Known and unexplored organic constituents in the earth's atmosphere, Environ. Sci. Technol., 41(5), 1514-1521.

¹³ Cotton, S. (2015, August, 25) Chemistry World, "Isoprene".
<https://www.chemistryworld.com/podcasts/isoprene-/8905.article>. [2017, March, 6].

¹⁴ Ibid.

in monitoring equipment. Temperatures in 2018 were 1.8-4.4 °F above normal, rainfall amounts 1.0-3.5 inches above normal. Weather and isoprene values are discussed in detail below.

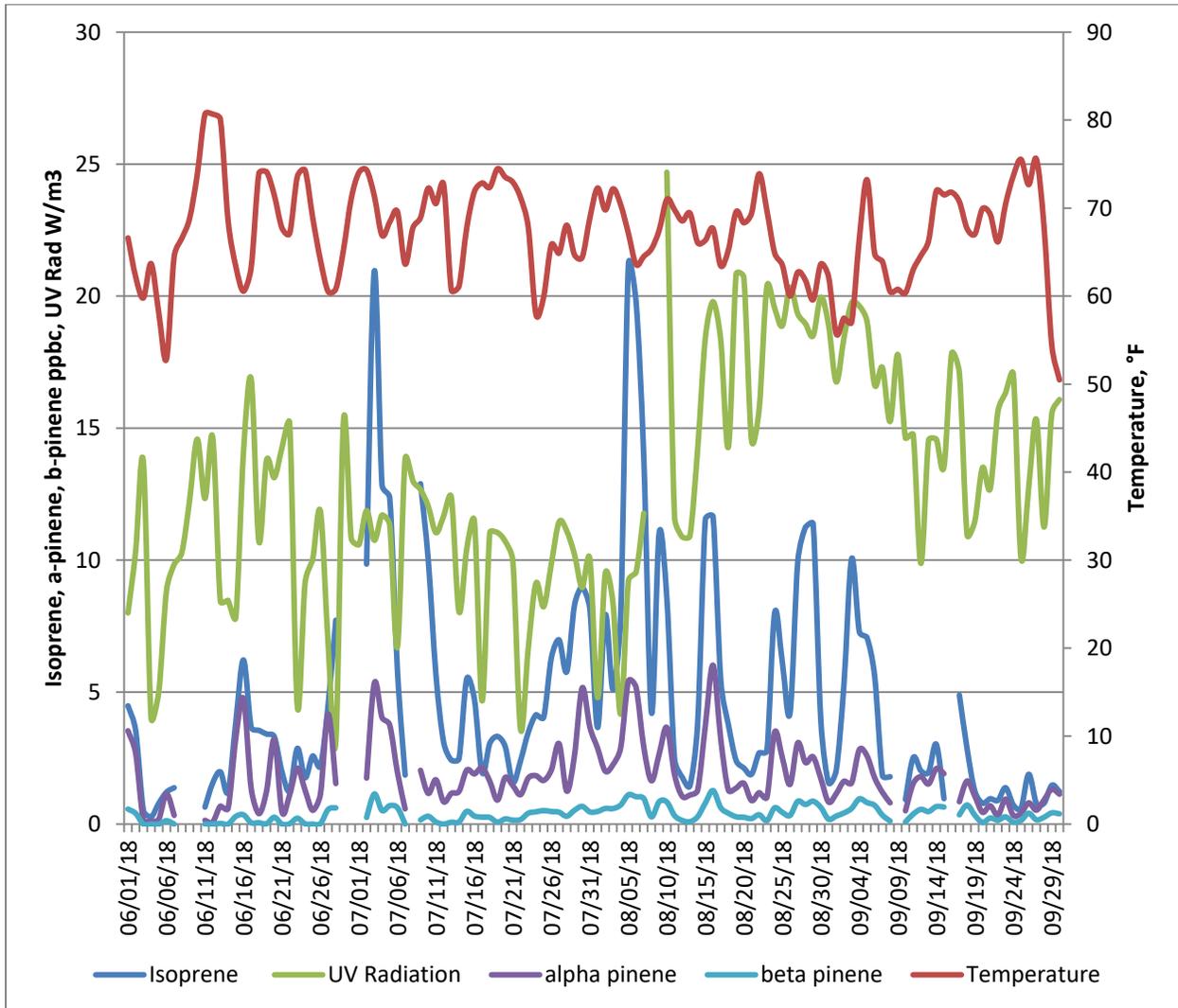
Figure 6-33: Isoprene Concentrations Since 2006



*2014 Gilson Road data only include September data up until September 10.

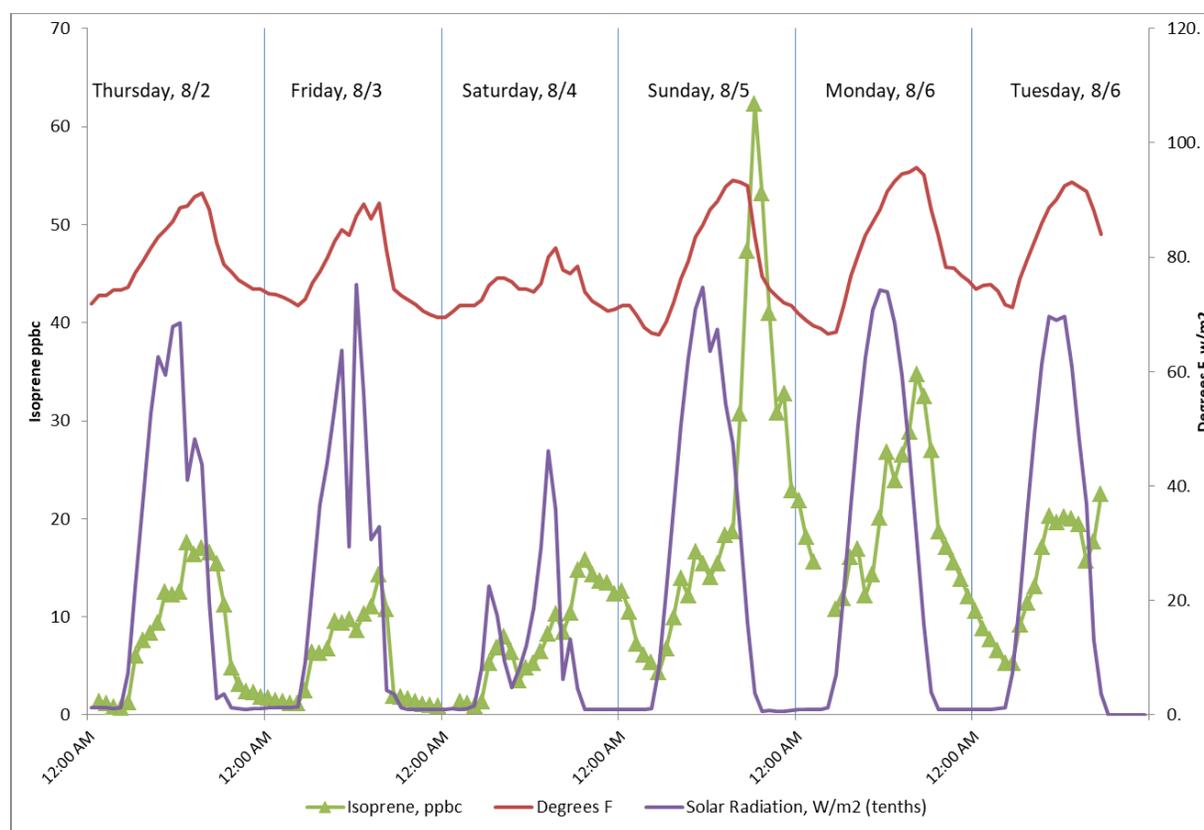
Figure 6-34 illustrates how isoprene and pinene concentrations vary with temperature and UV radiation at Moose Hill School. As noted in section 6.2, there was a high isoprene value measured here on August 5 that did not conform to the expected condition in relation to ambient temperature. Generally, ozone increases with higher daytime temperatures and stronger UV radiation. This effect is also seen when examining the diurnal characteristics of these three measurements (Figure 6-37).

Figure 6-34: 24 Hour Average Isoprene, α - and β -pinene, Temperature and UV Radiation at Moose Hill School 2018



A pattern emerges when one views the data in the days leading up to and following the highest isoprene reading on August 5 at Moose Hill School. As seen in Figure 6-35, temperature and solar radiation track fairly well with isoprene concentration on August 2 and 3. Temperature and solar radiation lag somewhat behind isoprene on August 4, and on August 5, the maximum isoprene concentration occurs well past the temperature and solar radiation peaks, and then seems to return back to the expected pattern in the days following, although isoprene data from the later part of August 7th and the early part of August 8 is missing. The cause of this anomaly is unknown. One study concluded that diurnal fluctuations in emissions are large and species specific, and must be considered when estimating emission rates for use in short-term regional atmospheric-chemistry models.¹⁵ The elevated isoprene measurement does not coincide with the highest ozone level measure here. This occurred on June 16 at 4 PM, when ozone was recorded at 75 ppb. This is discussed in section 7.

Figure 6-35: Isoprene, temperature, and solar radiation at Moose Hill School, August 2-6, 2018



In contrast to isoprene, α - and β -pinene show a diurnal pattern indicating that these species (mainly α -pinene) are emitted in the evening hours and their concentration decreases during the day as they react photochemically (Figure 6-36).

¹⁵ Funk, JL, CG Jones, et. al., Diurnal Variation in the Basal Emission Rate of Isoprene, *Ecological Applications*, 13(1), 2003, pp. 269–278.

Figure 6-36: Diurnal Isoprene, α - and β -pinene at Moose Hill School

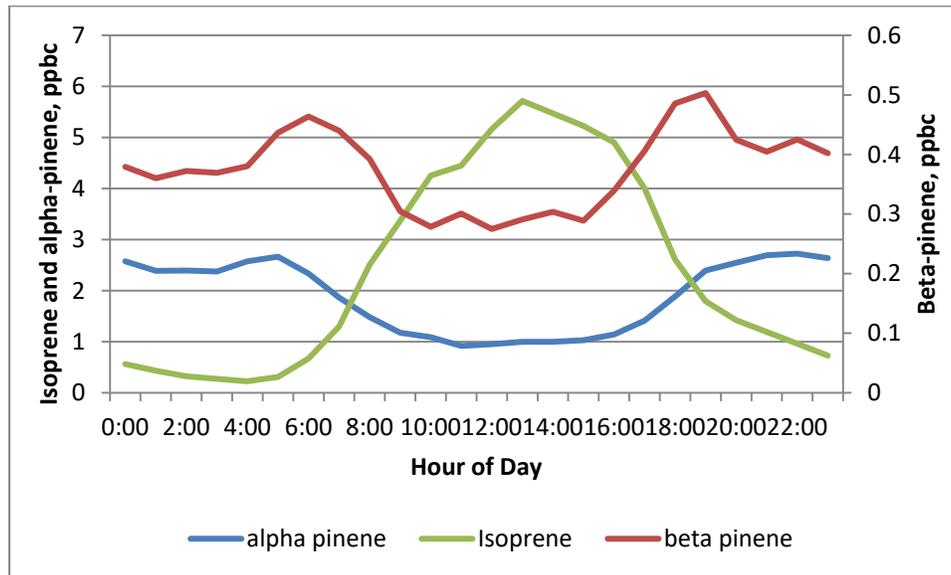


Figure 6-37 shows the relationship between isoprene and temperature at Miller State Park. Isoprene peaks on July 1 and July 16 show corresponding high temperature. UV radiation is not measured at this site.

Figure 6-37: 24 Hour Average Temperature and Isoprene at Miller State Park 2018

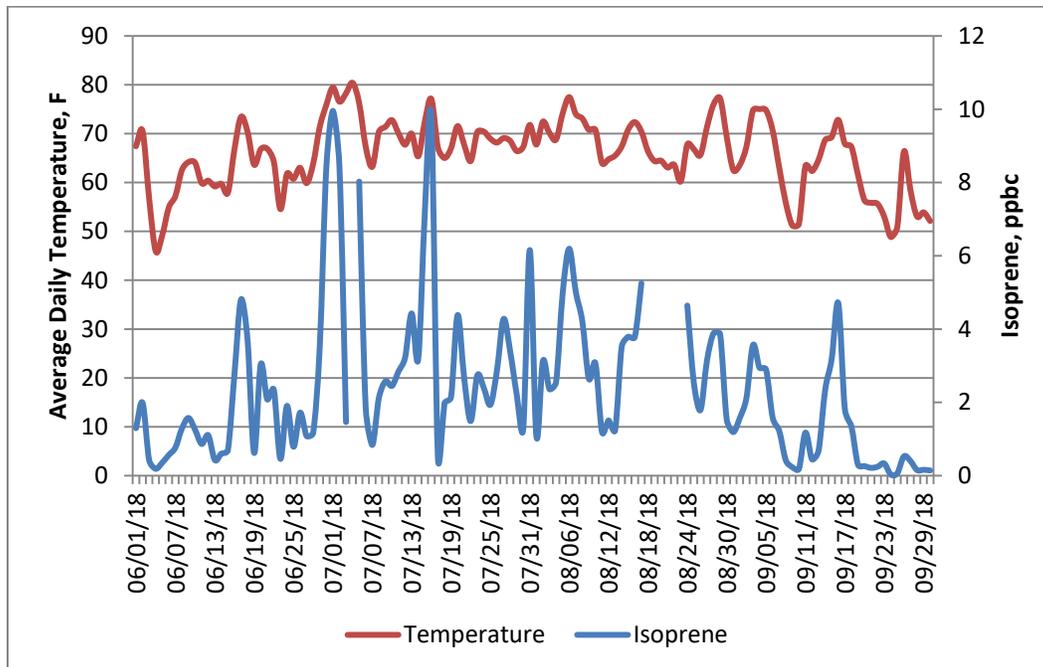
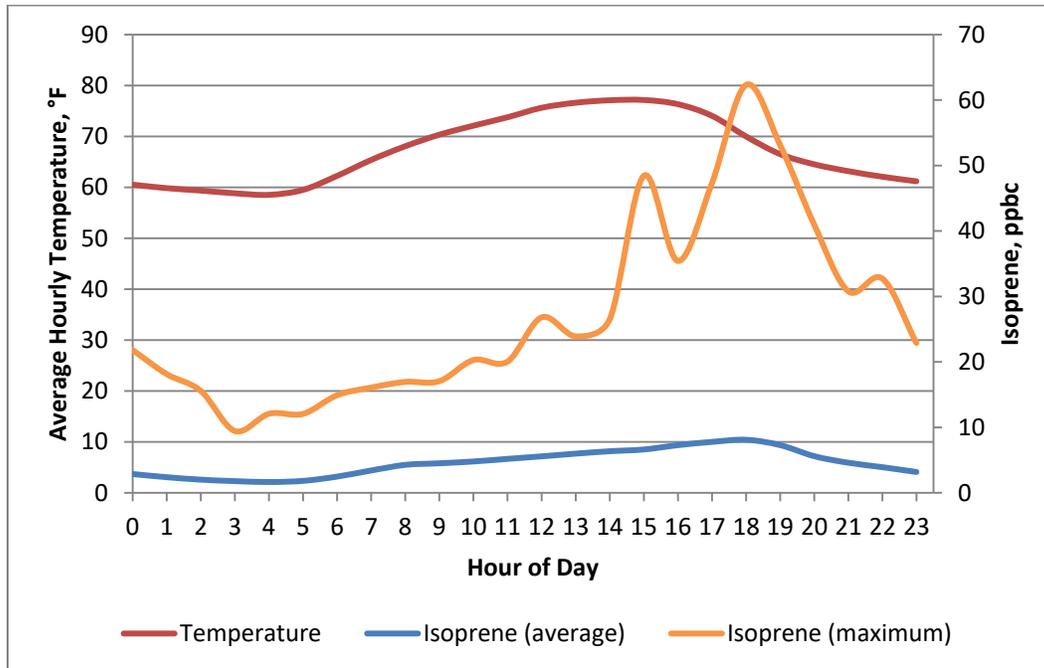


Figure 6-38 and 6-39 show the average diurnal and maximum isoprene concentrations and how they changed with temperature during the 2018 summer season. Generally, isoprene concentrations peak shortly after temperatures peak and into the early evening hours. On an individual day, hourly isoprene patterns are not as smooth as the average values over a season because peak concentrations often

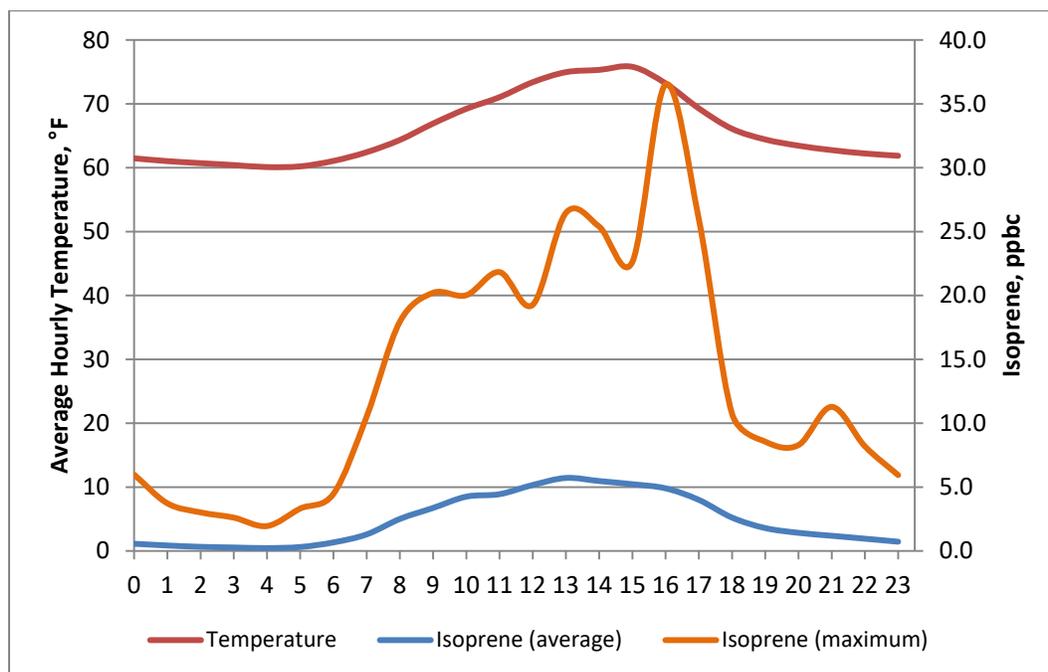
result from brief, isolated events; however, there is an obvious decline once the sun sets. Maximum isoprene values peak at 18:00 after air temperatures have peaked at Moose Hill School. This peak is highly influenced by the high value (62.3 ppb) recorded on 8/5/2018 as previously discussed.

Figure 6-38: Daily Average Hourly Isoprene, Temperature and UV Radiation at Moose Hill School 2018



Unlike Moose Hill School, average and maximum isoprene values at Miller State Park peak between midday and early afternoon, correlating more closely with temperature.

Figure 6-39: Daily Hourly Average and Maximum Isoprene and Average Temperature at Miller State Park 2018



7. PAMS Season Ozone - 2018

Above normal temperatures (+1.8-4.4 °F) and rainfall amounts (+1-3.5 inches) characterized all four months of the 2018 PAMS season. Data from Concord, New Hampshire, indicates the cool, dry high pressure that dropped into New England in June resulted in warm days and cool nights for most of the month, dropping down to 42 degrees on June 26, the coldest temperature observed in the last week of June for more than a decade. This was followed by low pressure that brought more than an inch of rain on June 28 and ushered in heat and humidity featuring seven straight days of temperatures in the 90s, the longest heat wave since 2002. Cooler, dryer weather prevailed until mid-July but heat and humidity returned near the end of the month, and continued well into August. Periods of heavy rain were experienced in early to mid-August, notably on August 8 when nearly 3 inches of rain fell. This and other frequent storms that characterized August led to this month being the wettest on record in Concord. There were a few breaks in heat and humidity but it returned at the end of the month to finish the summer as the sixth warmest and fourth wettest on record. Most of September was warm with only brief periods of cooler weather. From September 3 to 6, the temperature topped 90 degrees on three out of the four days. A few passing storms brought occasional heavy rainfall, including almost 2 inches on September 10 and 11. The persistent warmth and humidity made September 5 warmest on record. Table 7-1 summarizes the ozone exceedances that occurred in New Hampshire for 2018. The early season events occurring on top of Mt. Washington in April and May are related to possible exceptional events. One exceedance is seen at Moose Hill School in May but this was before VOC monitoring had begun. Two exceedances were measured at New Hampshire’s seacoast in Rye in July and August. An exceedance of the 8-hr standard occurs when an 8-hr averaged value during a day is greater than 0.070 ppm. Recording an exceedance of the ozone standard does not necessarily mean a violation of the standard has occurred. A violation of the 8-hr standard occurs if the three-year average of the annual 4th highest daily maximum 8-hour values at a specific site is greater than 0.070 ppm. The last time this

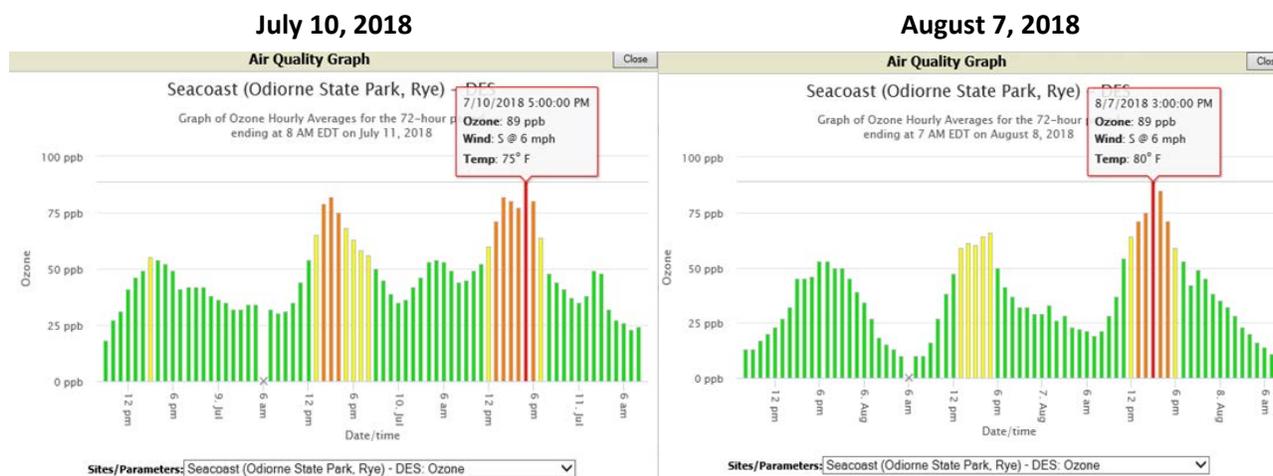
occurred in New Hampshire was 2010, representing the 2008-2010 design value period. The 8-hour average ozone reading at the PAMS sites for July 10 was 49 and 53 ppb for Miller State Park and Moose Hill School, respectively. On August 7, Miller State Park had an 8-hour average of 40 ppb. Moose Hill School on that date averaged 37 ppb.

Table 7-1: 2018 Ozone Exceedances in New Hampshire

Monitor Location	Date	Concentration (ppm)	
Summit of Mt Washington	4/14/2018	0.071*^	*Possible Exceptional Event ^ Not during the PAMS monitoring season
Summit of Mt Washington	5/18/2018	0.075*^	
Londonderry	5/26/2018	0.072^	
Rye	7/10/2018	0.075	
Rye	8/7/2018	0.071	

The graphs below (Figure 7-1) show the hourly ozone averages at Rye, New Hampshire on both dates for the 72-hour period before, during, and after the exceedances.

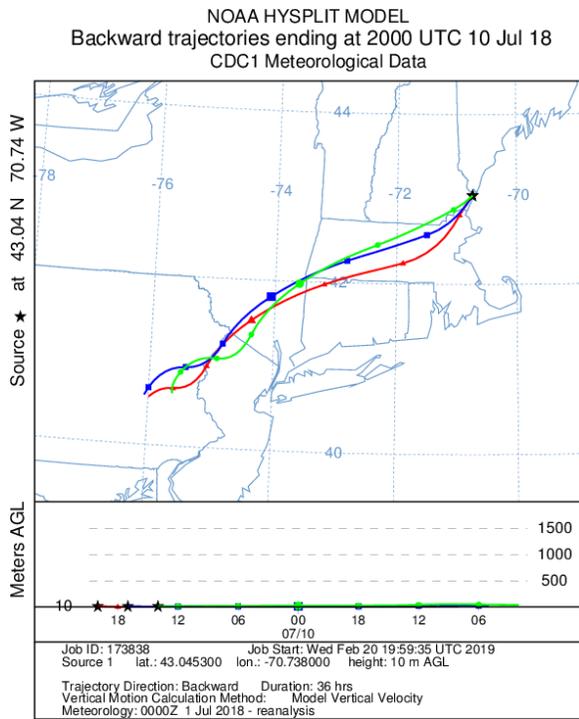
Figure 7-1: Hourly Ozone Data for Exceedance Days



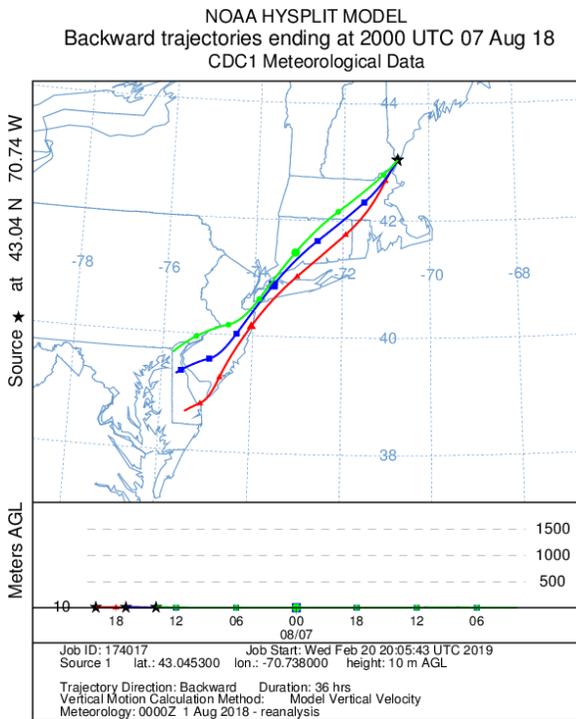
Information available from NOAA using the HYSPLIT Trajectory Model¹⁶ indicates that the ozone likely emanated from outside the region on both occasions. These trajectories (Figure 7-2) show ozone concentrations originating 36 hours prior to the time of the highest ozone concentration at the Rye, New Hampshire monitoring site (AQS ID 33-015-0016)(red line) and at 3 and 6 hours (green and blue lines, respectively) prior to the highest reading. Each mark on the trajectories represents a 6-hour interval. Wind direction frequency diagrams (Figure 7-3) support the ozone trajectory, i.e., the ozone air mass came from a predominantly south/southwest direction.

¹⁶ [NOAA HYSPLIT Trajectory Model](#)

Figure 7-2: Ozone backward trajectory
July 10, 2018

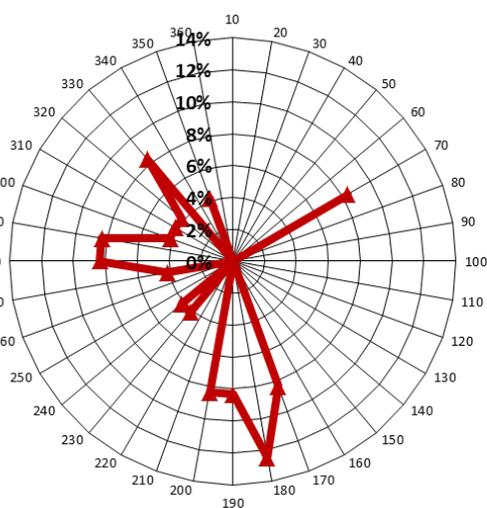


August 7, 2018

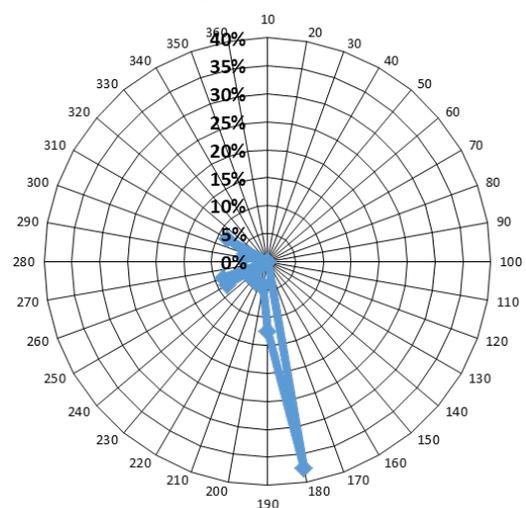


Wind direction frequency diagrams (Figure 7-3) support the ozone trajectory, i.e., the ozone air mass came from a predominantly south/southwest direction.

Figure 7-3: Wind Direction Frequency Chart at Rye, New Hampshire
July 10, 2018



August 7, 2018

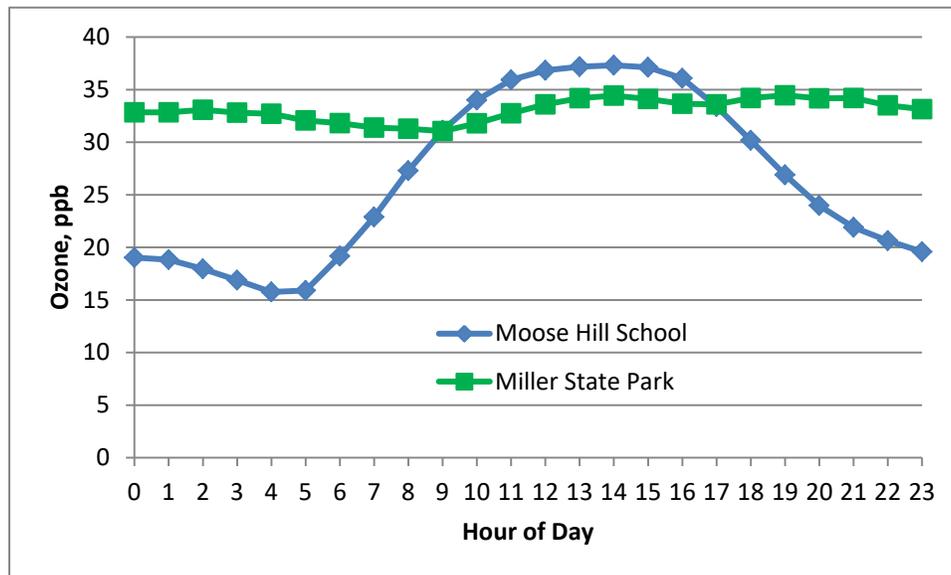


8. Ozone Measurements at the PAMS Sites

Ozone concentrations at Moose Hill School, located at a lower elevation and in a more urban setting, display a typical diurnal pattern, related to solar radiation and temperatures increasing during the day. The effect is aided by emissions from traffic and commercial activity, such as power generation that result in the release of nitrogen oxides. The pattern is reversed later in the day as these conditions reverse.

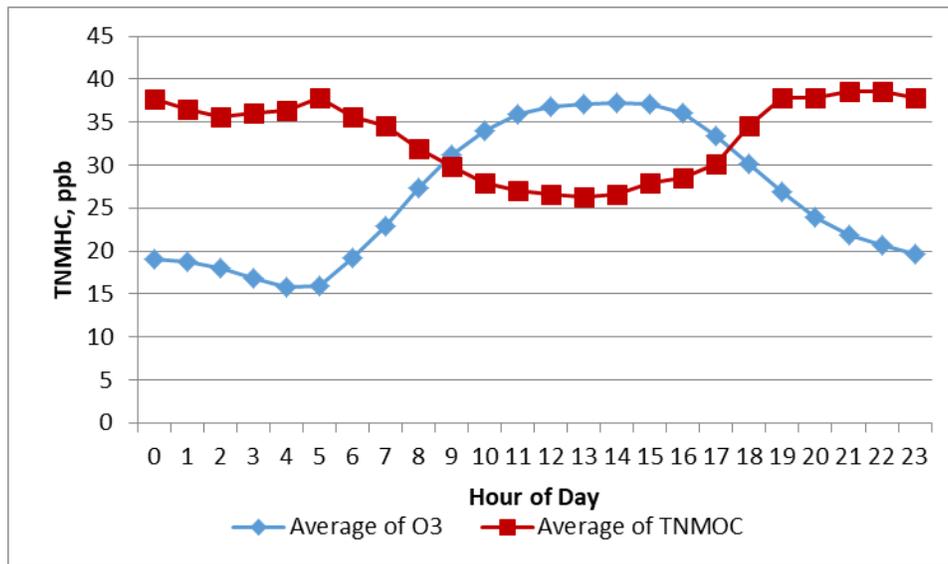
Conversely, much of the ozone pollution at high elevations is transported by winds from other states. The results from the high elevation ozone monitoring site at Miller State Park (Figure 8.1) show ozone concentrations change little throughout the day and that average concentrations are greater than at the Moose Hill School site. The two sites are 25 miles apart and there is a 1,945-foot difference in elevation.

Figure 8-1: Average Seasonal Diurnal Ozone Concentrations for Moose Hill School and Miller State Park



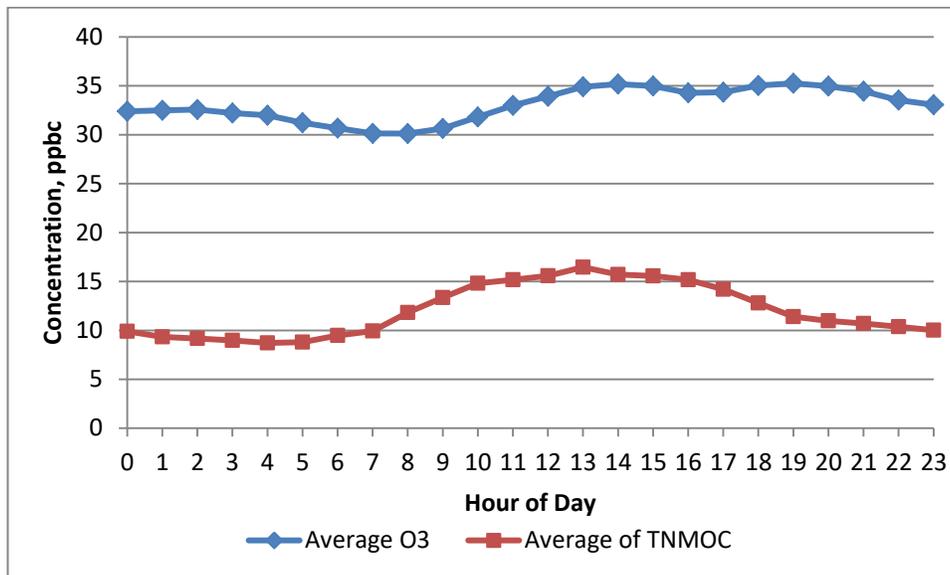
TNMOC and ozone show a symbiotic relationship at Moose Hill School. At ground level, early morning traffic increases the emissions of nitrogen oxides and VOC's; as traffic dies down they begin to react, forming nitrogen dioxide. Then, as sunlight intensifies later in the day, the nitrogen dioxide is broken down and its byproducts form ozone. Once the sun starts to set, the production of O₃ is halted, any leftover remains in the atmosphere and is consumed by several different reactions.

Figure 8-2: Hourly TNMOC/Ozone Londonderry PAMS 2018



Mountain top ozone is a result of higher background concentrations, less mixing of the air that would result in elimination of ozone through surface contact and chemical reactions, and faster transport of pollution from a larger region.

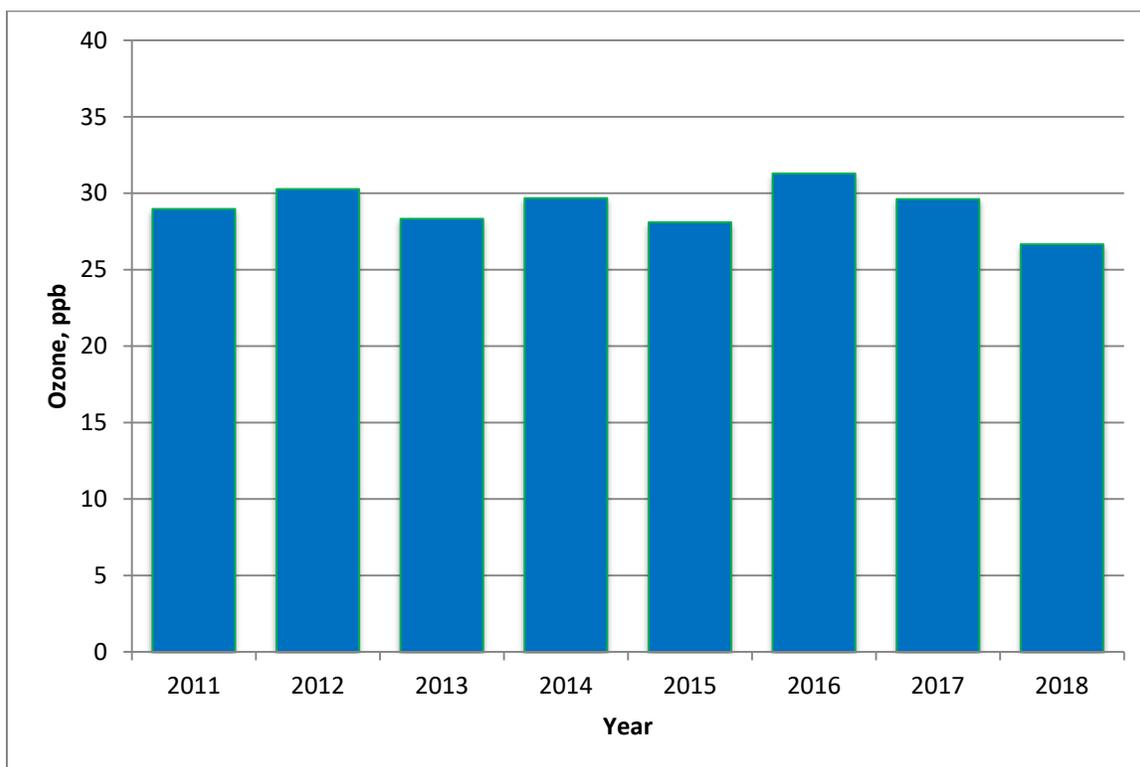
Figure 8-3: Hourly TNMOC/Ozone Miller State Park PAMS 2018



Concentration (ppbc) is along Y-axis and Hour of day is indicated along X-axis.

Figures 8-4 and 8-7 depict average ozone concentration trends during the PAMS season at both New Hampshire sites. Although PAMS monitoring only began at Moose Hill School in 2015, ozone monitoring has taken place there since its inception in 2011.

Figure 8-4: Moose Hill School PAMS Seasonal Ozone Averages 2011-2018



The Moose Hill School site in Londonderry saw no ozone exceedances during the PAMS season and only one in May of 2018. June topped the PAMS season with the highest average monthly ozone (Table 7-2). The highest ozone reading at this location was 75 ppb that occurred on June 18 at 4 PM.

Table 8-1: Average and Maximum Monthly Ozone Concentrations by Month at Moose Hill School 2018

Month	Ozone, ppb	
	Average	Maximum
June	30	75
July	29	67
August	24	65
September	19	44

On June 18 at 4 PM, the hourly ozone concentration is seen rising only slightly with the temperature on that date, and then quickly jumping at 4 PM followed by a sharp increase in relative humidity (Figure 8-5). The highest winds speeds for the month were recorded in Concord on June 18. These conditions and the back trajectory for the 75 ppb reading suggest that the ozone may have been transported from the New York/New Jersey region (Figure 8-6).

Figure 8-5: Hourly Ozone, Nonmethane Hydrocarbons and Meteorological Conditions at Moose Hill School June 18, 2018

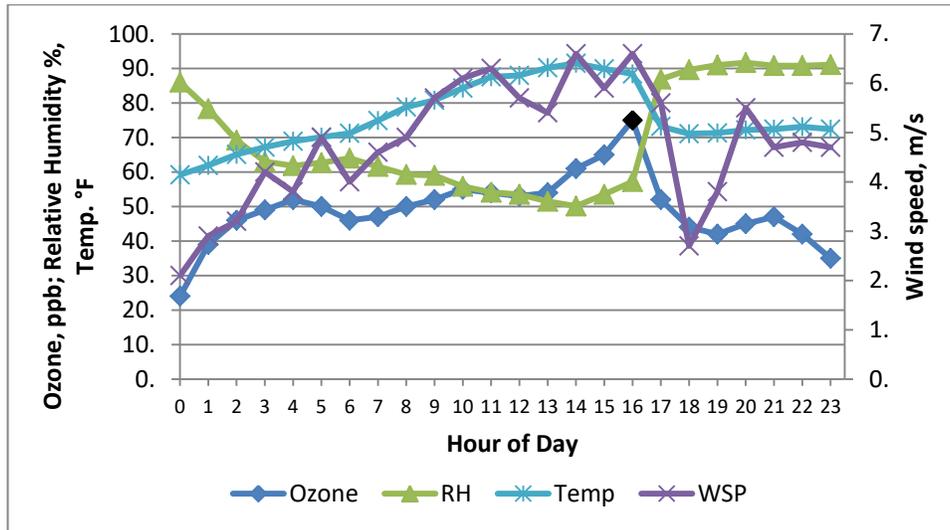
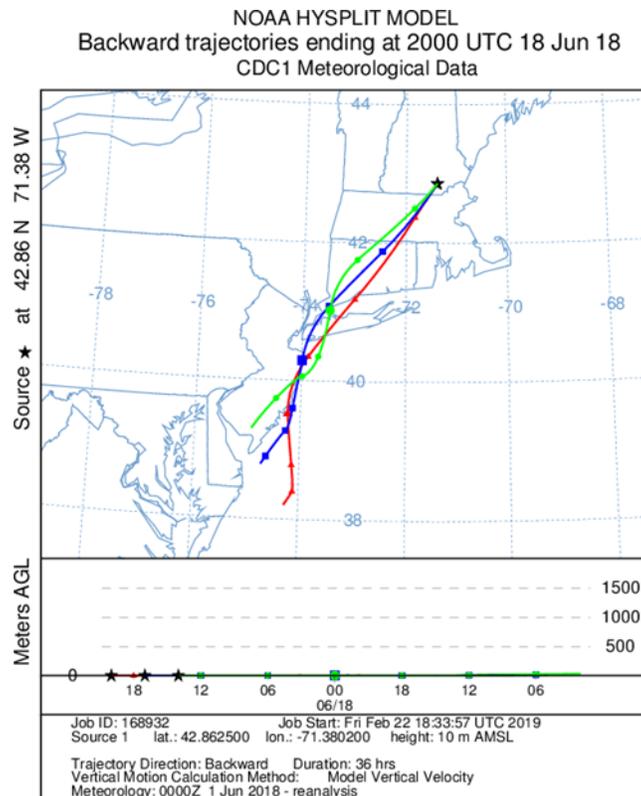
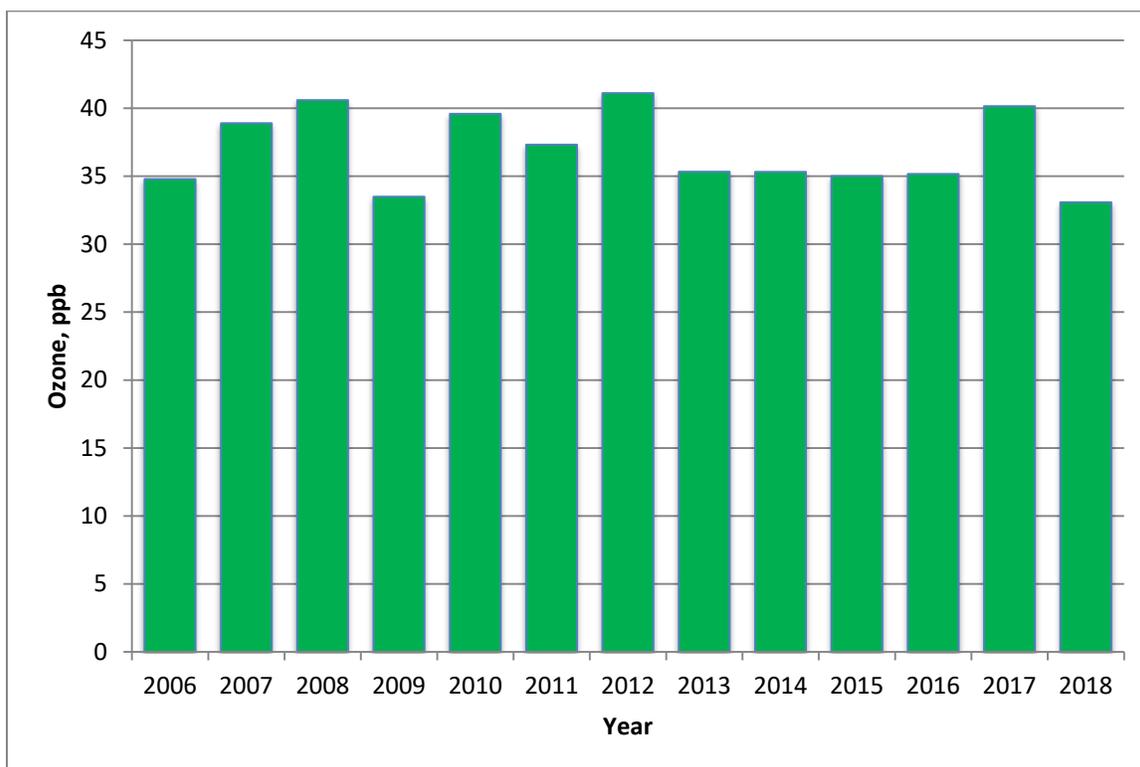


Figure 8-6: Back Trajectory for Ozone Concentration at Moose Hill School, June 18, 2018



Ozone values at Miller State Park have been very steady for four seasons until 2017 when the average increased by 5 ppm. In 2018, the average ozone concentration there was 33 ppb.

Figure 8-7: Miller State Park PAMS Seasonal Ozone Averages 2006-2018



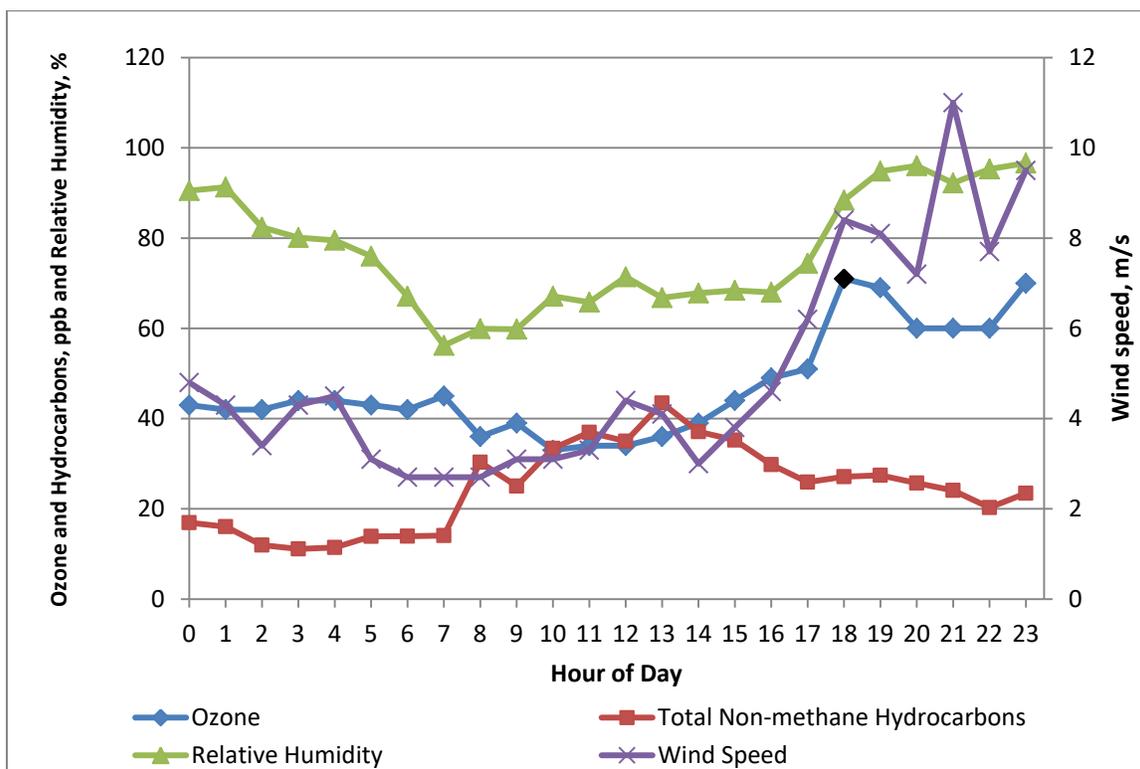
As shown in Table 8-2 below, July had the highest monthly average of ozone at this site. The highest concentration measured here was 71 ppb that occurred on July 16 at 6 PM.

Table 8-2: Average and Maximum Monthly Ozone Concentrations by Month at Miller State Park 2018

Month	Ozone, ppb	
	Average	Maximum
June	35	65
July	36	71
August	33	58
September	28	54

On July 16 at 6 PM, other high concentrations occurred on this day – 70 ppb at 11 PM and 69 ppb at 7 PM (Figure 8-8). This graph also shows the concentration of total nonmethane hydrocarbons for the same time period. As shown in this figure, the highest ozone concentration of the day lags behind that of hydrocarbons, which are dominated by the compound isoprene. The high reading followed a period of meteorological conditions conducive to ozone formation, specifically, low winds and low midday relative humidity.

Figure 8-8: Ozone, Nonmethane Hydrocarbons and Meteorological Conditions at Miller State Park on July 16, 2018



9. CONCLUSION

In conclusion, NHDES had a successful year of PAMS data collection. As changes to PAMS regulations take effect this year, New Hampshire is in the forefront as we already have implemented many of these changes in the 2018 PAMS season, including new instrumentation and software and the collection of additional data. Carbonyl sampling and mixing height will be conducted in Londonderry at the Moose Hill School site beginning of 2019.

Meteorological conditions for the 2018 PAMS season were characterized by above average temperatures and rainfall amounts. The months of July and August were warmer on average than in 2017. In addition to these differences, 2018 marked the installation of new, more effective PAMS monitoring equipment at the Moose Hill School. This resulted in increased capture efficiency leading to much higher VOC levels measured there as well as the addition of two new compounds, α - and β -pinene. The period from 2015-2017 saw the total PAMS VOC concentration declining slightly each year, with concentrations around 38% higher at the more urban Moose Hill School site. In 2018, Moose Hill School average daily total PAMS VOCs measured at Moose Hill School was 26.6 ppbc, an 85% increase. Miller State Park average daily total PAMS VOCs was up 24% from 2017. At both sites, biogenic isoprene (and α -pinene at Moose Hill School) was dominant, as was ethane, known to be increasing globally, and propane, which may also be a result of increased natural gas processing. Observed increases in compounds groups such as BTEX and SOAP at Moose Hill School may be a function of increased instrument sensitivity. Even with the increases seen at both sites in 2018, New Hampshire's air quality continues to improve. Additional monitoring scheduled to take place at that site in the near future will

also broaden our understanding of the chemistry taking place leading to ground level ozone formation. That stated, as we hone our understanding of climate change and its implications, the PAMS program and NCORE monitoring sites hold promising support platforms to understand current/existing atmospheric conditions and track potential changes over the long term.