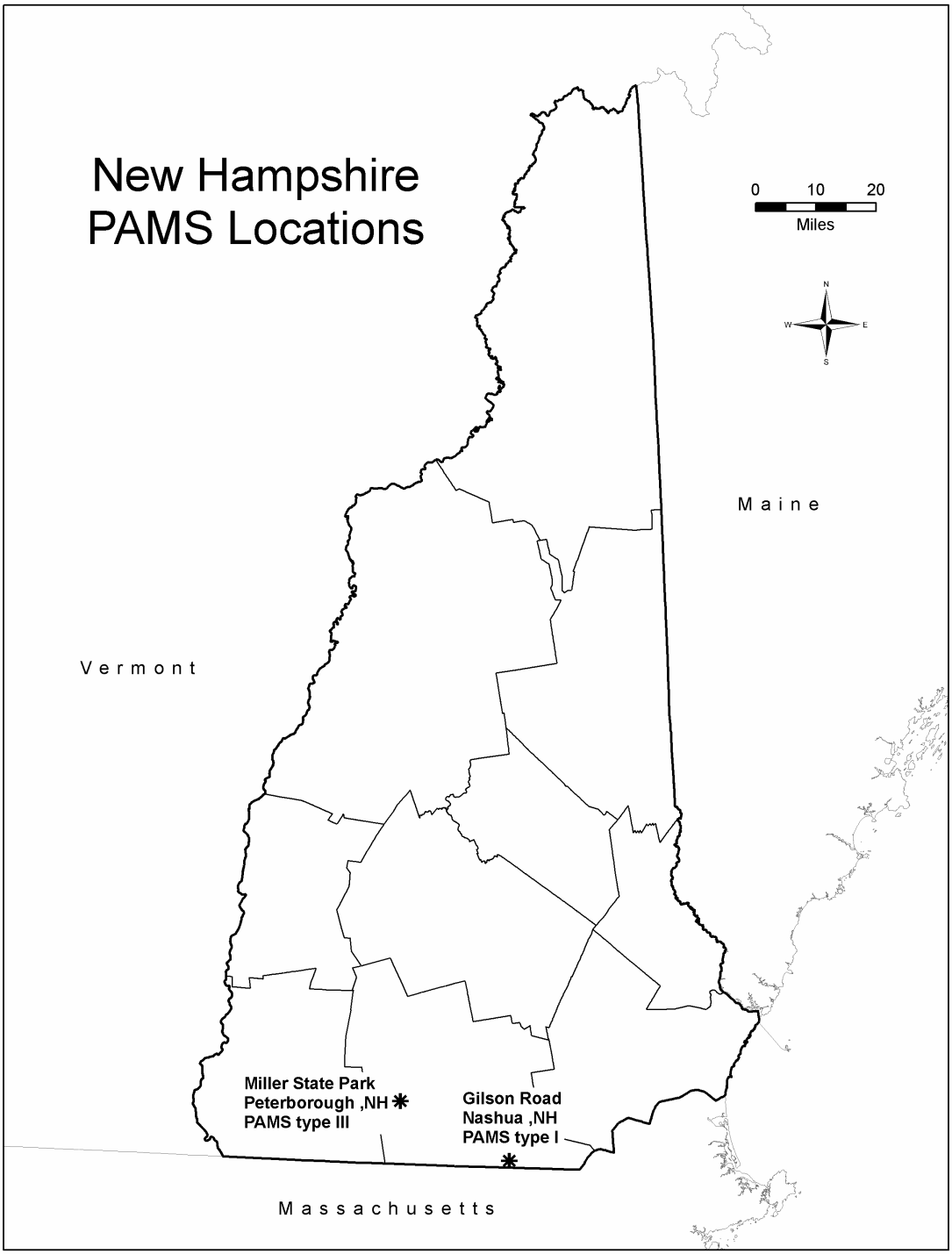
NEW HAMPSHIRE DEPARTMENT OF ENVIRONMENTAL SERVICES
2010 PAMS REPORT

2010 proved to be a very good year for data capture for photochemical monitoring in New Hampshire. The Photochemical Assessment Monitoring Stations (PAMS) collect a total of 54 volatile organic compounds (VOC's) on an hourly basis, 24 hours a day, seven days a week during the months of June, July, August, and September. This marked our 5th year of photochemical monitoring at our Type III site atop of Pack Monadnock in Peterborough, and our 6th year at our Type I site at Gilson Rd. in Nashua. These sites are both located in Hillsborough County, but are separated by approximately 2,090 feet in elevation. Aside from the excellent data capture and quality that came along with 2010, so did a couple of ozone exceedances accompanied by hot, dry conditions which had not been seen in the two previous years. This report will review the highlights of the 2010 PAMS season and update trend data.

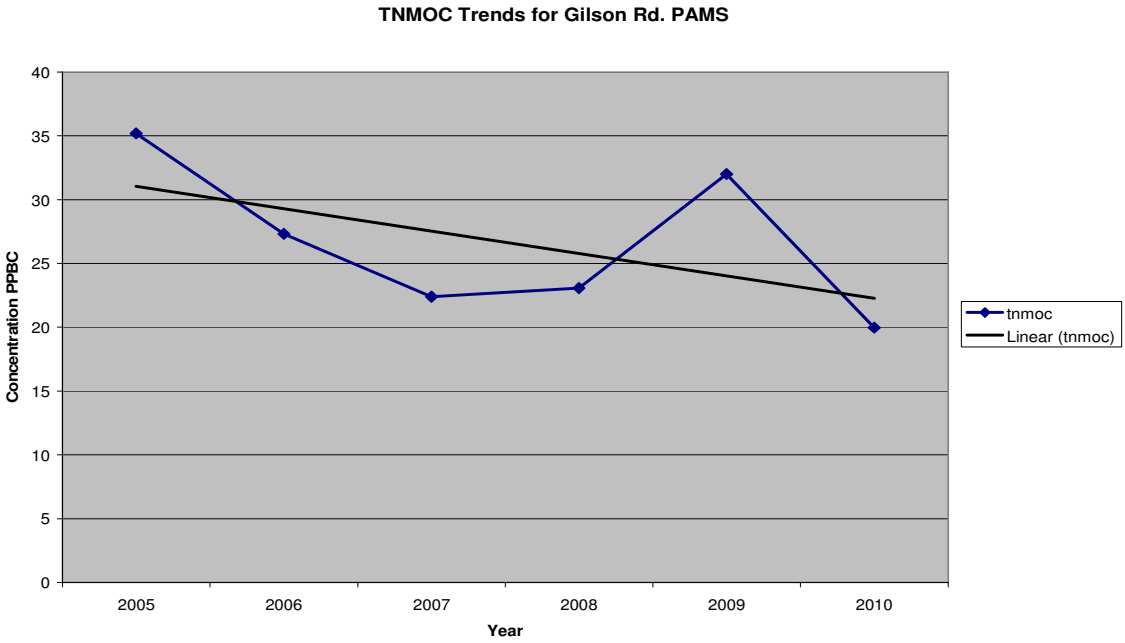
The ozone precursors at both monitors are analyzed using PerkinElmer ozone precursor systems consisting of a Gas Chromatograph (GC) and Thermal Desorber (TD). The TD collects ambient air samples on an hourly basis for approximately 40 minutes. A 600mL sample volume is drawn through with a vacuum pump to a Nafion dryer, which removes water from the sample, and then enters a specially designed trap. The trap is cooled to -30°C, which causes the VOC's to absorb onto the surface, the trap is then rapidly heated to 325°C and the VOC's are desorbed and swept onto the transfer line and ultimately the CG columns. With the use of a timed Dean's switch, the low molecular weight hydrocarbons are separated on a PLOT column while the higher molecular weight compounds are retained on a BP1 column and detected via Flame Ionization Detectors. Species are identified based on retention time and concentrations are determined by the area of the data peak.

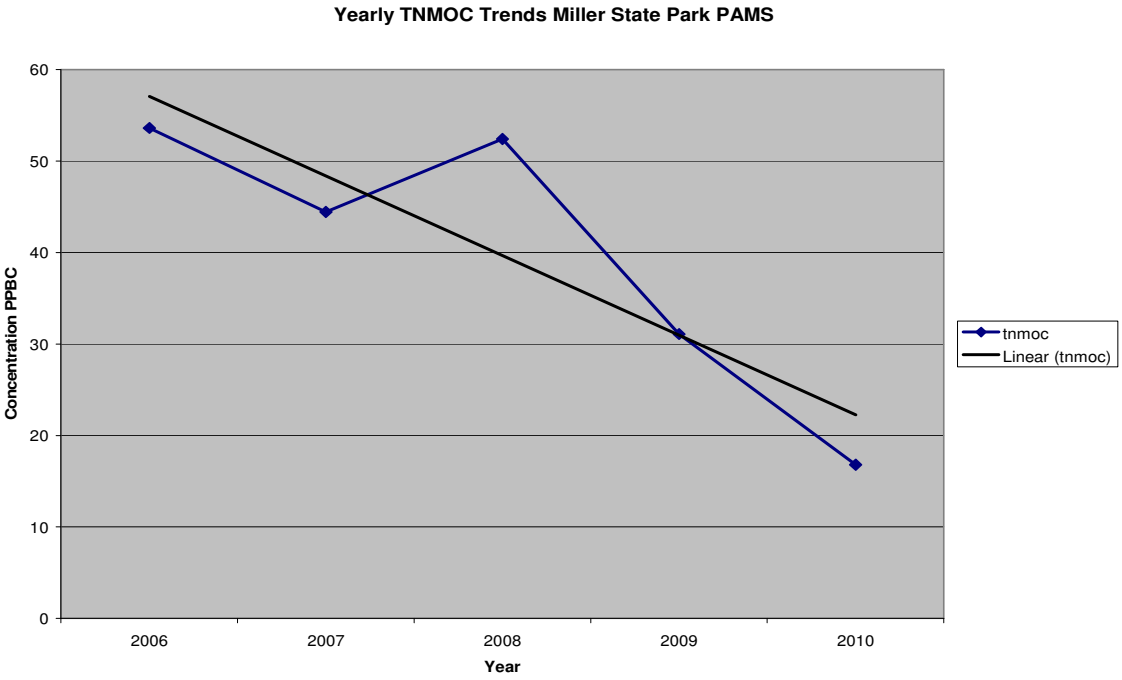
While 2010 proved to be a dry and hot summer and there were an increase in days where the ozone standard was exceeded, we continue to see a downward trend of most PAMS species at both of the NH sites on a year to year basis. This, among other conclusions will be highlighted in this year-end report.


New Hampshire
PAMS Locations
0 10 20
Miles
N
W
E
S
Maine
Vermont
Miller State Park
Peterborough ,NH
PAMS type III
Gilson Road
Nashua ,NH
PAMS type I
Massachusetts

TNMOC TRENDS

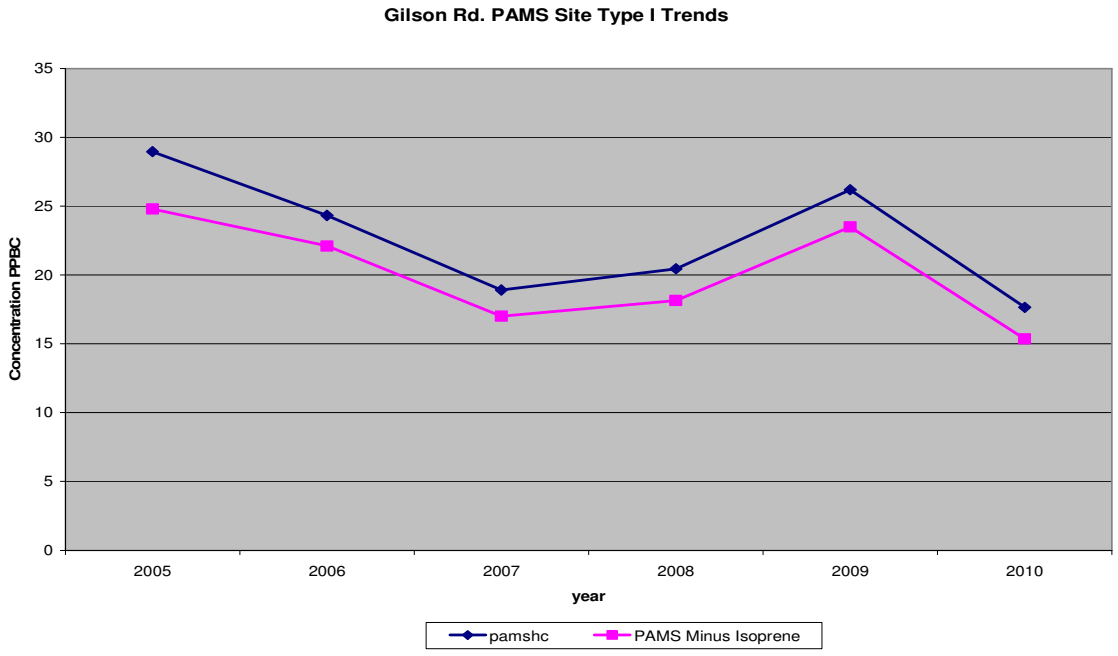
As shown below, TNMOC is on a decline at both of the NH PAMS sites, although a more steep descent appears at Miller State Park, 2009 data at Gilson Rd. was heavily influenced by a paving project in the vicinity of the site. 2008 data at Miller was also a questionable year with the installation of all new instruments and some carryover of high molecular weight hydrocarbons which elevated TNMOC values.

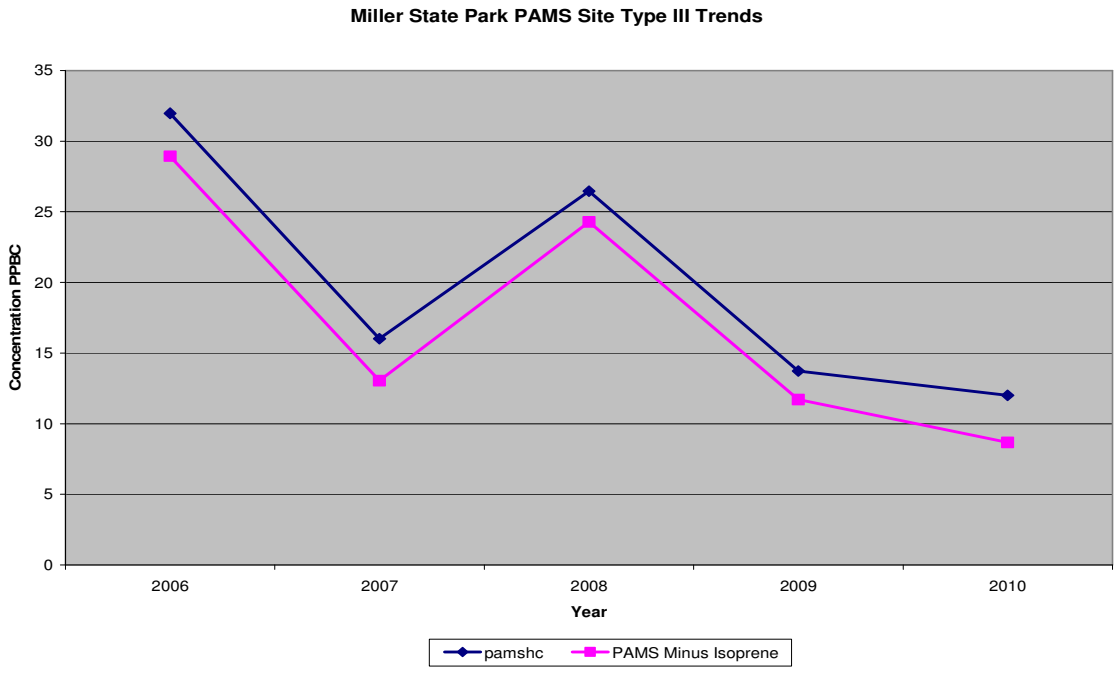




PAMS TARGET SPECIES TRENDS

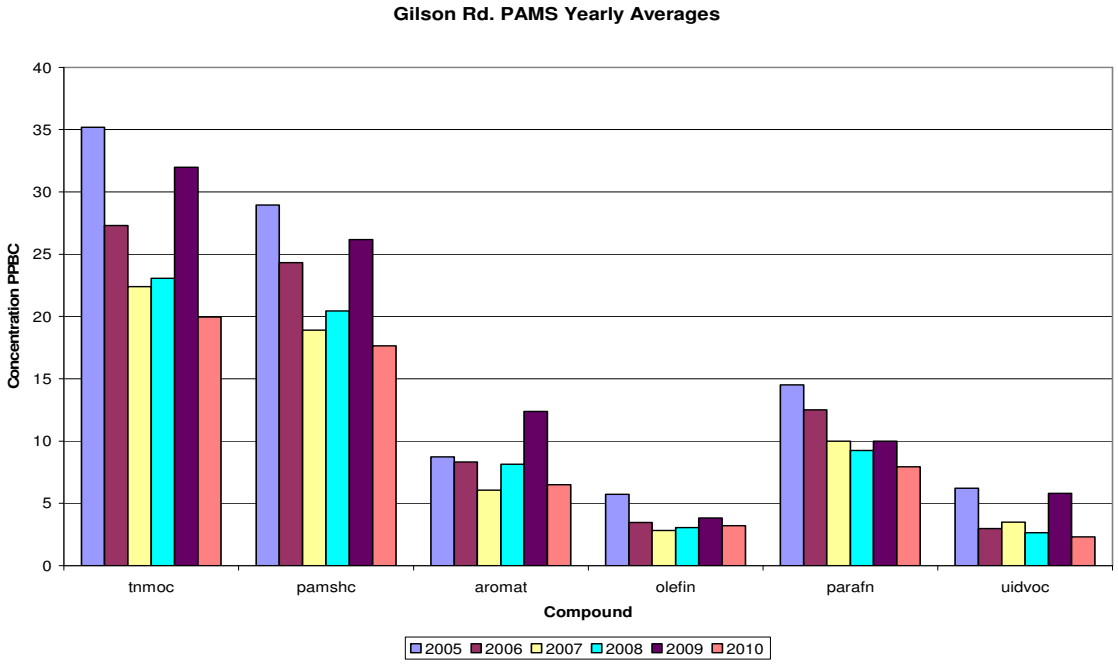
Another look at trends, this time including the sum of PAMS compounds compared to PAMS minus Isoprene concentrations. These graphs are a preliminary look at how important Isoprene is to the total PAMS values. Isoprene accounts for approximately 10% of the PAMS target species at NH PAMS sites on an annual basis.
Again, the 2009 spike is attributed to a local paving influence at Gilson Rd. and the 2008 spike at Miller is due to the installation of new instrumentation and some compound carryover.

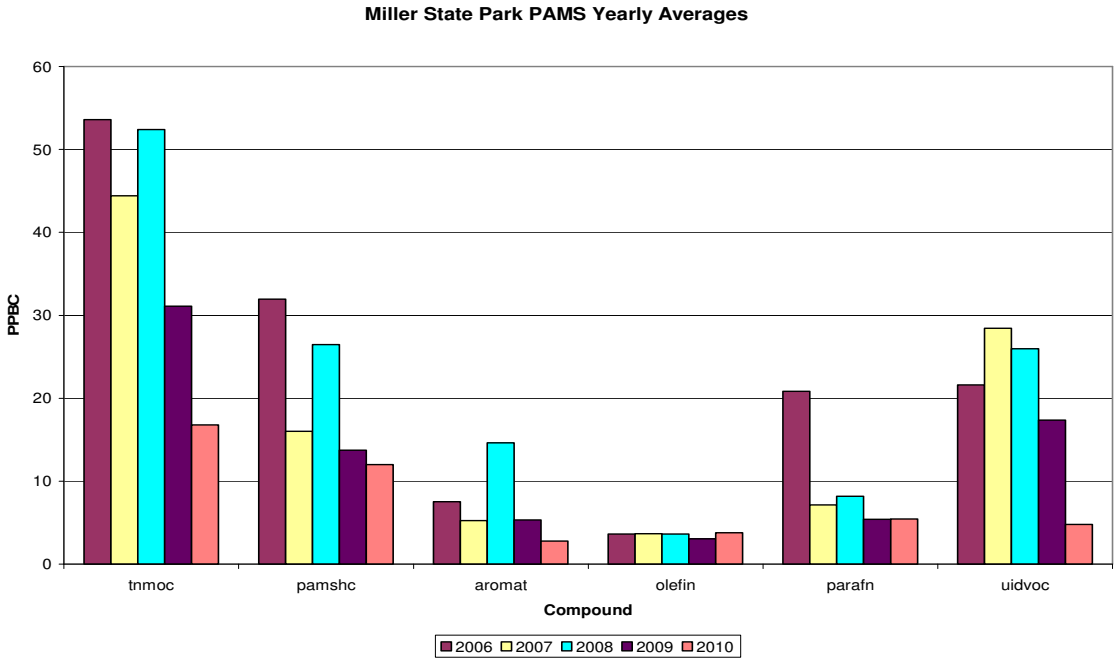




TRENDS BY FUNCTIONAL GROUP

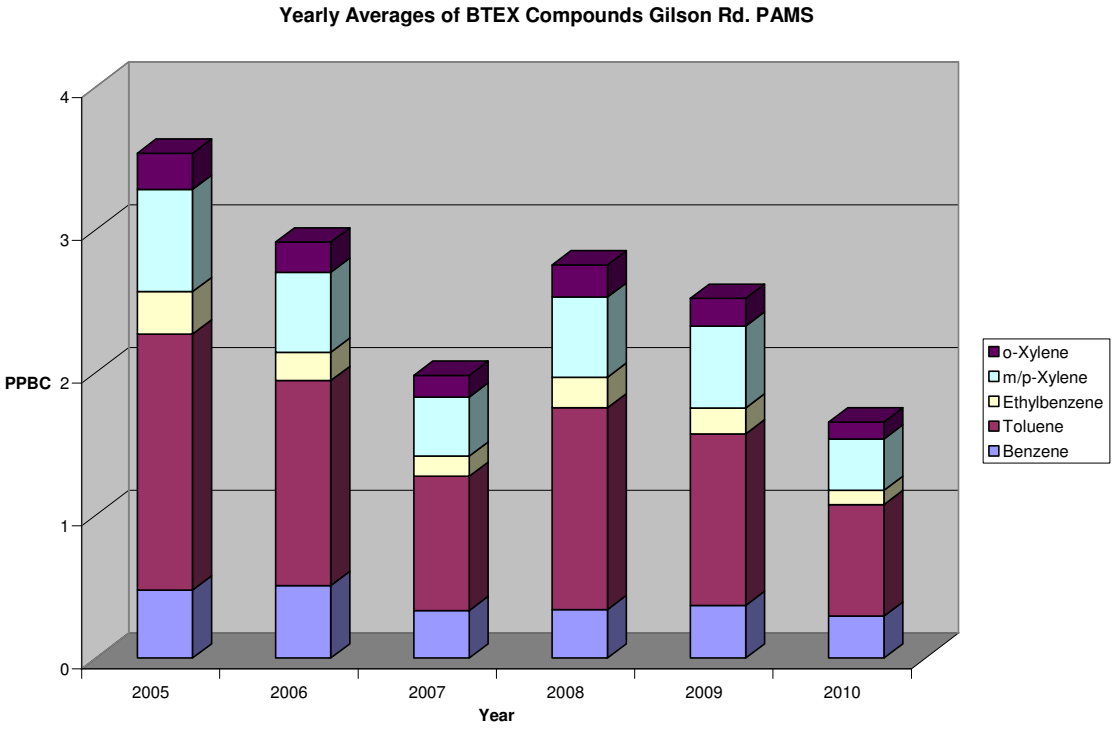
Most compound concentrations have declined in 2010, isoprene and hexane being the major exception at Miller State Park as well as an increasing benzene trend. Very slight increases of n-hexane, n-undecane, ethane, and acetylene were observed at Gilson Rd. Also note the significant decrease in unidentified compounds at Miller SP. This is mostly attributed to the compound 1,-chloro-1,1-difluoroethane, which has been presumed to occur at higher concentrations during periods of clouds and rain atop the mountain. This appears to be reaffirmed considering the dry, hot summer of 2010.

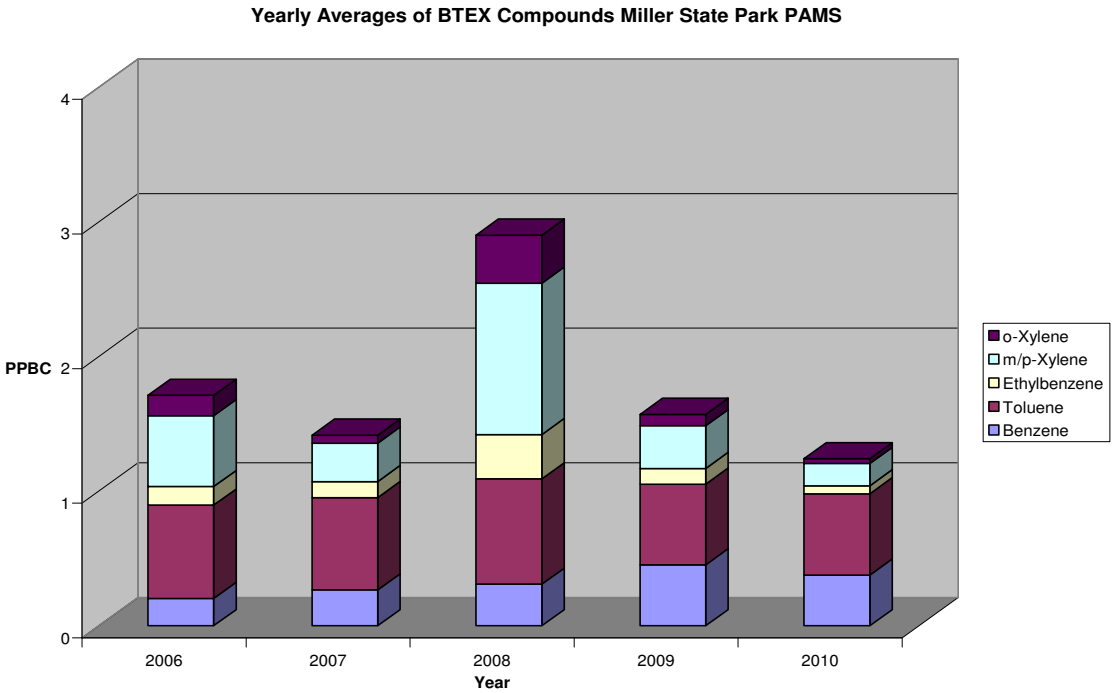




TRENDS OF BTEX COMPOUNDS

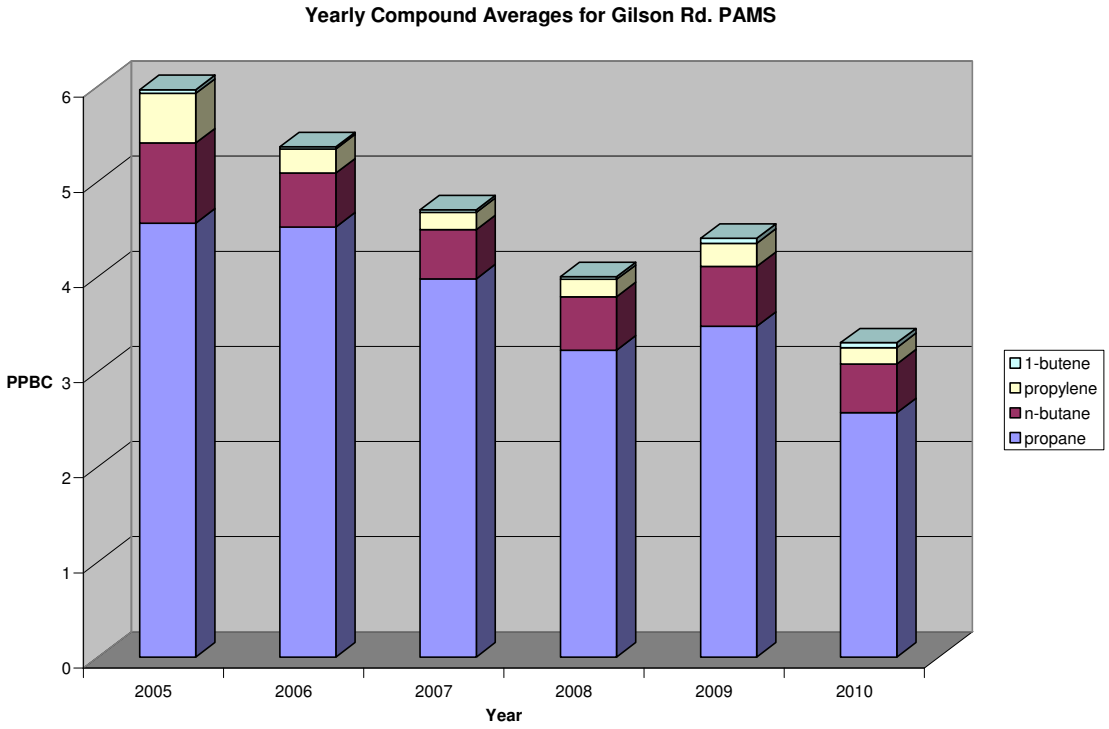
A look at BTEX compounds at the PAMS sites over the years, again there is a downward trend. 2008 Miller data was influenced by carryover of certain BTEX compounds due to the installation of new instrumentation that year.

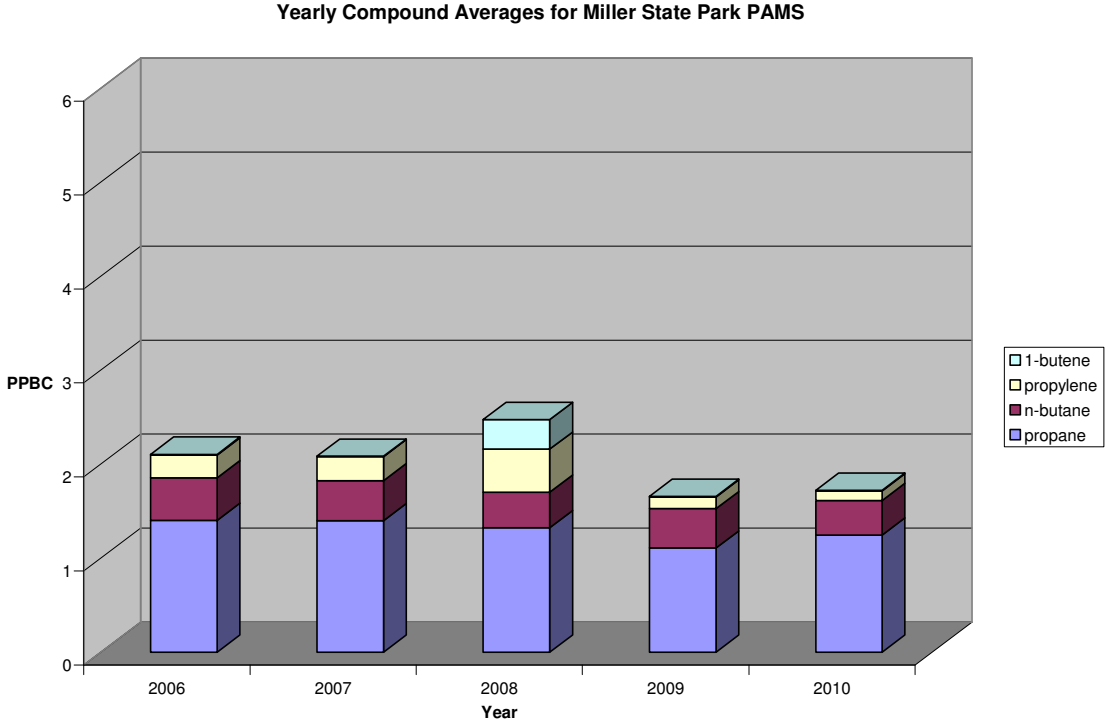




TRENDS FOR LIQUID PETROLEUM PRODUCTS

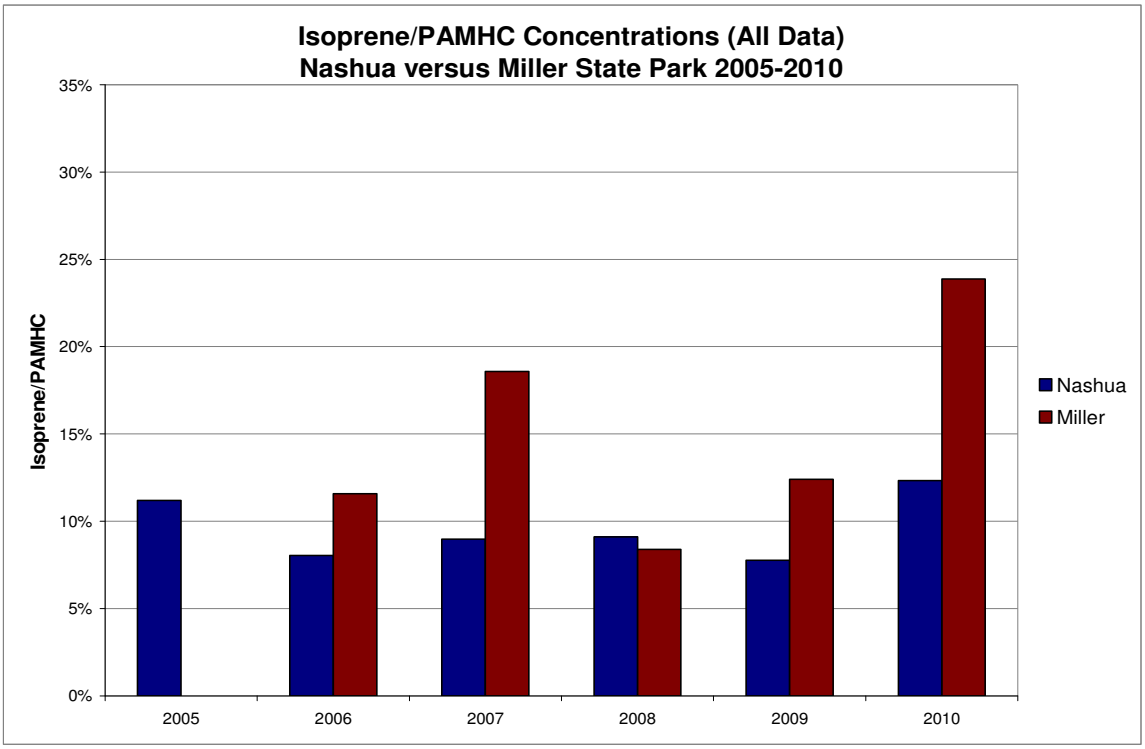
Liquefied petroleum compounds, most commonly associated with heating, cooking and transportation sources.

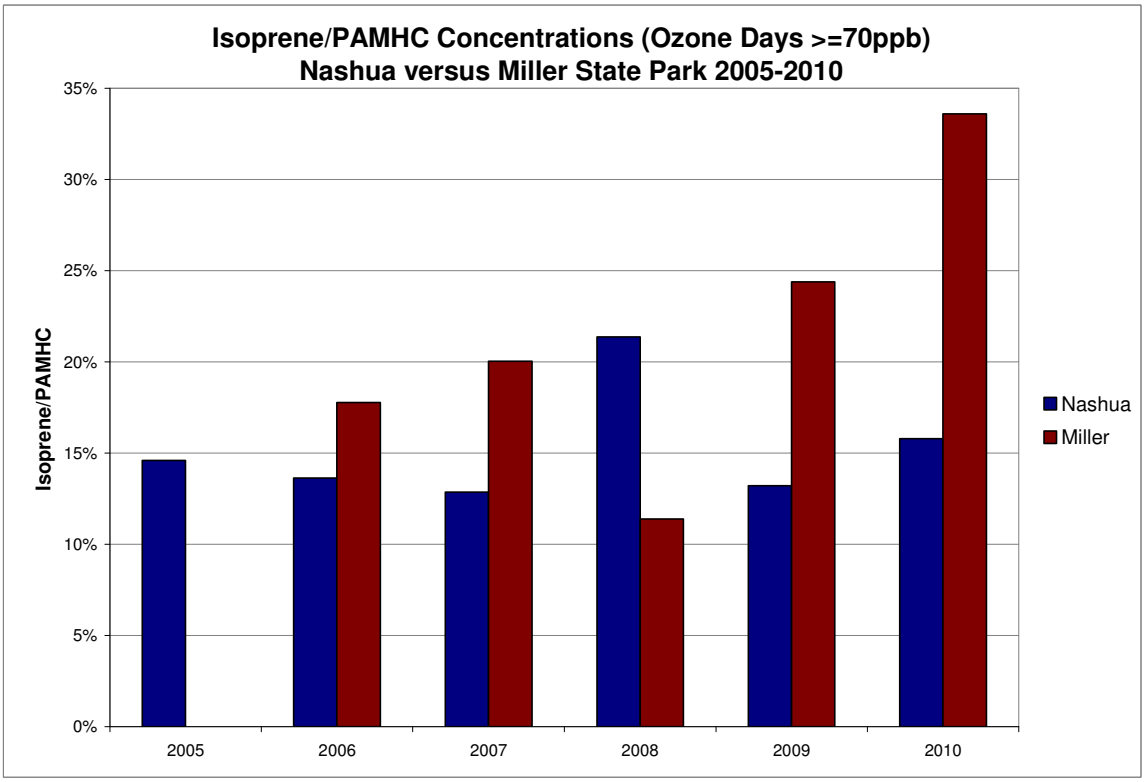




TRENDS OF ISOPRENE TO TOTAL PAMS TARGET SPECIES

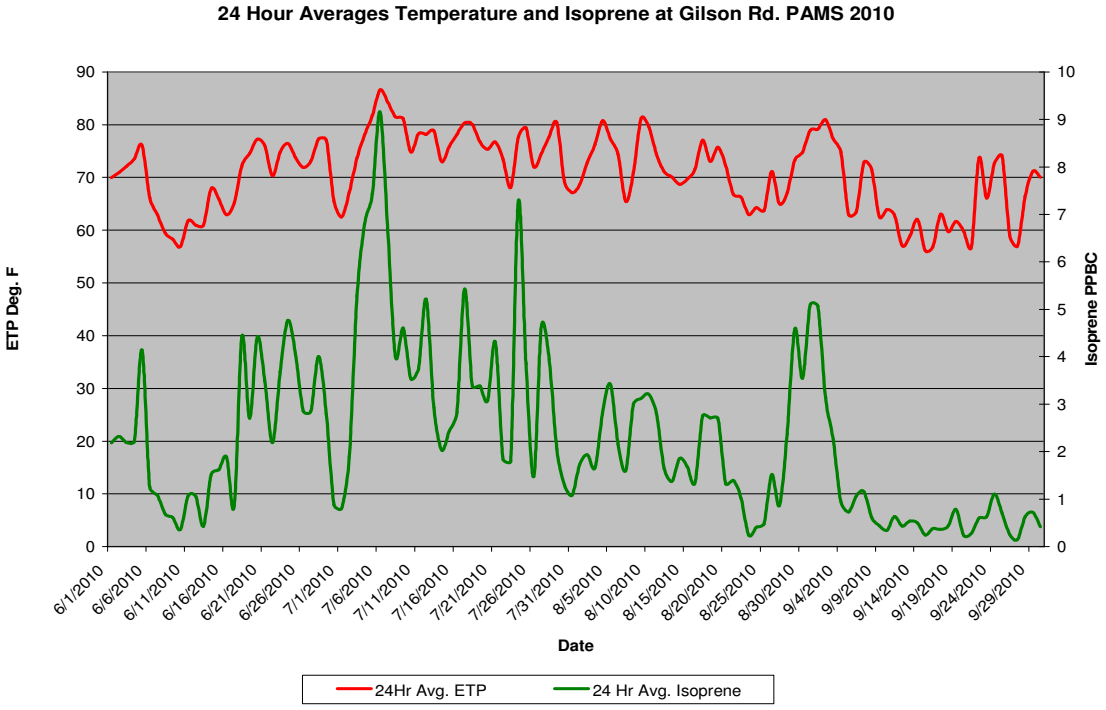
These graphs reinforce the importance of Isoprene at the NH PAMS stations and their contribution to the total PAMS concentrations. Percentages increase at both sites during high ozone days indicating the ozone forming potential of isoprene.

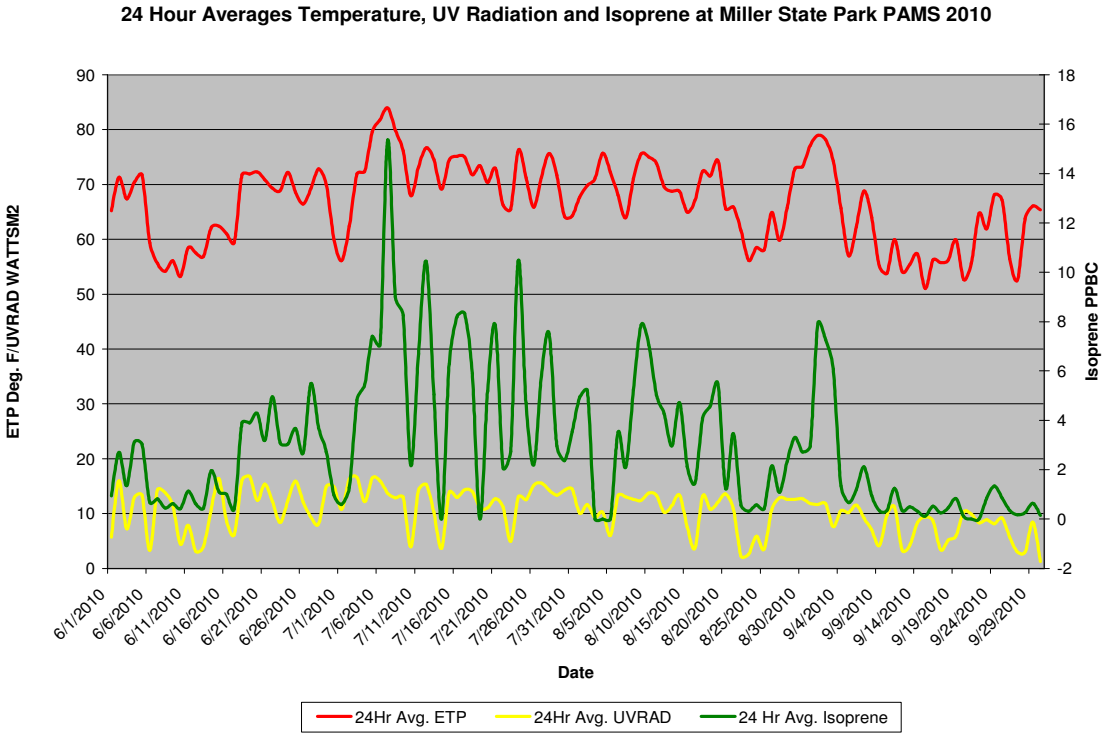




2010 SEASONAL TRACKING SUMMARY FOR TEMPERATURE, UV RADIATION AND ISOPRENE

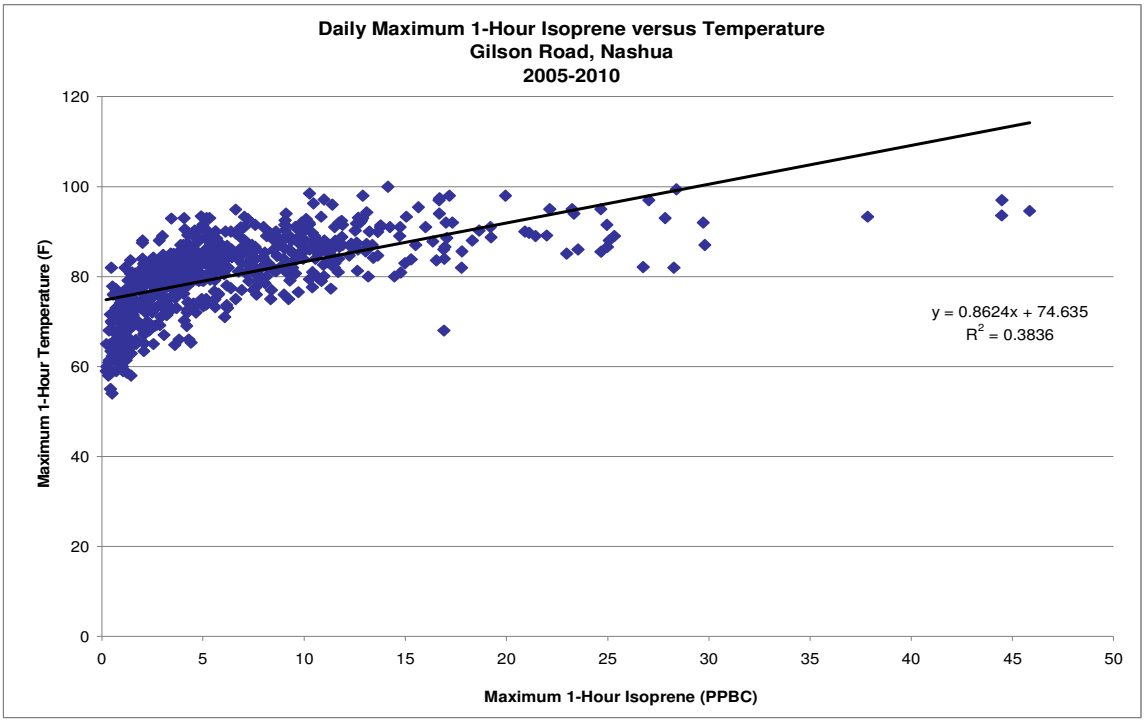
Here, the correlation of isoprene and temperature is examined as well as UV radiation at Miller State Park in 2010. As seen, there is a good comparison of the two proving that isoprene is most present during the hottest days.

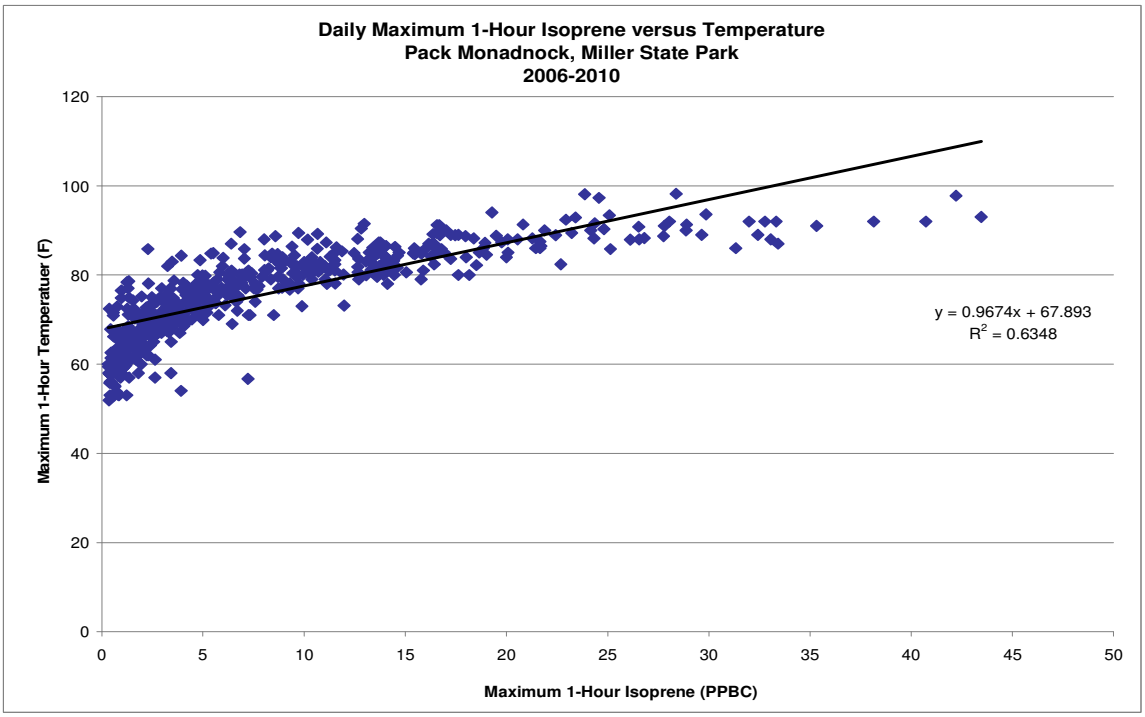




CORRELATION OF ISOPRENE TO TEMPERATURE (all years)

Note the higher R2 value associated with the Pack Monadnock data. Isoprene at Miller State Park appears to trend well with increasing temperature and UV radiation during mid-afternoon, while Isoprene at Gilson peaks at a later hour, after the peak in temperature, as seen in the graphs below. The results support that to a large degree higher temperatures lead to higher local isoprene emissions.

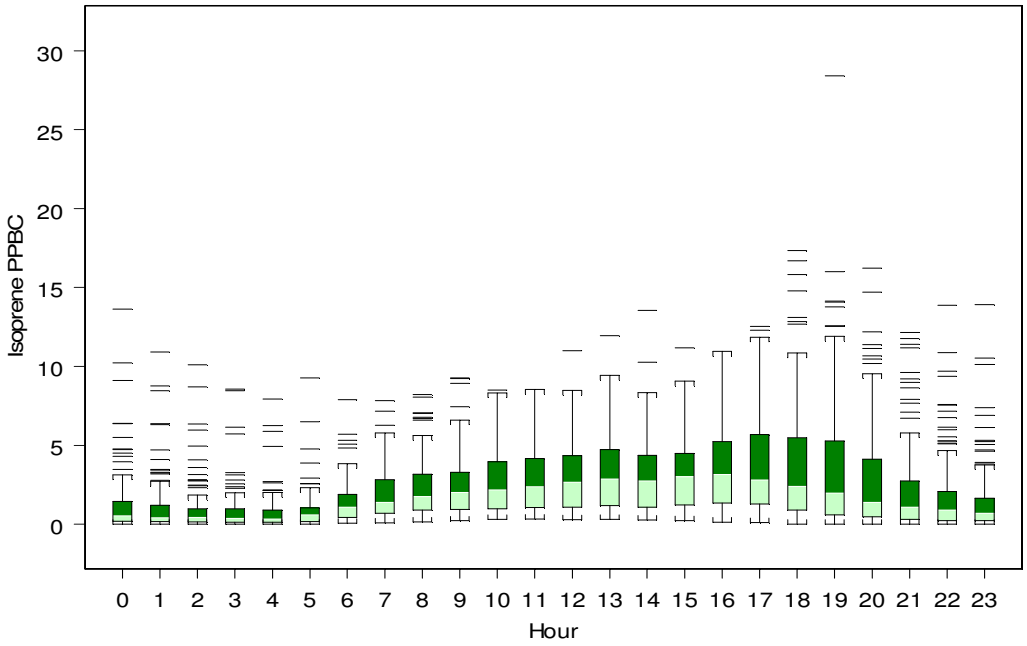




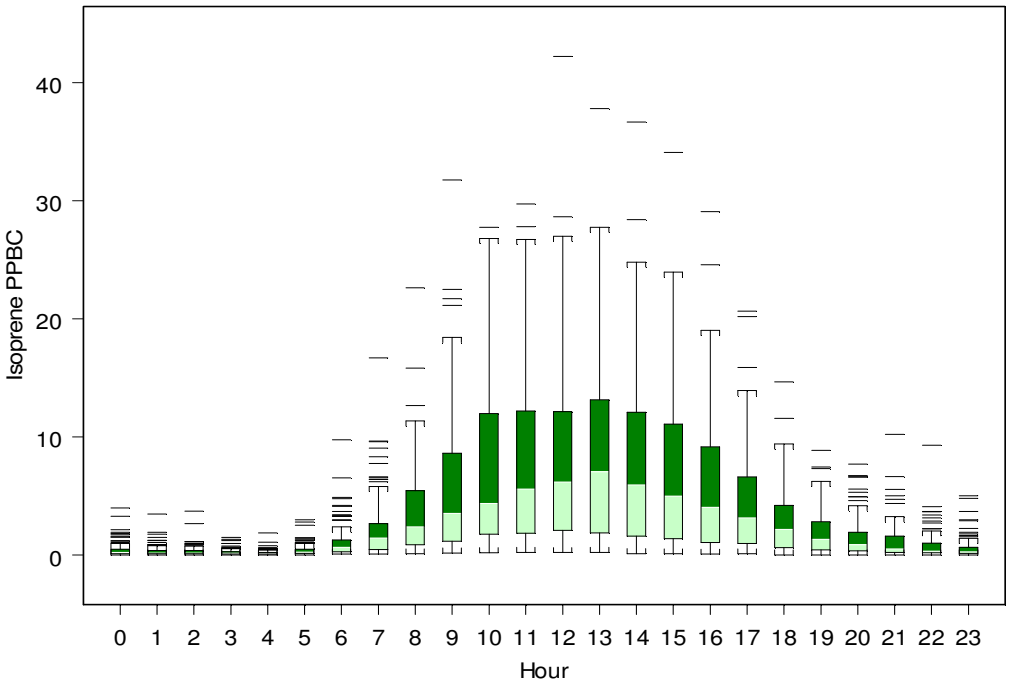
2010 AVERAGE DIURNAL PATTERNS FOR ISOPRENE

Hourly data for the 2010 PAMS season is graphed above, and is consistent with previous years. Again the difference in the diurnal pattern of Isoprene is quite noticeable at Gilson Rd. compared to the more expected pattern at Miller State Park. Miller peaks during max UV around noon to 1 pm while Gilson peaks during mid to late afternoon.

Isoprene Concentrations by Hour of Day at Gilson Rd. PAMS 2010

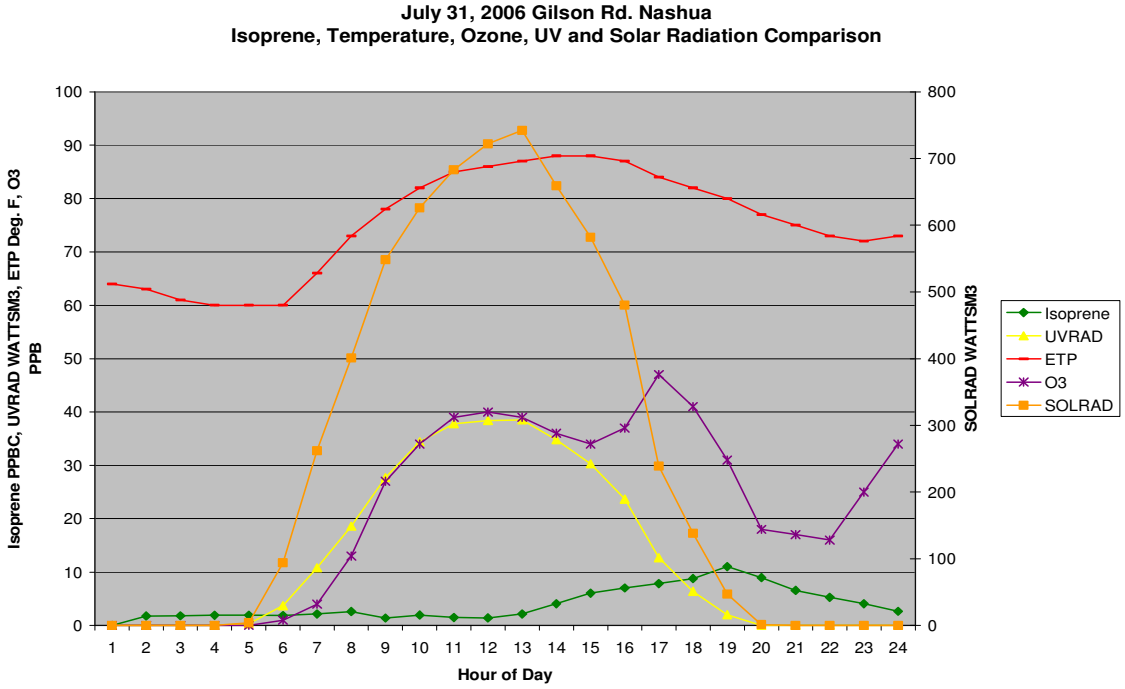


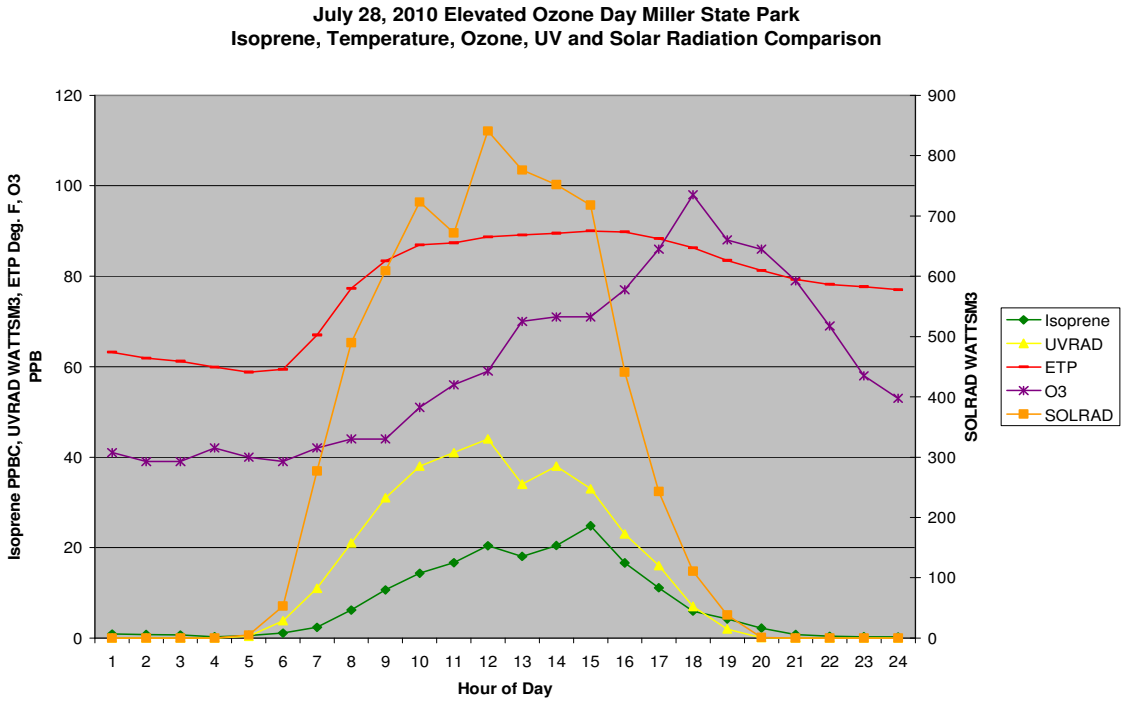
Isoprene Concentrations by Hour of Day at Miller State Park PAMS 2010

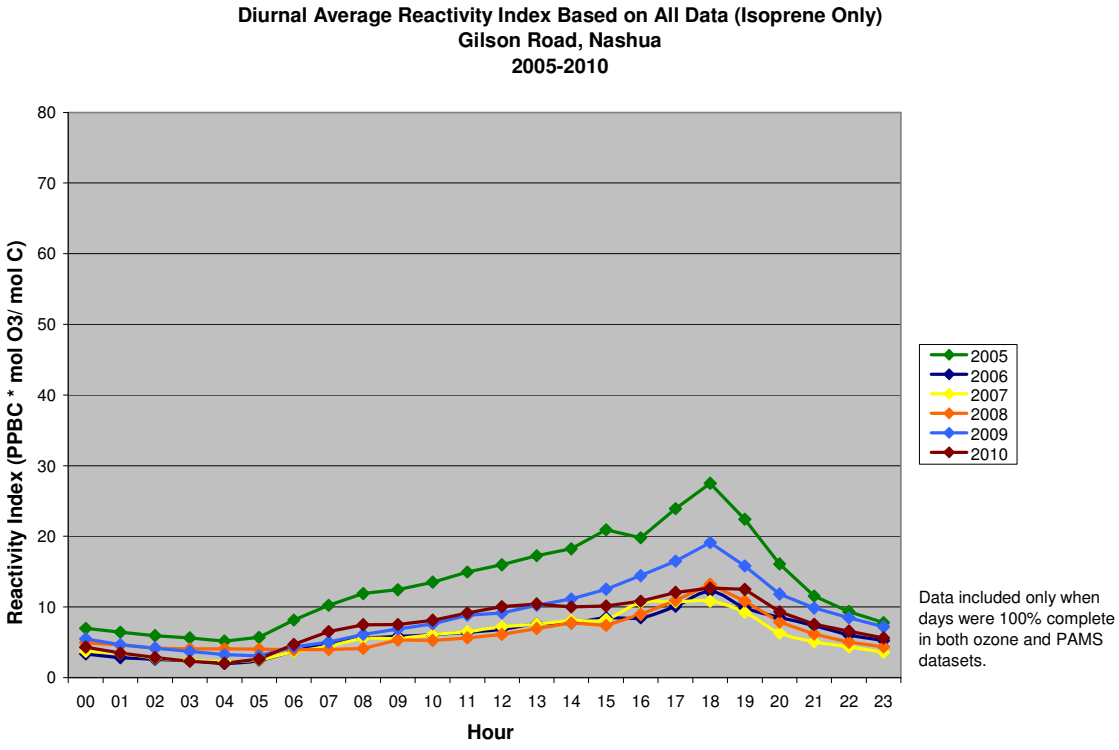


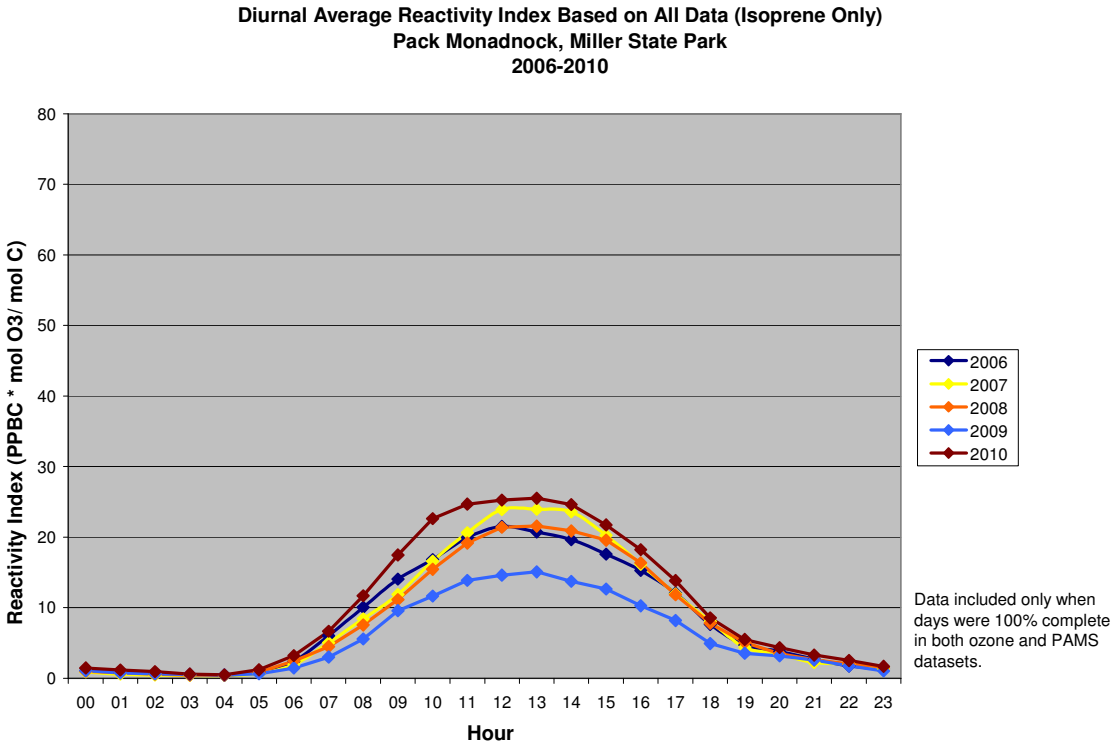
2006 AND 2010 EPISODE COMPARISON TRACKING OF O3, ISOPRENE, TEMPERATURE AND SOLAR RADIATION

Solar and UV Radiation sensors were installed at the Gilson Rd. PAMS site for 2006 then subsequently moved to Miller. We know that temperature and sunlight play a major role in Isoprene production which is showcased nicely in the Miller graph above. However the major difference at Gilson Rd. has been steadily seen even going back to 2006 data.





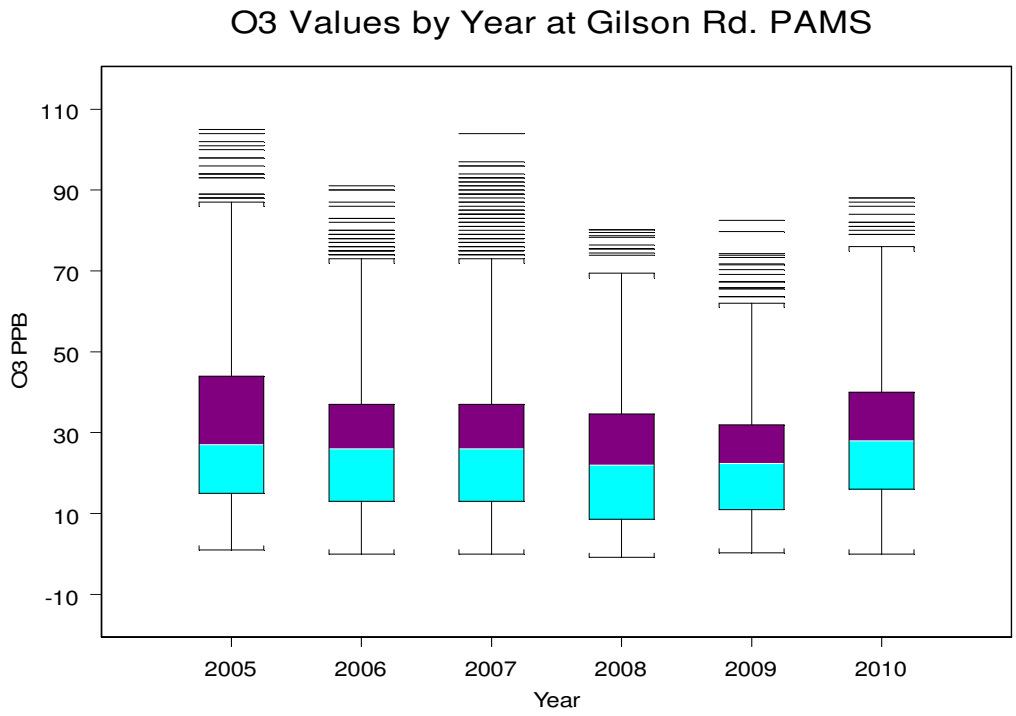


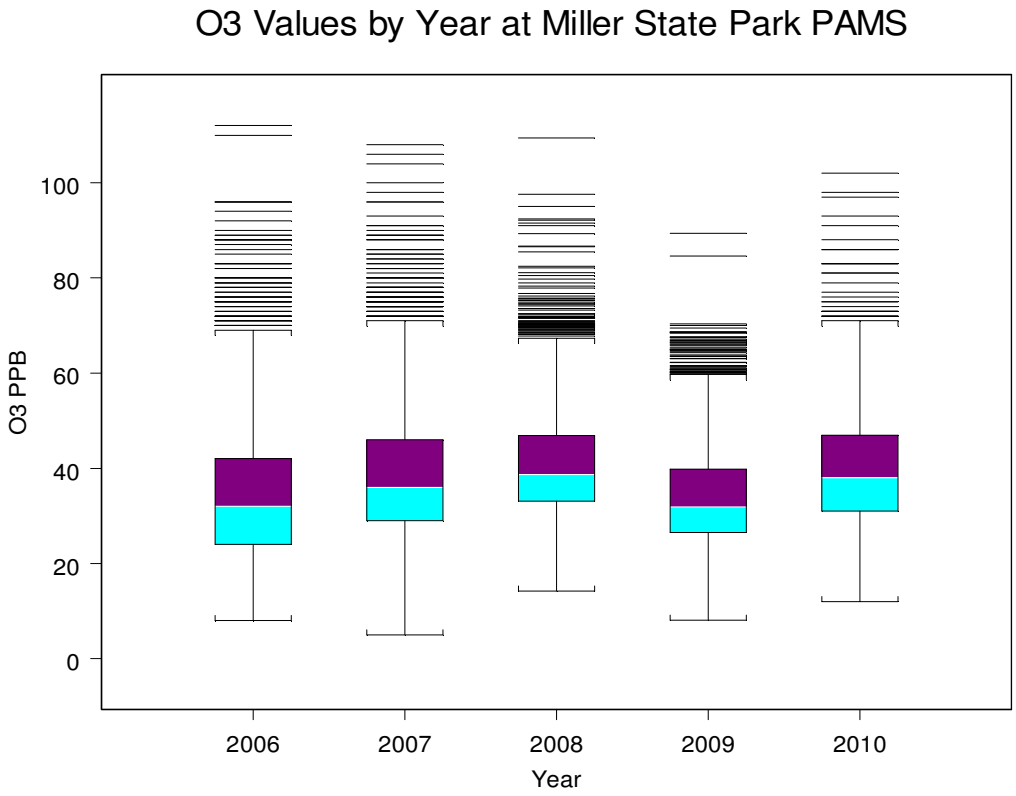


The site patterns remain consistent since PAMS monitoring started at both sites.

OZONE TRENDS: BOX AND WHISKER PLOTS

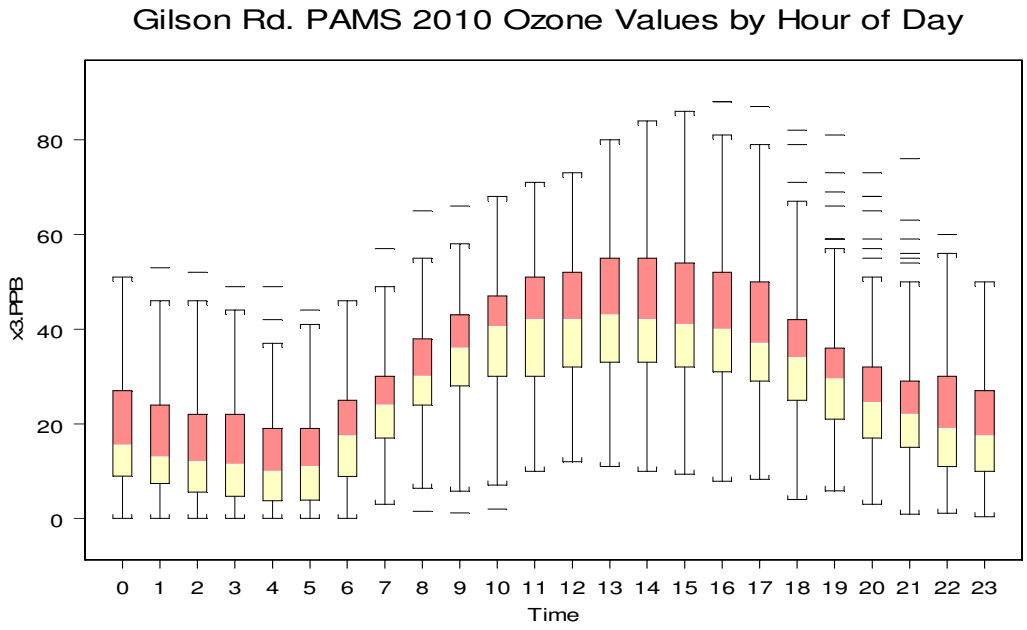
Ozone levels at both sites show an increase in 2010 over the previous couple of years.

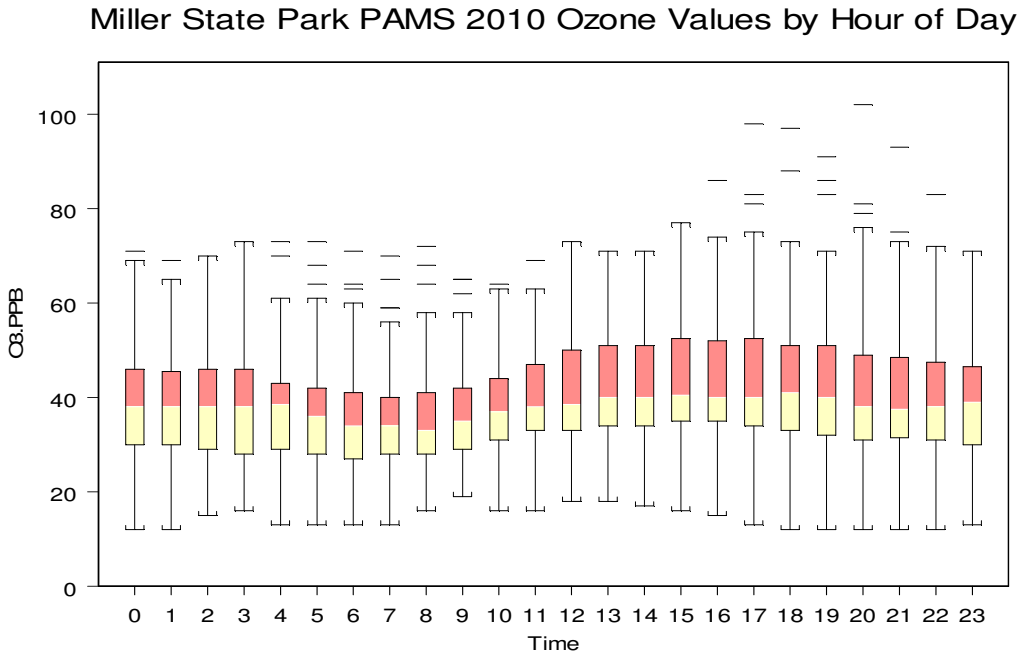




2010 AVERAGE DIURNAL OZONE PATTERN BOX AND WHISKER PLOTS

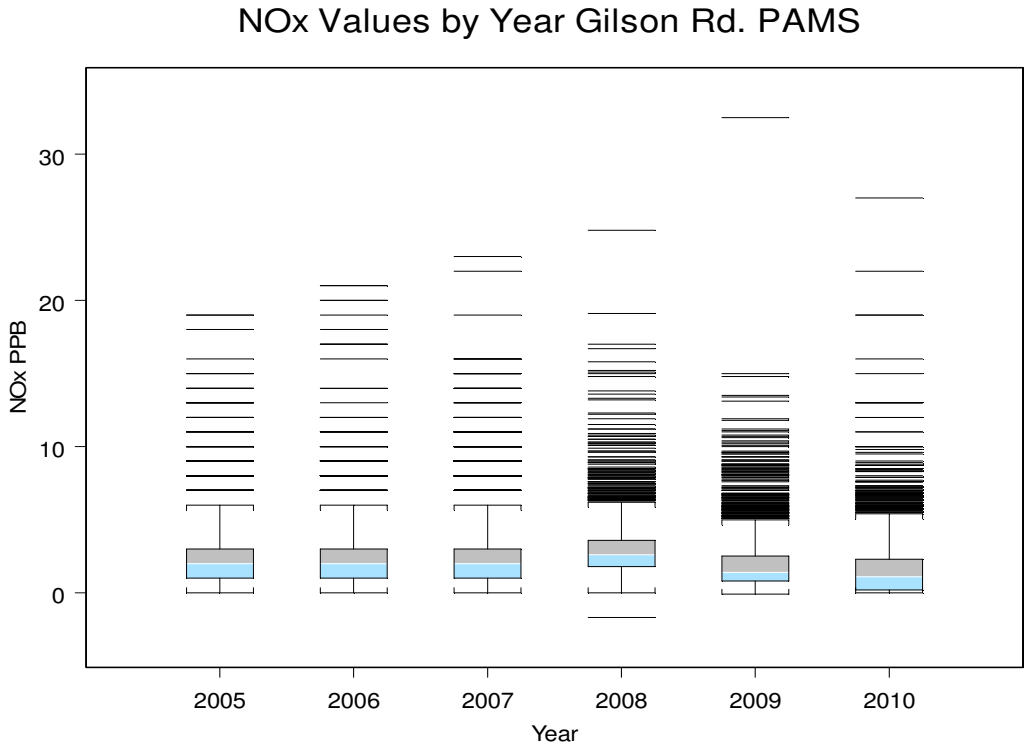
Due to the high elevation of the Miller site (2290 ft.), there is much less of a diurnal pattern with Ozone as is typical with higher elevation sites. Ozone is not depleted at night due to minimal effect of ozone removal mechanisms at ground level and direct exposure to the atmospheric transport layers; it remains constant throughout the day. Miller is exposed to the impacts of long range transport without the overnight removal process and is therefore more likely to exceed the standard. Higher elevations of ozone at this elevation could be used in tracking air pollution as it enters the lower elevations of southern NH.

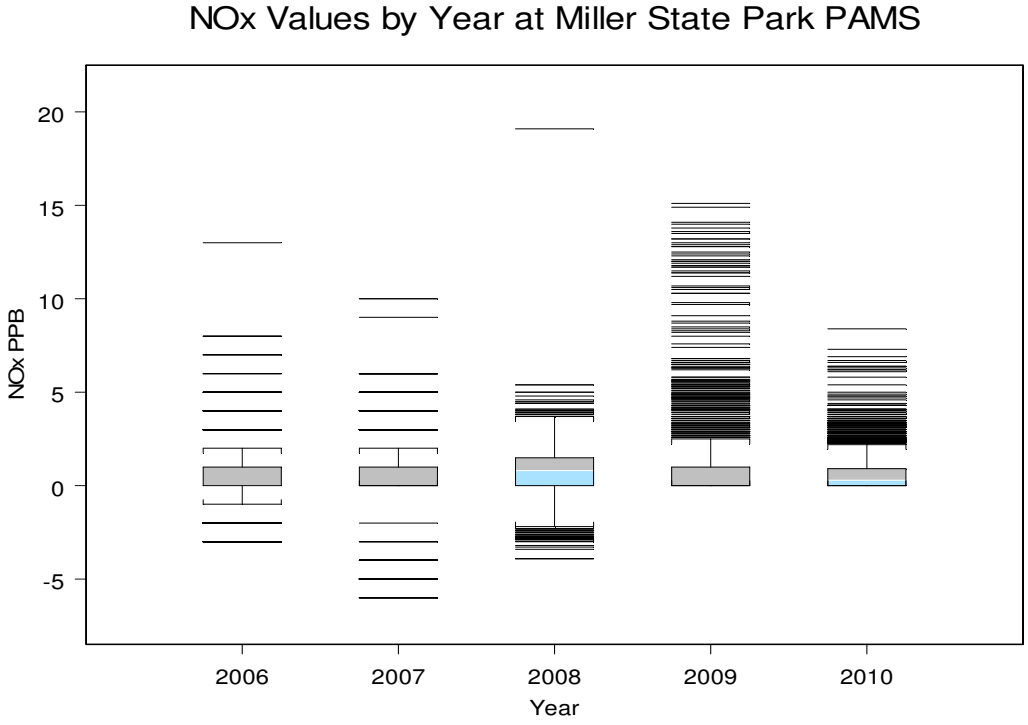




NOx TRENDS: BOX AND WHISKER PLOTS

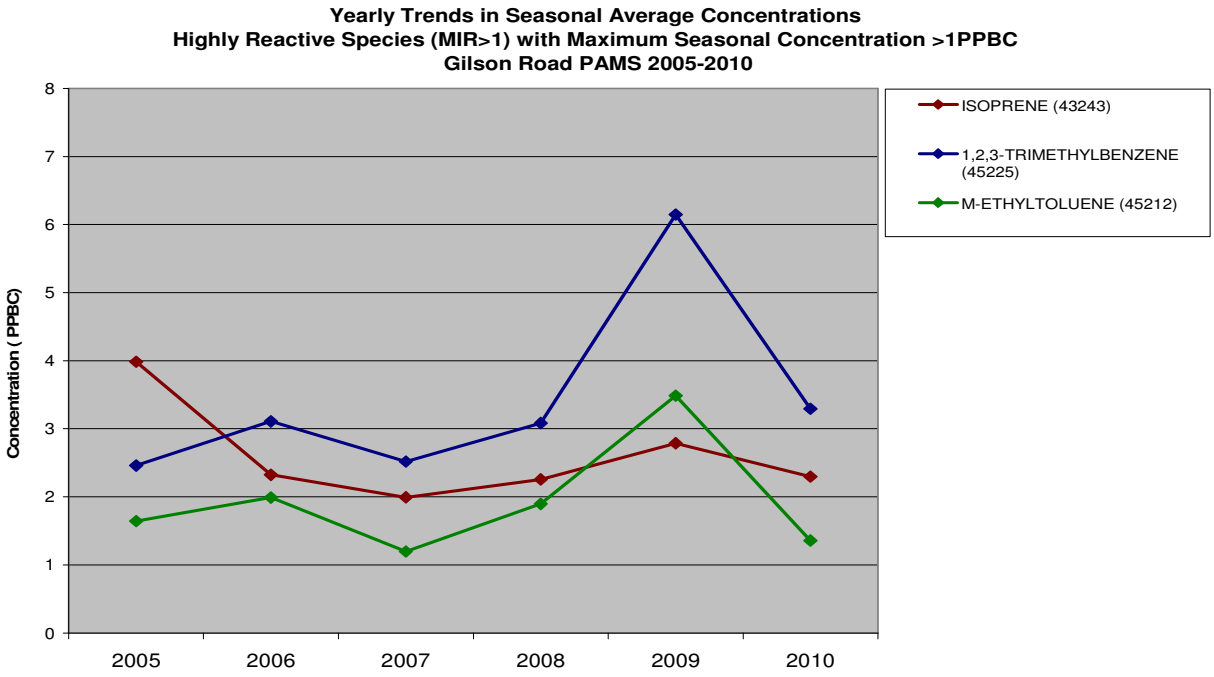
Overall, NOx values at Miller are much lower than at Gilson Rd. This is typical of measurements made in higher elevations (atmospheric boundary layer) and is compounded by Miller's rural location.

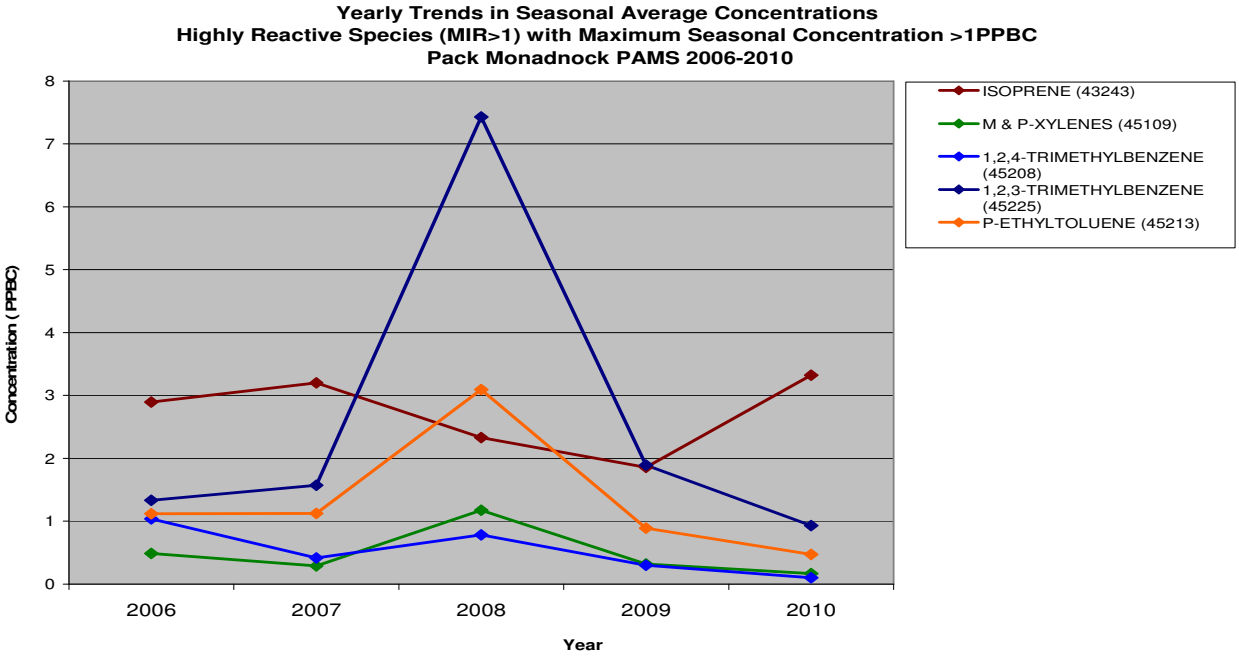




TRENDS OF MOST PHOTOCHEMICALLY REACTIVE PAMS SPECIES

Aside from the anomalies associated with paving at Gilson Rd. in 2009 and the carryover with the 2008 Miller data, the compounds follow the expected trends, including the increase in isoprene due to the weather associated with the summer of 2010.

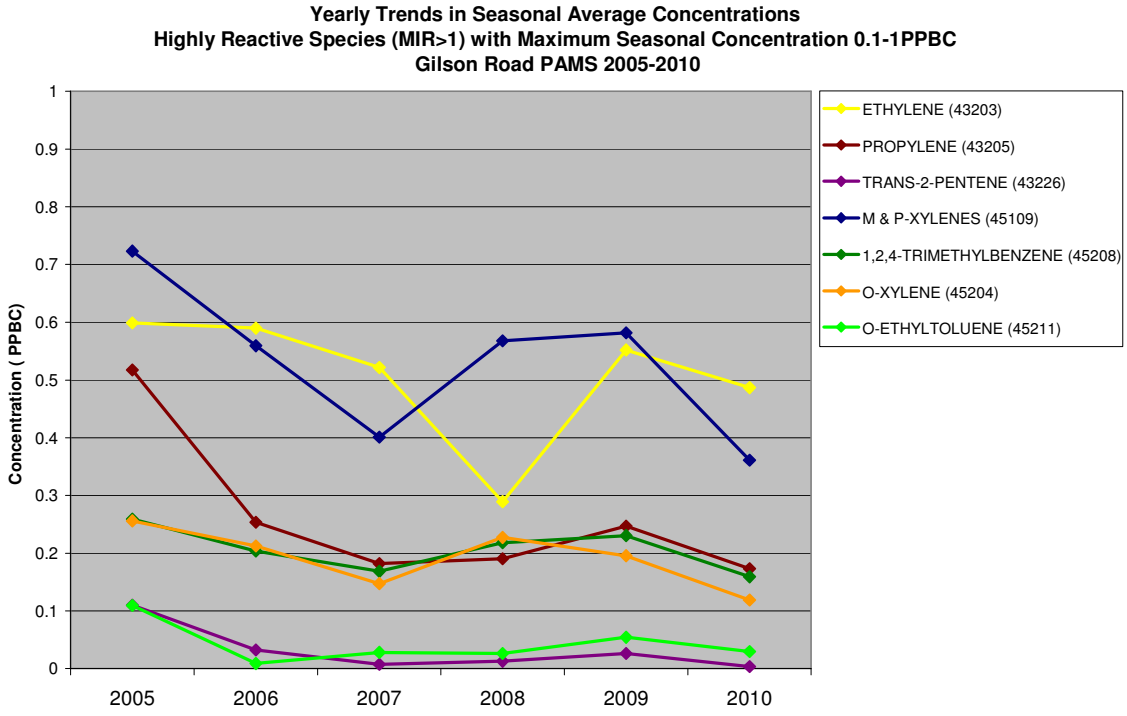


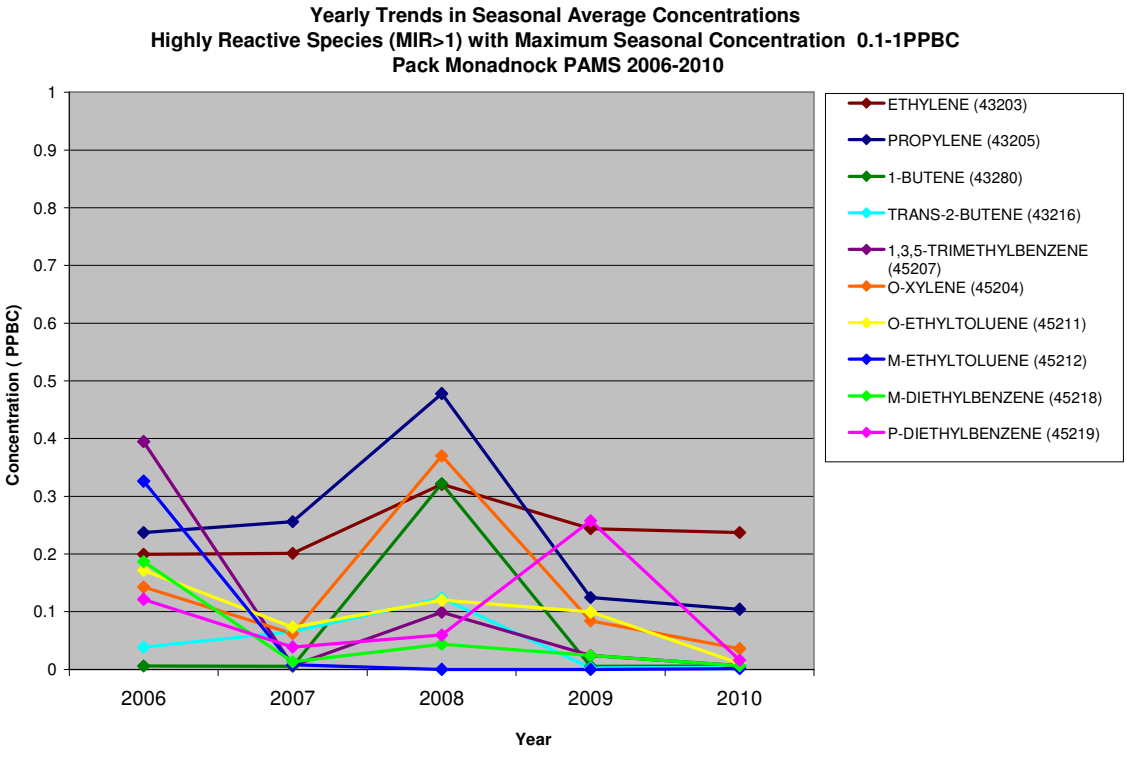


TRENDS OF MOST PHOTOCHEMICALLY REACTIVE PAMS SPECIES

(continued)

Aside from the anomalies associated with paving at Gilson Rd. in 2009 and the carryover with the 2008 Miller data, the compounds follow the expected trends.



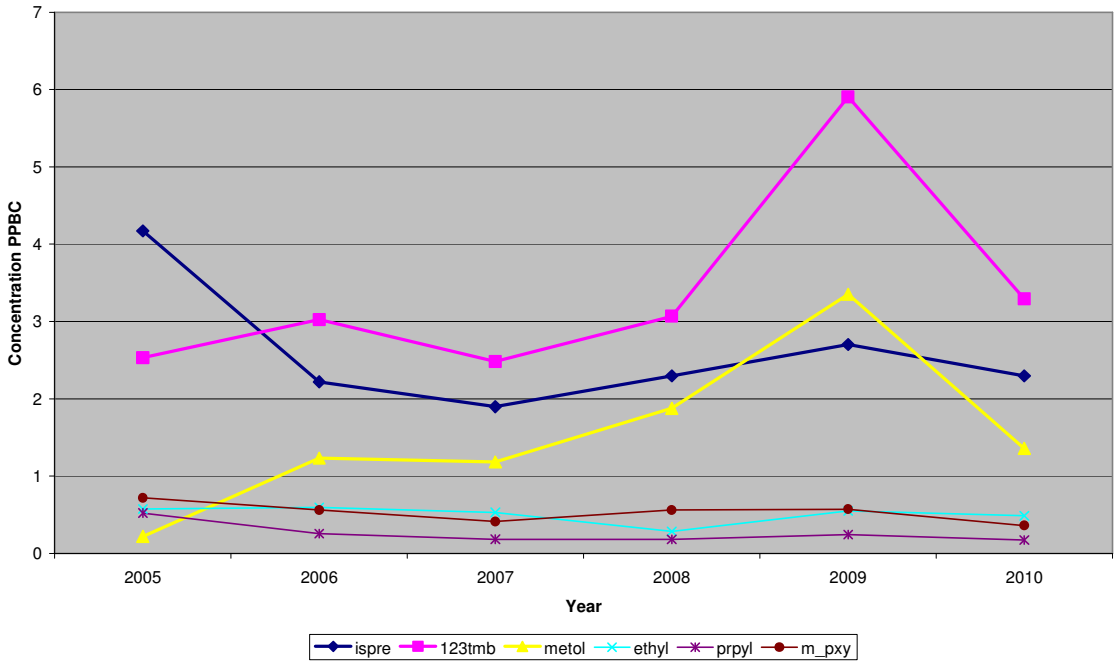


TRENDS OF MOST PHOTOCHEMICALLY REACTIVE PAMS SPECIES

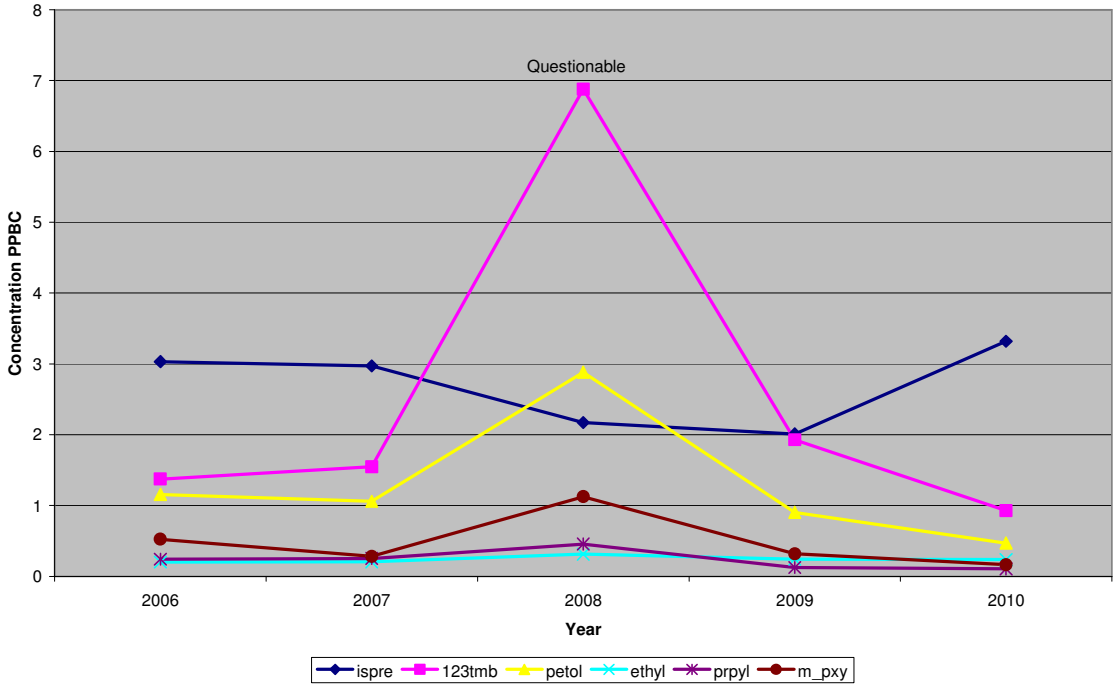
(continued)

Aside from the anomalies associated with paving at Gilson Rd. in 2009 and the carryover with the 2008 Miller data, the compounds follow the expected trends.

Average Trends of Most Common Photochemically Reactive Species
Gilson Rd. PAMS



Yearly Trends of Most Common Photochemically Reactive Species Miller State Park PAMS



Seasonal 24-hour Max Values at Gilson Rd. for Toxic PAMS Species Compared to the Ambient Allowable Limit

PAMS Parameter	AAL Ug/m3	Max 24 Hour Average (ug/m3)						Max as % of AAL
		2005	2006	2007	2008	2009	2010	
PROPYLENE (43205)	35,833	0.55	0.34	0.30	0.33	0.35	0.20	0.00%
CYCLOPENTANE (43242)	25,595	0.23	0.23	0.16	0.13	0.15	0.10	0.00%
ISOPENTANE (43221)	36,875	2.04	2.50	1.56	1.41	1.23	1.13	0.01%
PENTANE (43220)	36,875	3.13	1.39	0.85	0.74	0.76	0.61	0.01%
2-METHYLPENTANE (43285)	36,875	0.60	0.78	0.21	0.35	0.25	0.18	0.00%
3-METHYLPENTANE (43230)	36,875	0.41	0.48	0.20	0.30	0.20	0.25	0.00%
HEXANE (43231)	885	0.59	0.58	0.47	0.74	0.51	1.18	0.13%
BENZENE (45201)	6	0.51	0.74	0.36	0.42	0.37	0.29	12.91%
CYCLOHEXANE (43248)	6,000	0.25	0.21	0.21	0.48	0.19	0.29	0.01%
HEPTANE (43232)	8,249	0.56	0.34	0.18	0.32	0.25	0.12	0.01%
METHYLCYCLOHEXANE (43261)	23,958	0.21	0.21	0.11	0.16	0.10	0.06	0.00%
TOLUENE (45202)	5,000	2.37	2.67	1.39	1.97	1.60	1.77	0.05%
OCTANE (43233)	7,000	0.32	0.13	0.10	0.13	0.09	0.07	0.00%
ETHYLBENZENE (45203)	1,000	0.36	0.36	0.18	0.39	0.57	0.14	0.06%
M & P-XYLENES (45109)	1,550	0.88	0.96	0.68	1.15	2.04	0.45	0.13%
STYRENE (45220)	1,000	0.88	0.13	0.22	0.07	0.06	0.13	0.09%
O-XYLENE (45204)	1,550	0.32	0.36	0.26	0.40	0.40	0.16	0.03%
NONANE (43235)	15,625	0.21	0.13	0.21	0.10	0.11	0.07	0.00%
1,3,5-TRIMETHYLBENZENE (45207)	619	0.11	0.12	0.09	0.32	0.17	0.09	0.05%
1,2,4-TRIMETHYLBENZENE (45208)	619	0.32	0.39	0.32	0.39	0.31	0.18	0.06%

Seasonal 24-hour Max Values at Miller State Park for Toxic PAMS Species Compared to the Ambient Allowable Limit

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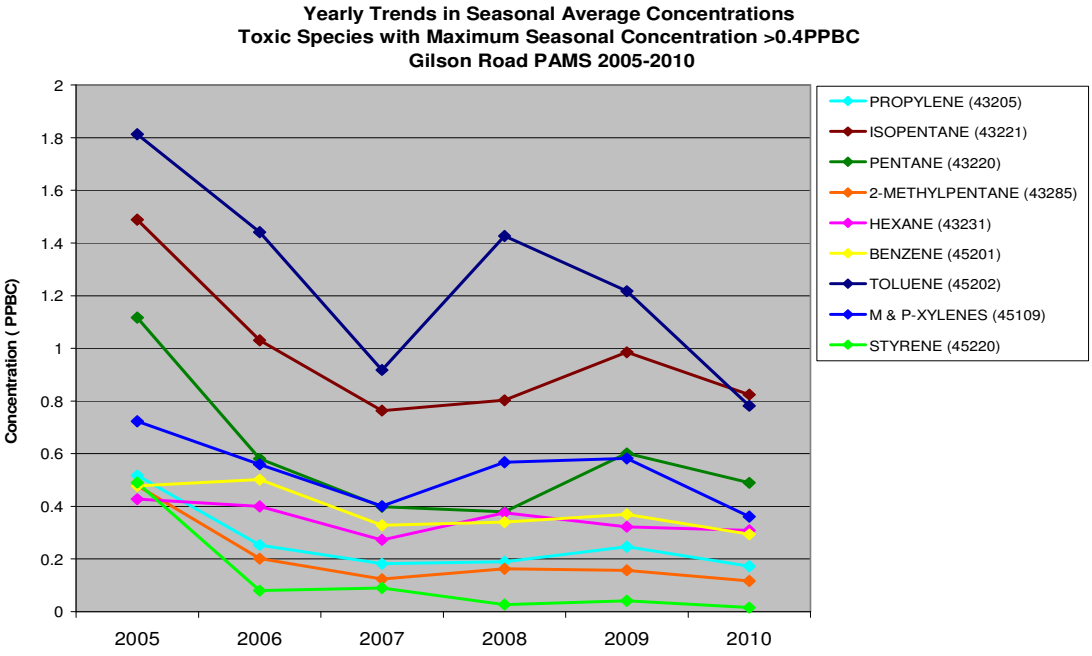
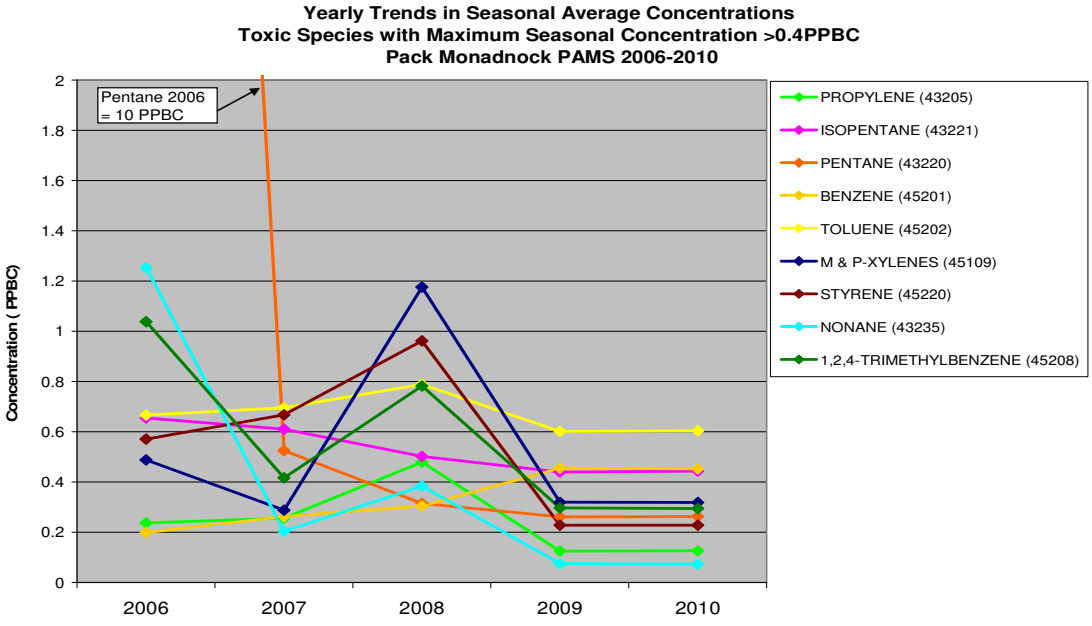
		2006	2007	2008	2009	2010	
PROPYLENE (43205)	35,833	0.28	0.25	0.46	0.15	0.20	0.00%
CYCLOPENTANE (43242)	25,595	0.42	0.53	1.63	0.09	0.29	0.01%
ISOPENTANE (43221)	36,875	1.03	1.09	0.70	0.89	0.75	0.00%
PENTANE (43220)	36,875	45.41	7.63	0.55	0.45	0.38	0.12%
2-METHYLPENTANE (43285)	36,875	0.19	0.27	0.04	0.06	0.04	0.00%
3-METHYLPENTANE (43230)	36,875	0.13	0.17	0.01	0.04	0.03	0.00%
HEXANE (43231)	885	0.21	0.27	0.19	0.32	1.36	0.15%
BENZENE (45201)	6	0.31	0.33	0.32	0.41	0.73	12.79%
CYCLOHEXANE (43248)	6,000	0.14	0.05	0.02	0.08	0.04	0.00%
HEPTANE (43232)	8,249	0.71	0.16	0.15	0.17	0.13	0.01%
METHYLCYCLOHEXANE (43261)	23,958	1.23	0.15	0.15	0.11	0.16	0.01%
TOLUENE (45202)	5,000	1.00	1.05	1.11	1.01	0.77	0.02%
OCTANE (43233)	7,000	0.91	0.17	0.27	0.11	0.06	0.01%
ETHYLBENZENE (45203)	1,000	0.35	0.20	0.59	0.21	0.15	0.06%
M & P-XYLENES (45109)	1,550	1.88	0.37	2.38	0.46	0.23	0.15%
STYRENE (45220)	1,000	1.03	1.13	1.80	0.40	0.08	0.18%
O-XYLENE (45204)	1,550	0.60	0.13	0.67	0.15	0.08	0.04%
NONANE (43235)	15,625	8.83	1.33	0.57	0.23	0.08	0.06%
1,3,5-TRIMETHYLBENZENE (45207)	619	1.75	0.08	0.29	0.13	0.04	0.28%
1,2,4-TRIMETHYLBENZENE (45208)	619	3.91	1.34	0.79	0.53	0.14	0.63%

TRENDS FOR MOST COMMON TOXIC PAMS SPECIES

Most toxic compound concentrations are decreasing or maintaining with the exception of an increase in Benzene seen at Miller State Park since 2006.



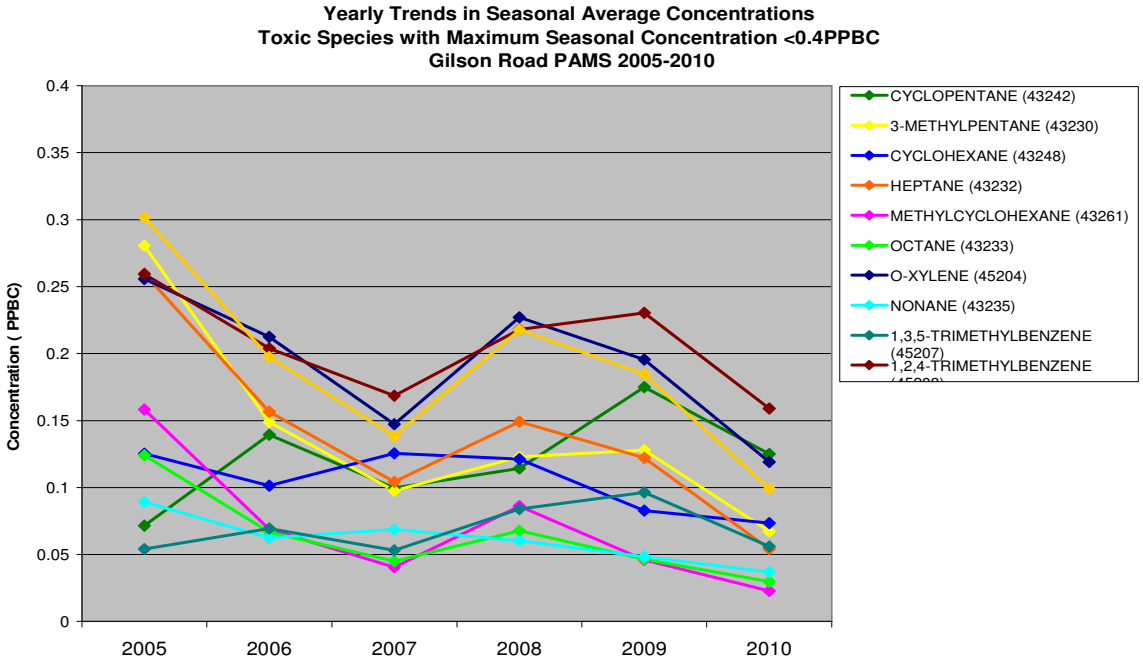


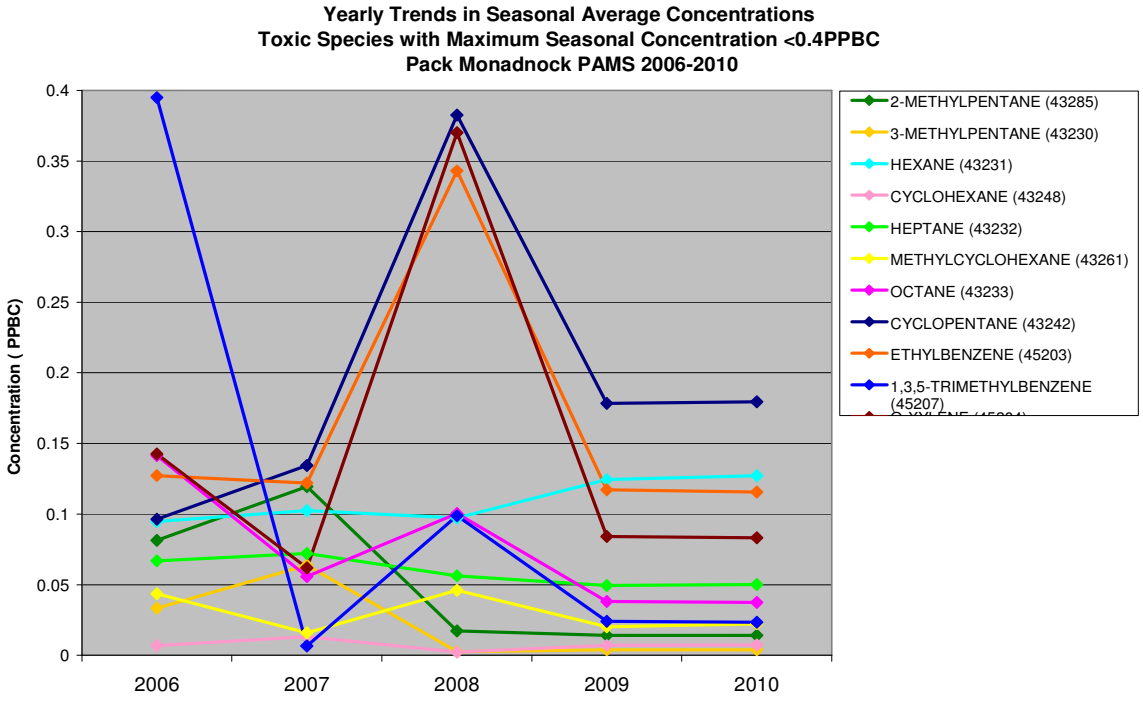
* High pentane in 2006 was due to co-elution with an unknown compound.

TRENDS FOR MOST COMMON TOXIC PAMS SPECIES

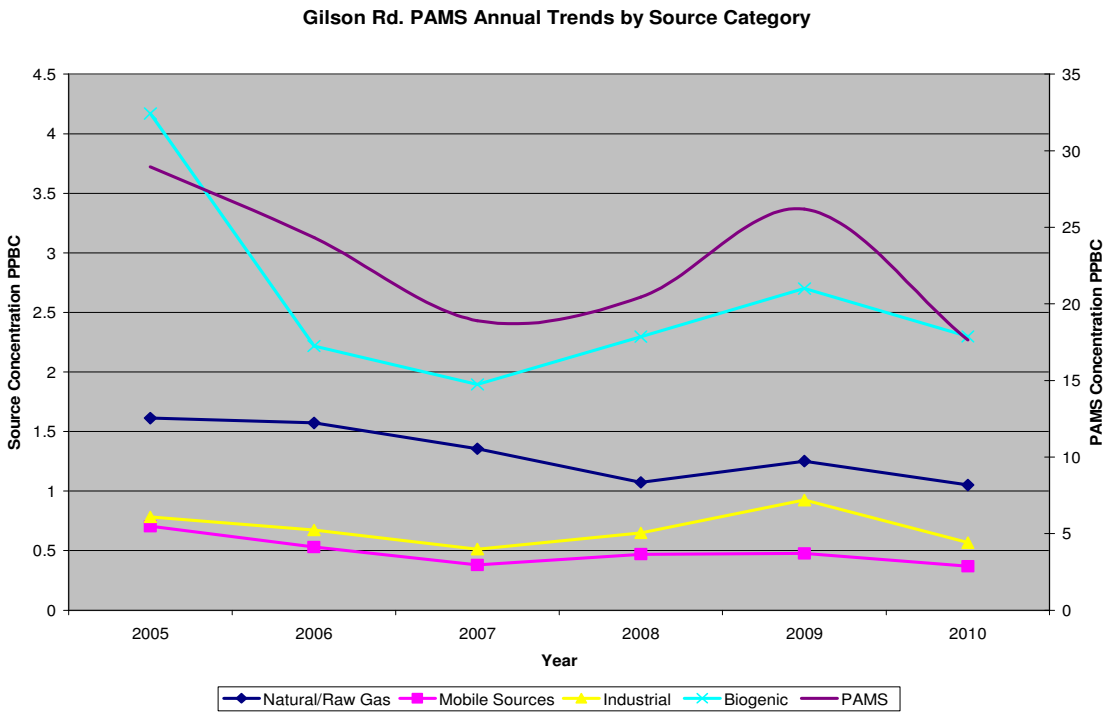
(Continued)

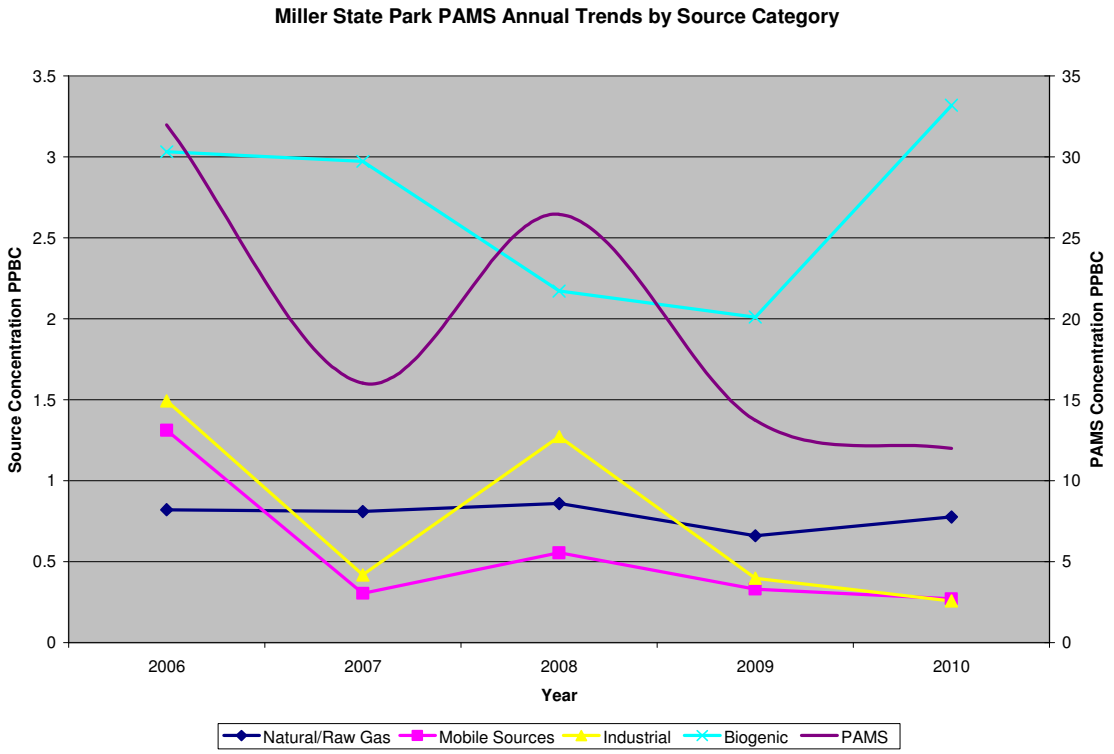
Again, most of the toxic compound concentrations are decreasing or maintaining with the exception of an increase in Hexane seen at Miller State Park.

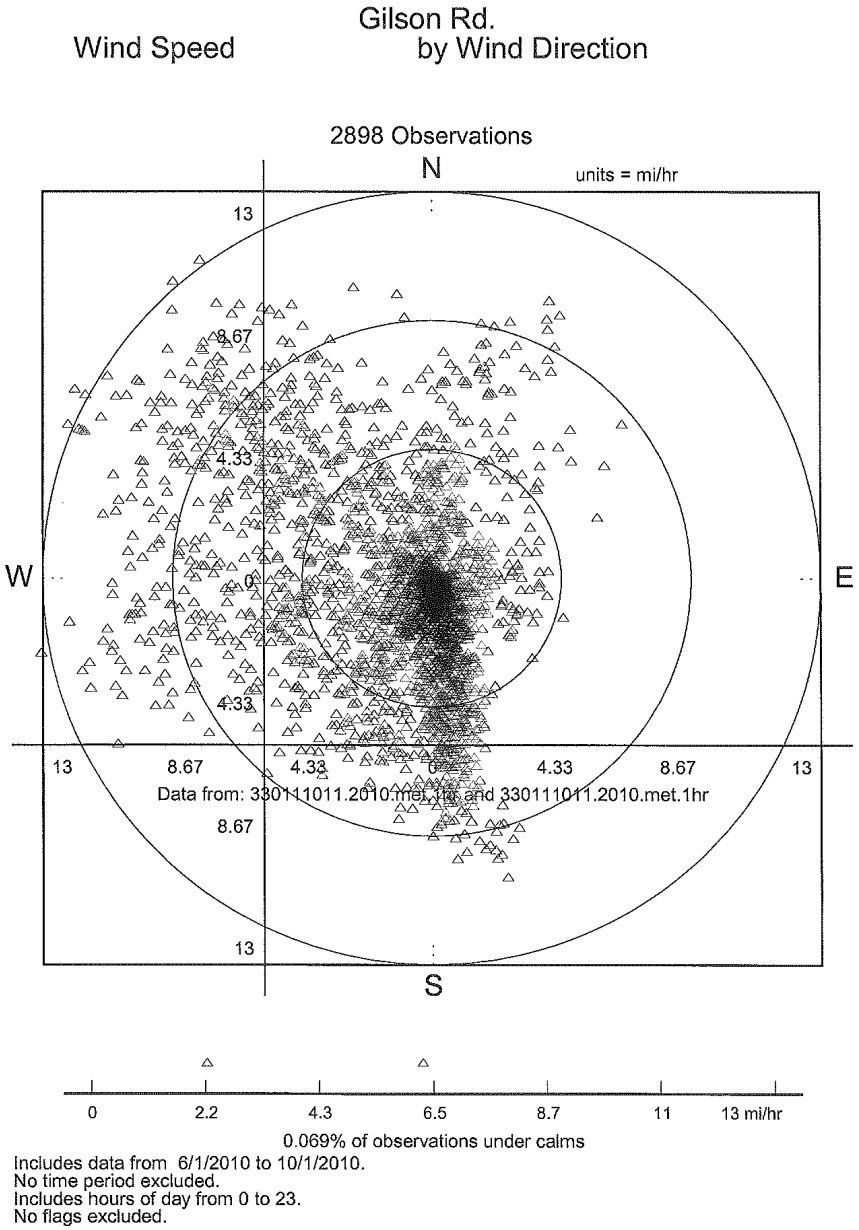




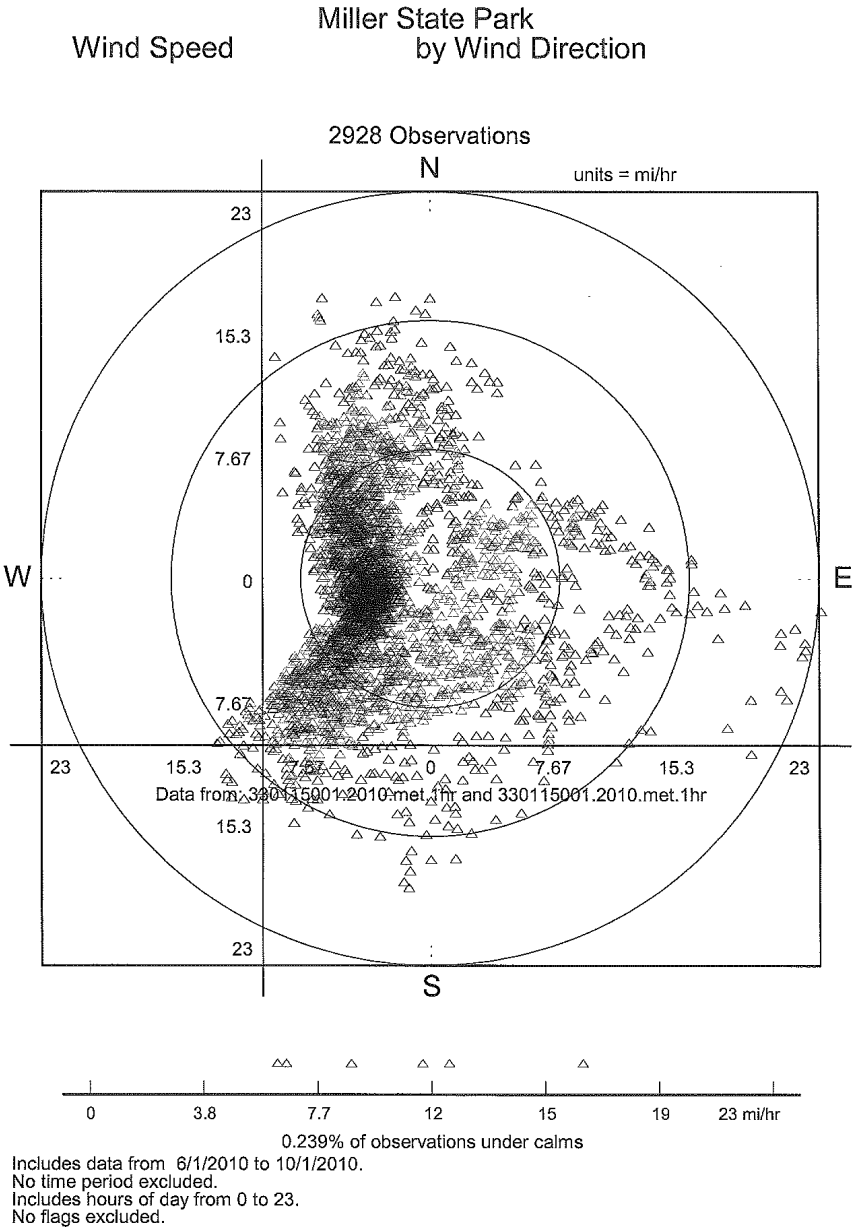
TRENDS BY LIKELY SOURCE CATEGORY





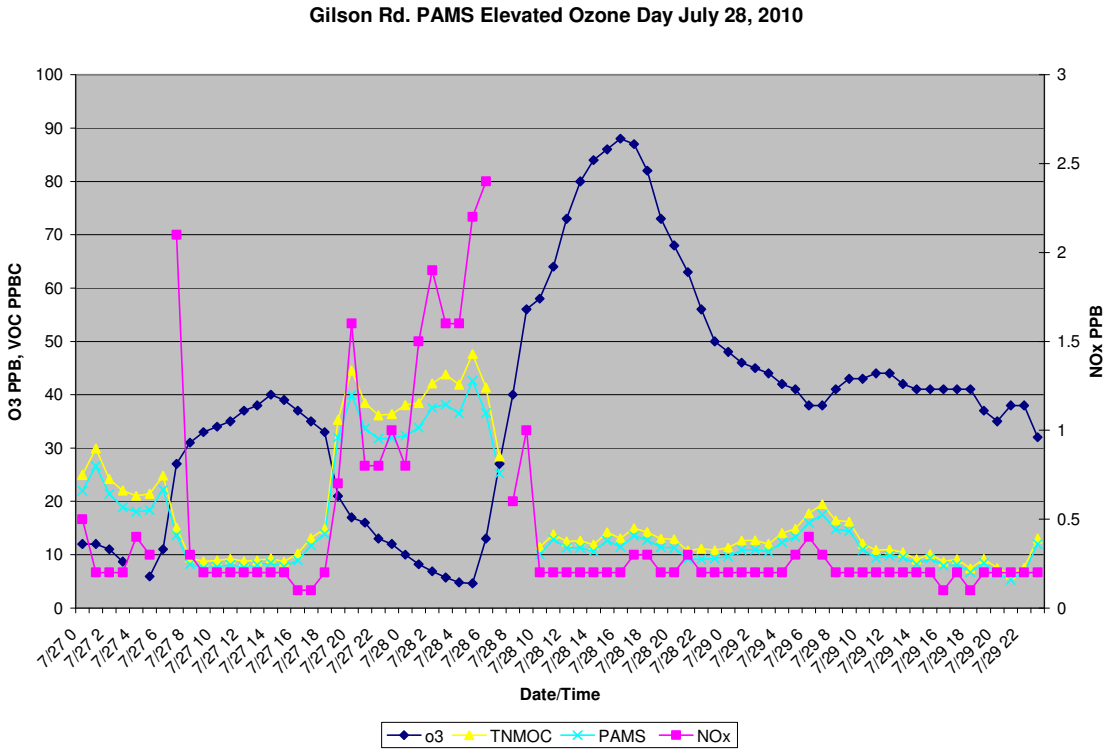


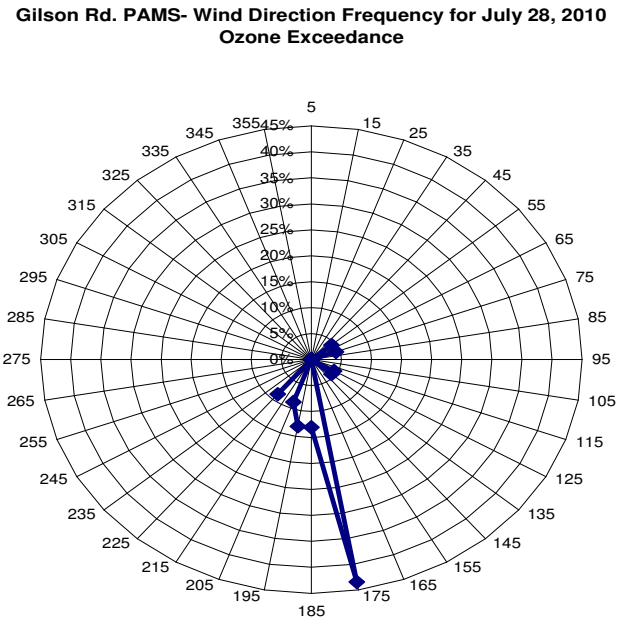
Wind speed and wind direction during the 2010 PAMS season at Gilson Rd. The majority of wind comes from the south, southwest.



Wind speed and wind direction during the 2010 PAMS season at Miller State Park. The majority of the winds come from the southwest and northwest.

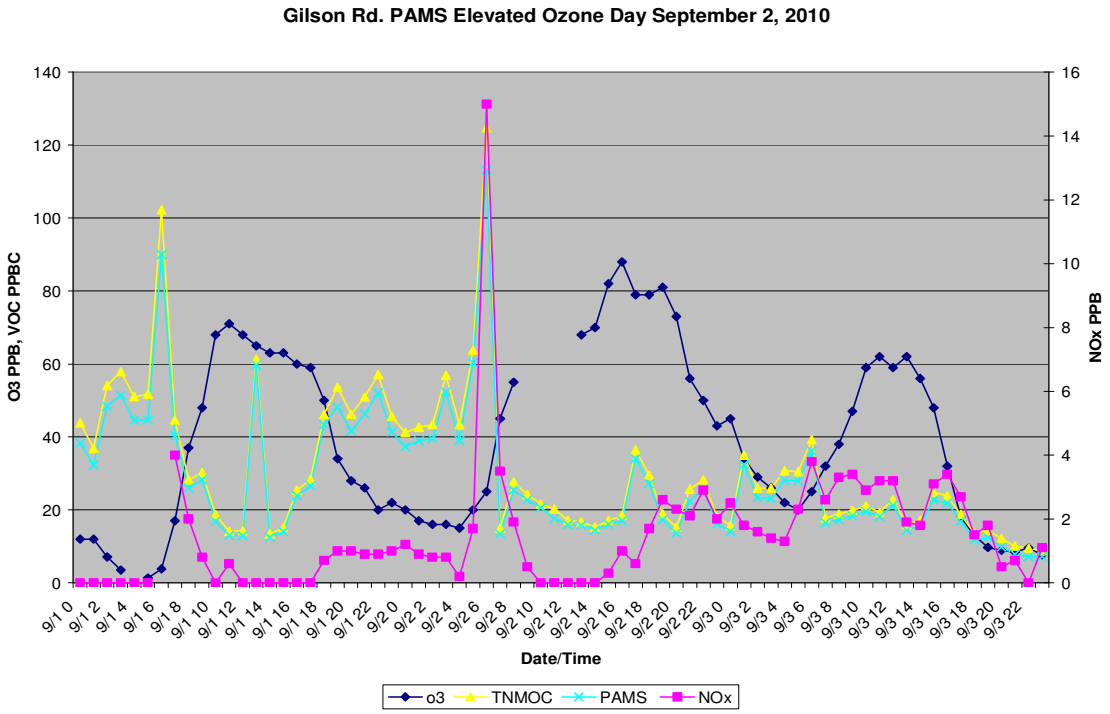
EPISODE SUMMARY FOR JULY 28, 2010 AT GILSON RD.

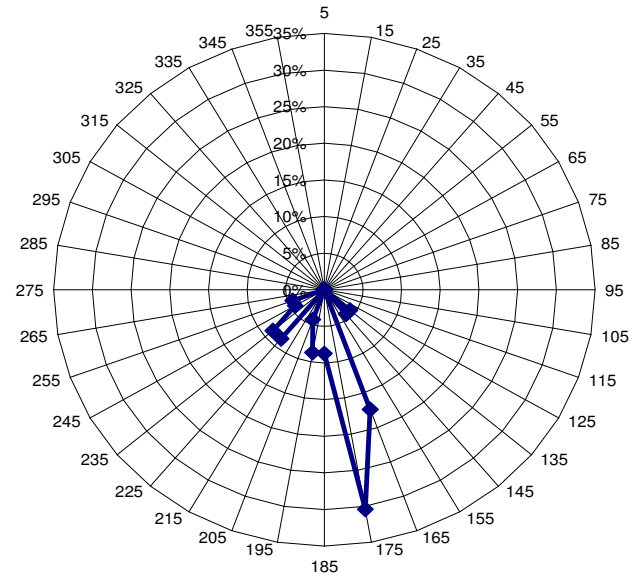




The 8 hour average for ozone at Gilson Rd. on July 28, 2010 was 0.081 ppm. Predominant winds were southerly and NOx levels correlate well with VOC spikes, both acting as O3 precursors for this event.

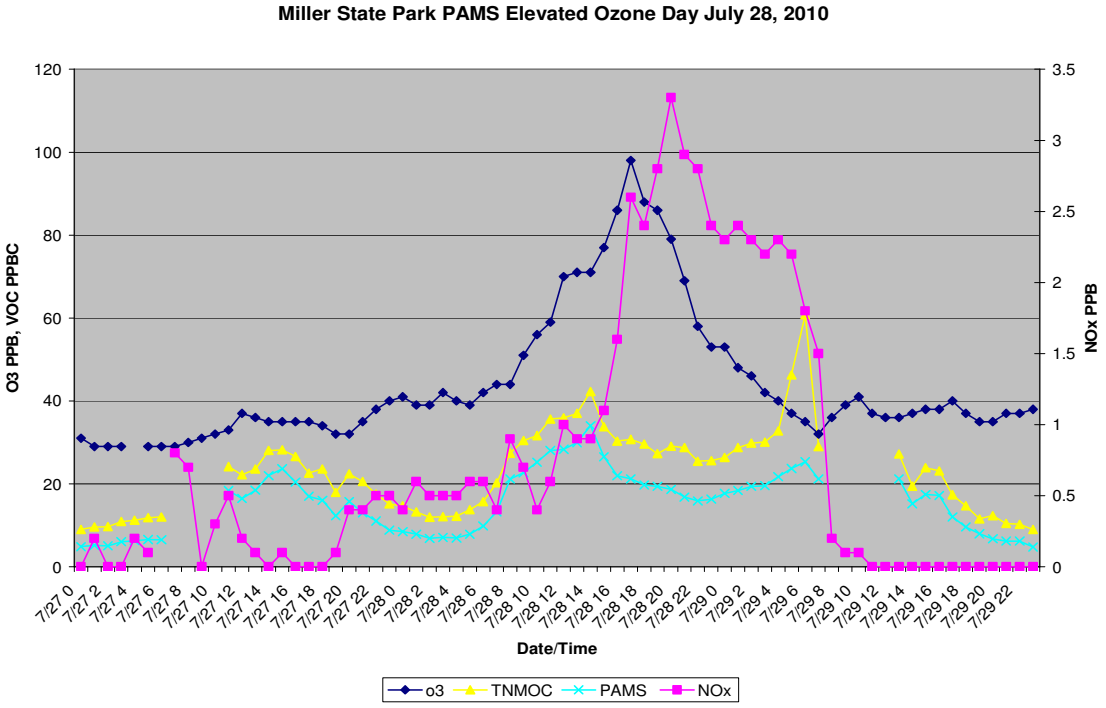
EPISODE SUMMARY FOR SEPTEMBER 2, 2010 AT GILSON RD.

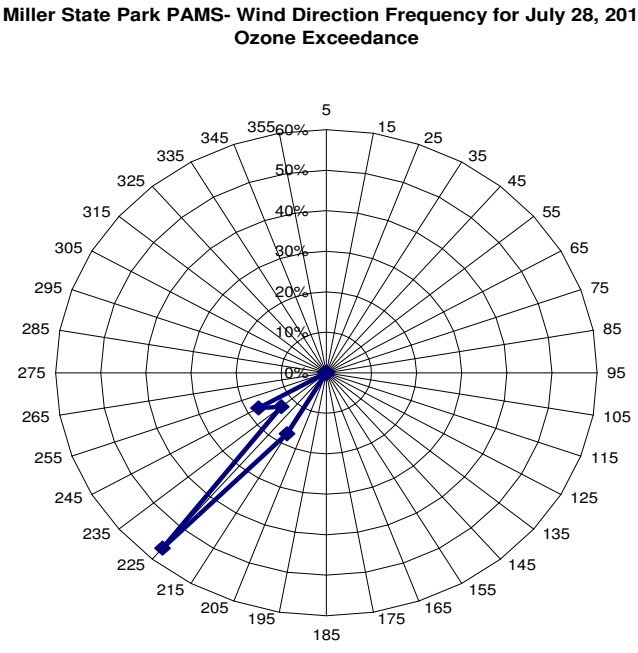




The 8 hour average for Ozone at Gilson Rd. on September 2, 2010 was 0.078 ppm. Winds predominately from the south.

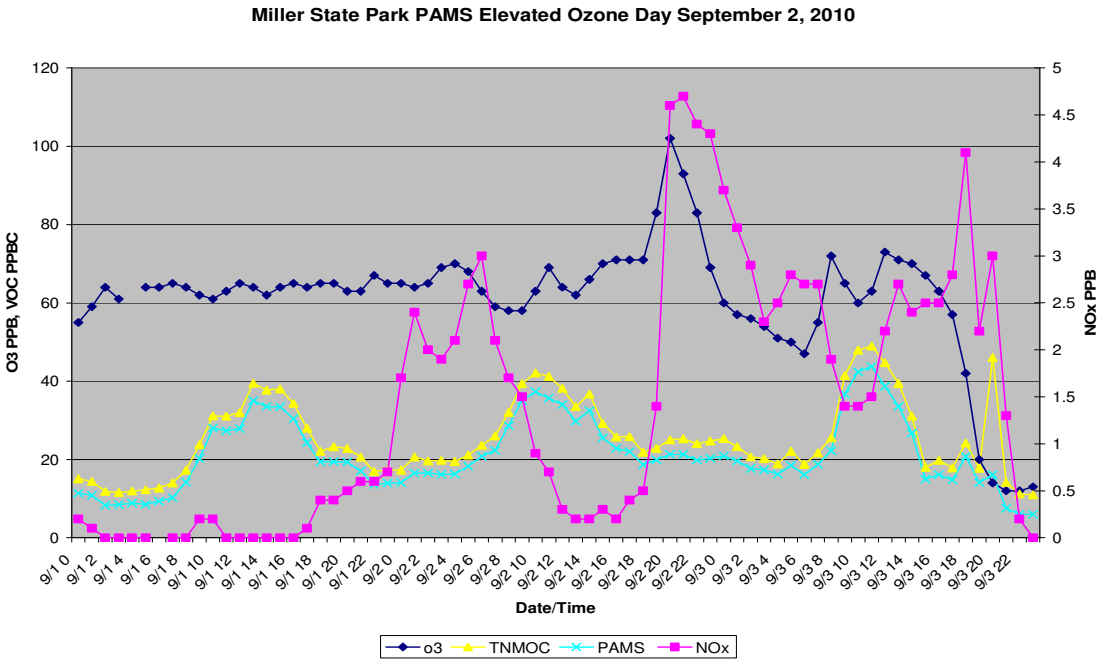
EPISODE SUMMARY FOR JULY 28, 2010 AT MILLER STATE PARK



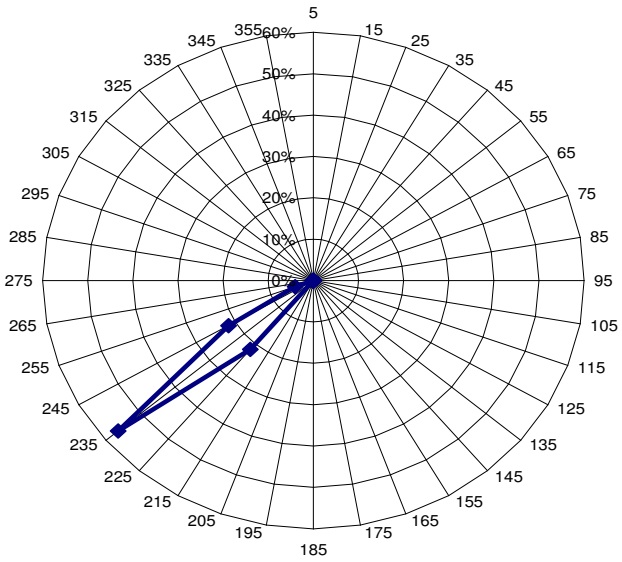


The 8 hour average for ozone at Miller State Park on July 28, 2010 was 0.082 ppm. NOx values peak at approximately the same time as O3 values with no clear peak of VOC concentrations, with winds from the southwest.

EPISODE SUMMARY FOR SEPTEMBER 2, 2010 AT MILLER STATE PARK

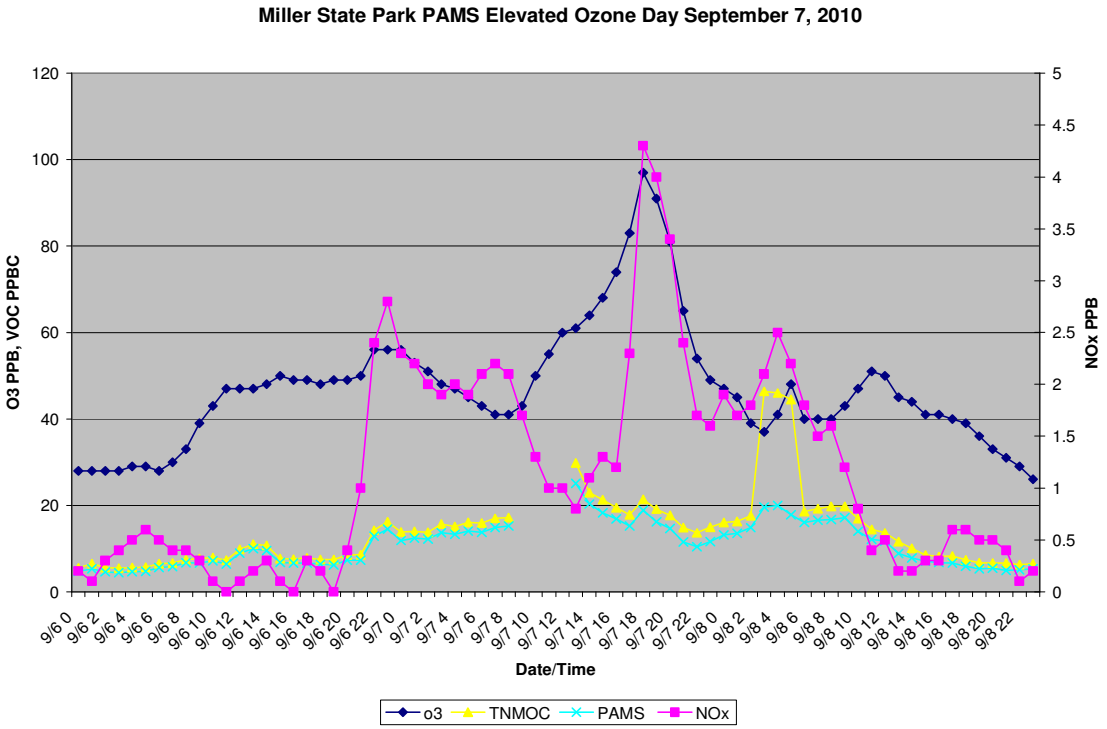


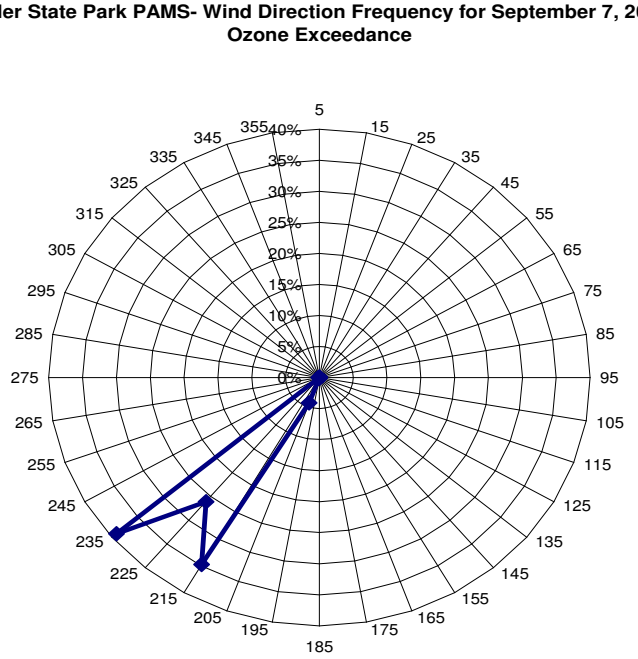
Miller State Park PAMS- Wind Direction Frequency for September 2, 2010 Ozone Exceedance



The 8 hour average for Ozone at Miller State Park on September 2, 2010 was 0.082 ppm. VOC concentrations peak around mid-day on the day before, the day of, and the day after the event. As typical, winds are coming from the southwest.

EPISODE SUMMARY FOR SEPTEMBER 7, 2010 AT MILLER STATE PARK





The 8 hour average for Ozone at Miller State Park on September 7, 2010 was 0.078 ppm with southwest winds.

DISCUSSION

2010 PAMS data showed trends of continued decline on average despite more favorable weather conditions. Isoprene being a major exception at Miller as it is heavily driven by high temperatures and increased solar radiation. As a result, the diurnal pattern of isoprene was explored in great detail after reviewing the 2010 data. It was determined that, as known, Isoprene concentrations increase with temperature however Isoprene at Miller may be more heavily driven by an increase in UV radiation than actual temperature, although both are contributing factors at the high elevation site. This pattern however is not seen at the lower elevation Gilson Rd. site. One thought was perhaps that the forest makeup had something to do with it; oak and spruce are the main Isoprene contributors here in the northeast, so perhaps different trees emitted Isoprene at different rates throughout the day. In response to this theory, the forest makeup within a two mile radius of each site was analyzed. The results are as follows:

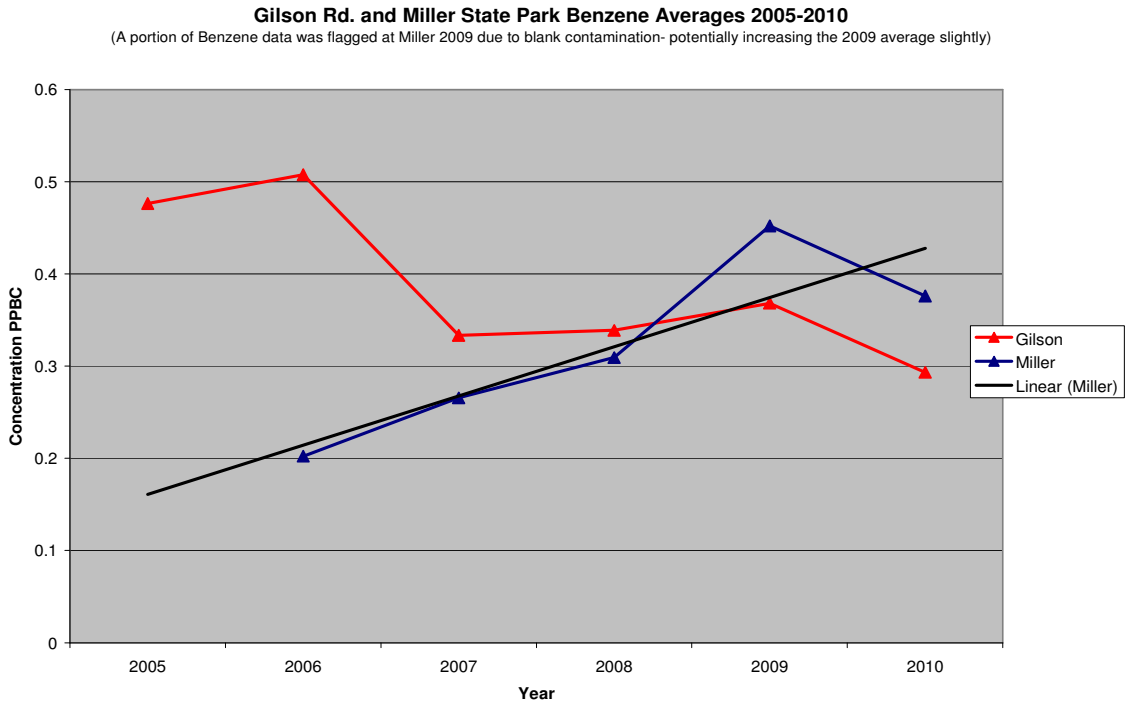
	Gilson Rd %	Miller State Park %
Background	8.37	0.00
Developed, High Intensity	2.05	0.00
Developed, Medium Intensity	7.19	0.09
Developed, Low Intensity	19.45	0.52
Developed, Open Space	4.40	0.38
Cultivated Crops	1.48	0.53
Pasture/Hay	7.27	3.79
Grassland/Herbaceous	0.63	0.00
Deciduous Forest	8.11	47.39
Evergreen Forest	23.55	23.22
Mixed Forest	2.85	22.06
Shrub/Scrub	1.86	0.09
Palustrine	6.02	0.55
Palustrine_1	2.16	0.43
Palustrine_2	0.34	0.04
Unconsolidated Shore	0.10	0.00
Barren Land	0.94	0.01
Open Water	3.23	0.91

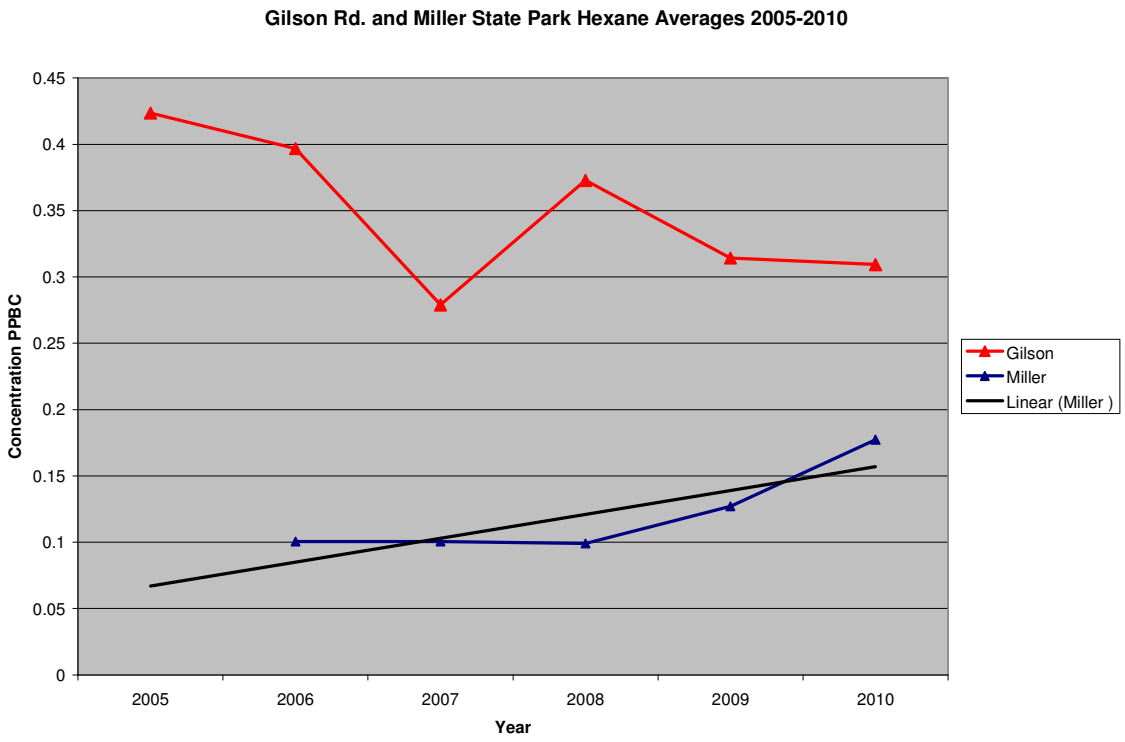
Key-

Developed, High Intensity	Includes highly developed areas where people reside or work in high numbers. Examples include apartment complexes, row houses and commercial/industrial. Impervious surfaces account for 80 to100 percent of the total cover.
Developed, Medium Intensity	Includes areas with a mixture of constructed materials and vegetation. Impervious surfaces account for 50 79 percent of the total cover. These areas most commonly include single family housing units.
Developed, Low Intensity	Includes areas with a mixture of constructed materials and vegetation. Impervious surfaces account for 20 49 percent of total cover. These areas most commonly include single family housing units.
Developed, Open Space	Includes areas with a mixture of some constructed materials, but mostly vegetation in the form of lawn grasses. Impervious surfaces account for less than 20 percent of total cover. These areas most commonly include large lot single family housing units, parks, golf courses, and vegetation planted in developed settings for recreation, erosion control, or aesthetic purposes
Cultivated Crops	Areas used for the production of annual crops, such as corn, soybeans, vegetables, tobacco, and cotton, and also perennial woody crops such as orchards and vineyards. Crop vegetation accounts for greater than 20 percent of total vegetation. This class also includes all land being actively tilled.
Pasture/Hay	Areas of grasses, legumes, or grass legume mixtures planted for livestock grazing or the production of seed or hay crops, typically on a perennial cycle. Pasture/hay vegetation accounts for greater than 20 percent of total vegetation.
Grassland/Herbaceous	Areas dominated by grammanoid or herbaceous vegetation, generally greater than 80% of total vegetation. These areas are not subject to intensive management such as tilling, but can be utilized for grazing.
Deciduous Forest	Areas dominated by trees generally greater than 5 meters tall, and greater than 20% of total vegetation cover. More than 75 percent of the tree species shed foliage simultaneously in response to seasonal change.
Evergreen Forest	Areas dominated by trees generally greater than 5 meters tall, and greater than 20% of total vegetation cover. More than 75 percent of the tree species maintain their leaves all year. Canopy is never without green foliage.
Mixed Forest	Areas dominated by trees generally greater than 5 meters tall, and greater than 20% of total vegetation cover. Neither deciduous nor evergreen species are greater than 75 percent of total tree cover.
Shrub/Scrub	Areas dominated by shrubs; less than 5 meters tall with shrub canopy typically greater than 20% of total vegetation. This class includes true shrubs, young trees in an early successional stage or trees stunted from environmental conditions
Unconsolidated Shore*	Unconsolidated material such as silt, sand, or gravel that is subject to inundation and redistribution due to the action of water. Characterized by substrates lacking vegetation except for pioneering plants that become established during brief periods when growing conditions are favorable. Erosion and deposition by waves and currents produce a number of landforms representing this class.
Barren Land (Rock/Sand/Clay)	Barren areas of bedrock, desert pavement, scarps, talus, slides, volcanic material, glacial debris, sand dunes, strip mines, gravel pits and other accumulations of earthen material. Generally, vegetation accounts for less than 15% of total cover.
Open Water	All areas of open water, generally with less than 25% cover of vegetation or soil.

As expected, the Gilson Rd. site shows more heavily developed areas within the vicinity, but with a much smaller percentage of deciduous and mixed forests than the Pack Monadnock site. Although interesting, it is not believed that this is the reason for the difference in the diurnal pattern of Isoprene at the two sites. With some further research, one possible explanation was found that, although Isoprene is primarily oxidized photochemically during daylight hours, late-day isoprene emissions that remain in the atmosphere at sunset undergo oxidation by NO_3 (Nitrate) in regionally polluted areas with large NO_x levels. Due to strong diurnal emission, isoprene reacts predominantly with the hydroxyl radical (OH) whereas the reaction with NO3 becomes more important at night.

Now with five years of data collection at Miller and six years at Gilson, historical trends can be observed including the increase of both Benzene and Hexane at Miller while both species show a decline at Gilson Rd.





Benzene is found in the air from emissions from burning coal and oil, gasoline service stations, and motor vehicle exhaust. Benzene levels in the air can be elevated by emissions from burning coal and oil, benzene waste and storage operations, motor vehicle exhaust, and evaporation from gasoline service stations. Once in the air, benzene reacts with other chemicals and breaks down within a few days. Benzene evaporates into the air very quickly; its vapor is heavier than air and may sink into low-lying areas, which makes the increase at Miller ever more thought provoking. It is reported that an EPA ruling will put a ceiling on the total benzene content of any gasoline produced after 2011.

Hexanes are also significant constituents of gasoline. They evaporate very easily into the air where it is then broken down within a few days. Hexane is noted to be one of the least photochemically reative hydrocarbons.

With that said, it will be very interesting to see what the 2011 data shows.