NESCAUM PAMS Workgroup Overview and Review of New Hampshire PAMS Data Analysis

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NEW HAMPSHIRE DEPARTMENT OF Environmental Services

Acknowledgements

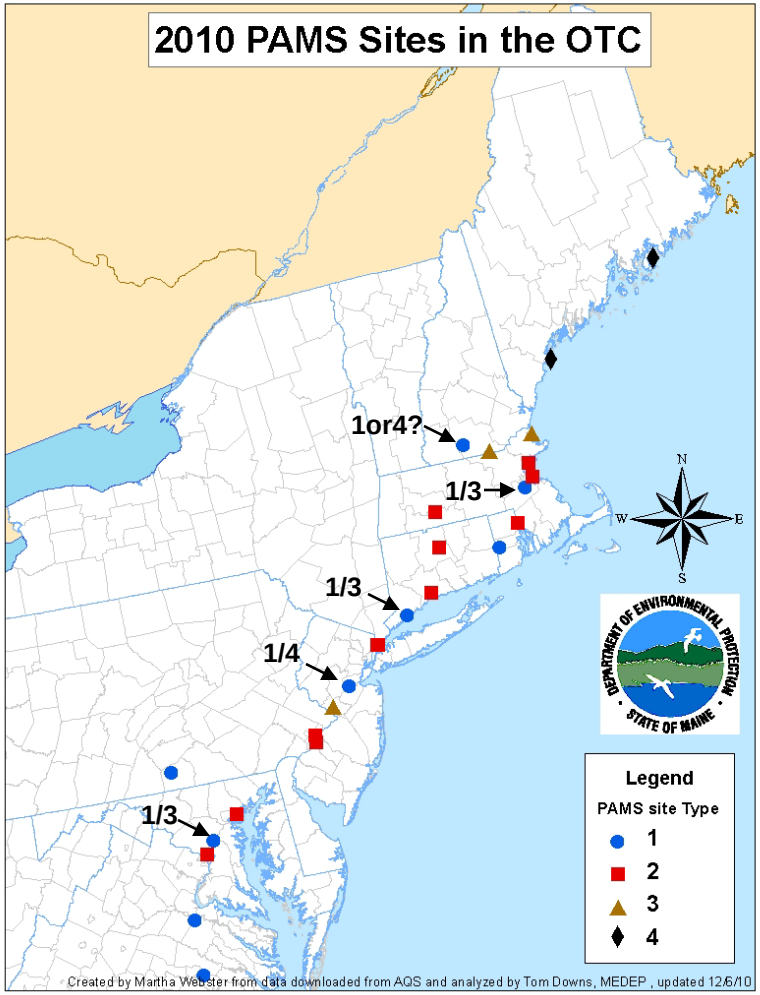
Tom Downs – MEDEP

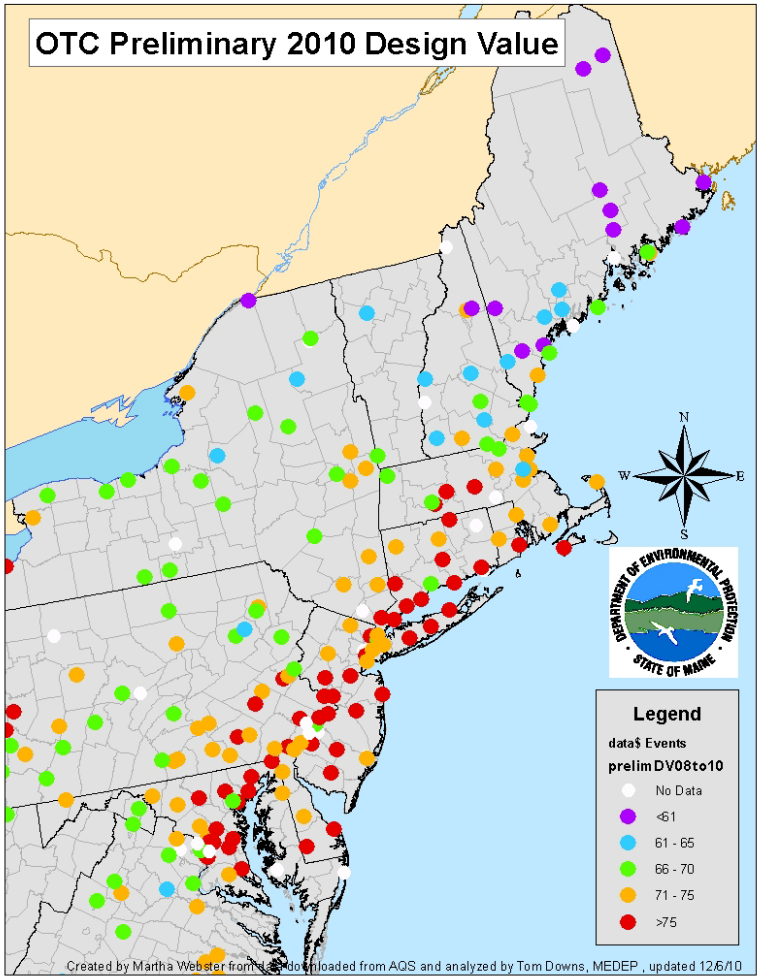
George Allen – NESCAUM

Jessica Sheldon and Lara Stumpo – NHDES

Many others involved in the NESCAUM PAMS Workgroup

2010 Regional PAMS Network





TYPE 1 – UPWIND/background site

TYPE 2 – MAXIMUM EMISSIONS site

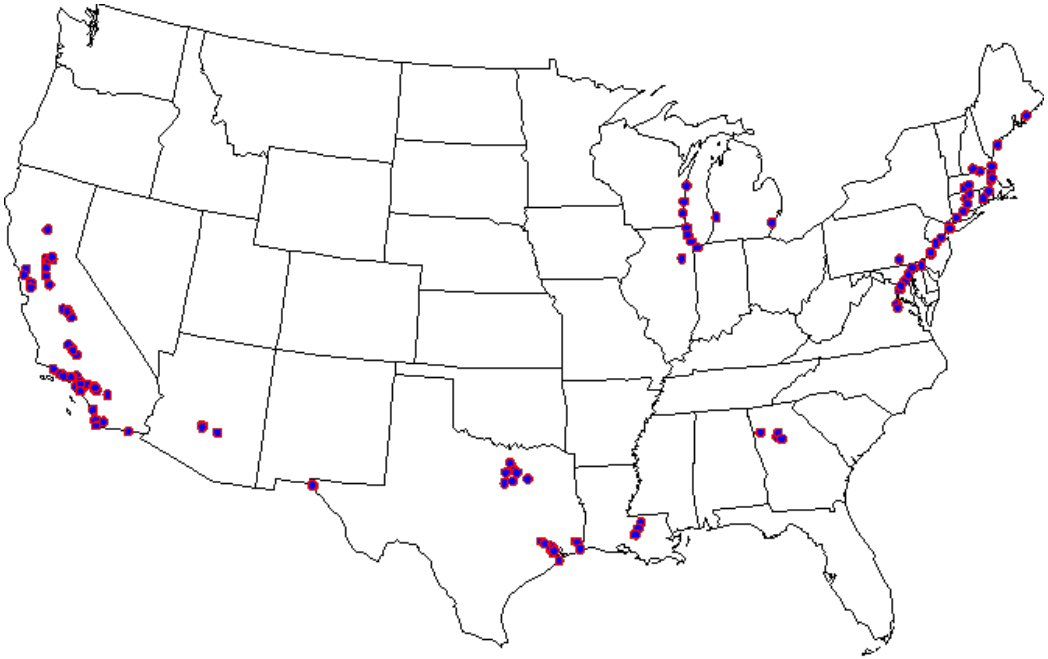
TYPE 3 – MAXIMUM OZONE concentration site

♦ TYPE 4 – Extreme DOWNWIND site

Overview of NESCAUM PAMS Workgroup's Efforts

Reviewed:

- EPA guidance
  - Focused on linking common species to emission sources.
  - Anticipated that major sources would become SIP focused
- Past EPA PAMS Analyses
  - Often focused on redundancies and how the network can be reduced



Overview of NESCAUM PAMS Workgroup's Efforts

Also Reviewed:

- Detection limits
- Common species
  - –Are some species too often below MDL to be useful?
  - –Are there species that should be added?
- Carbonyls – data quality, are they worth the cost?
- Is the newer, more sensitive or less expensive analytical techniques? (Synspec – gets more compounds including more biogenics)
- Data analyses by state

DATA PROCESSING

- Summary statistics calculated
  - Average concentrations (by site and by classification)
  - Percent of data below minimum detect levels
  - Percent data recovery rates

- QA checks
  - Check for qualifier flags and delete obvious invalid data
  - Check for units consistency and convert to correct units if necessary
  - Box plots to identify outliers?
  - Concern with the frequency of below minimum detects?

Overview of NESCAUM PAMS Workgroup's Preliminary Findings

Concluded:

- Data analysis should also be done regionally
- PAMS data critical for regional modeling efforts
- State survey found that many (but not all) states don't know or trust their carbonyl data quality. States still submitted data to AQS as required.
  - Known problems with acrolein – EPA pulled data from AQS
  - Suspected quality problems with other carbonyls – OAQPS looking into.
- Will look at Regional Network Needs Under New Ozone NAAQS Implementation rule

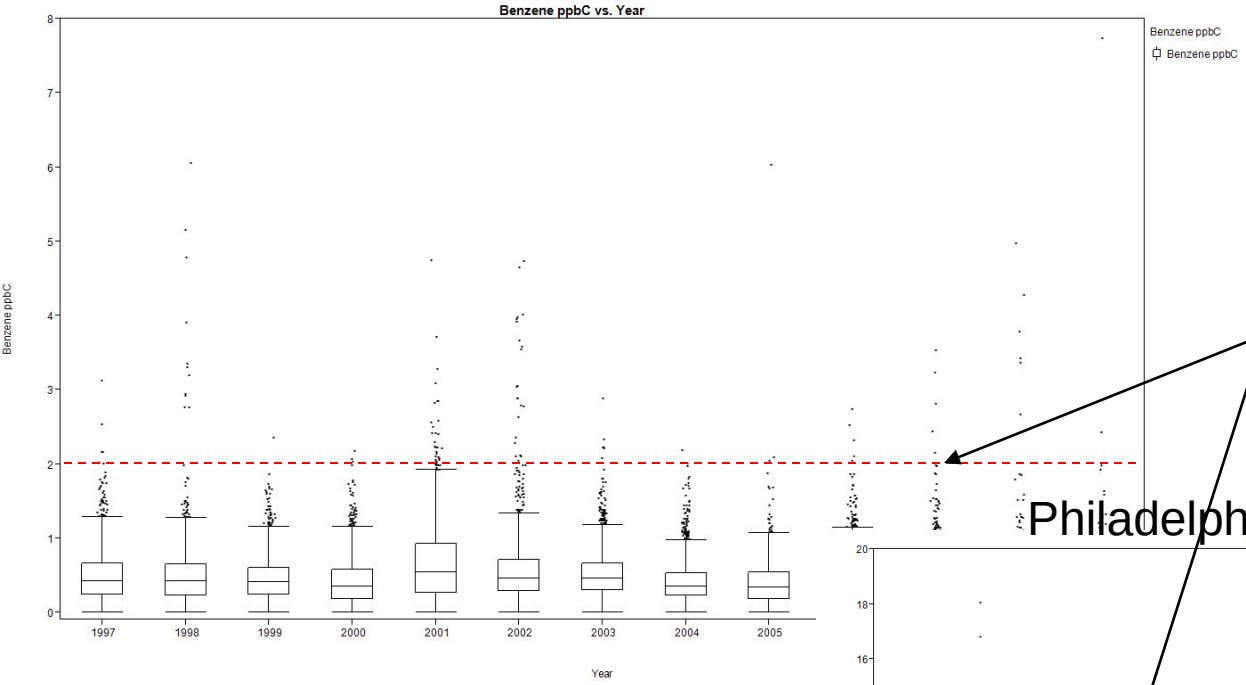
Should we analyze all 54-57 VOC species in future data analyses?

- On the ftp site - analyses for each site comparing trends for the full suite of VOC's vs. a reduced ("focused") PAMS species list of 23 and 7 compounds
  http://www.maine.gov/dep/ftp/DEP_PAMS/NESCAUM_PAMS_ANALYSES/

- Preliminary analyses are also included
  - % unidentified VOC's
  - Benzene/tolulene ratios
  - Ranking of VOC's

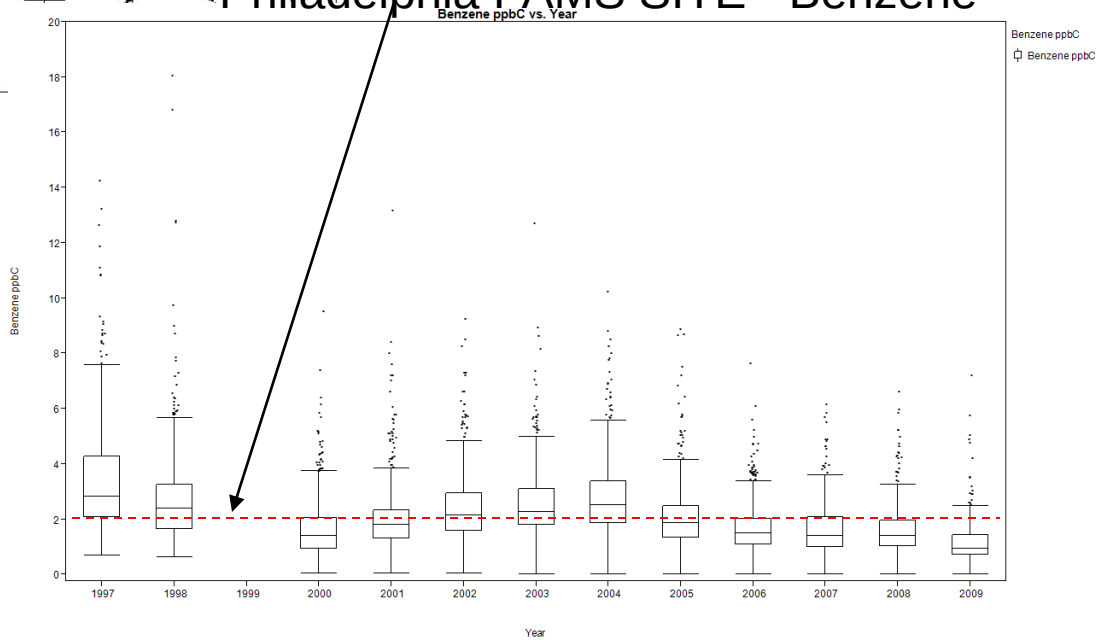
Annual Box and Whisker Plots by Site and Key Species

Cape Elizabeth, Maine PAMS SITE - Benzene



Comparative line drawn at 2ppbC

Philadelphia PAMS SITE - Benzene



SAS JMP statistical software used

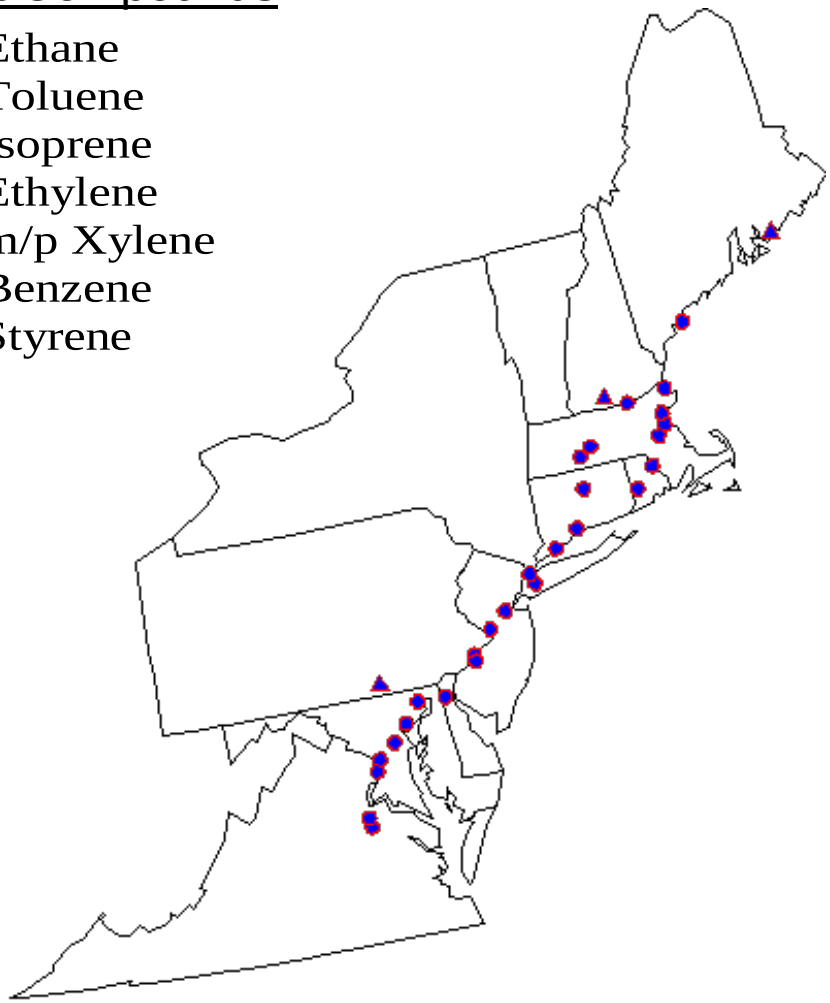
Sub-Grouping of 54 Target PAMS Compounds

23 Target Compounds

1. Propane
2. Ethane
3. Toluene
4. Isopentane
5. Isoprene
6. n-Butane
7. Ethylene
8. n-Pentane
9. Isobutane
10. 2,2,4-Trimethylpentane
11. m/p Xylene
12. 2-Methylpentane
13. Ethylbenzene
14. n-Hexane
15. Benzene
16. Propylene
17. Acetylene
18. o-Xylene
19. 1,2,4-Trimethylbenzne
20. n-Decane
21. Methylcyclohexane
22. n-Nonane
23. n-Octane

7 Target Compounds

1. Ethane
2. Toluene
3. Isoprene
4. Ethylene
5. m/p Xylene
6. Benzene
7. Styrene



Rankings of VOC's during 0500-0800 hours of an Ozone event day (8-hr > 70 ppb)

ALL hourly sites		TYPE 1 sites		TYPE 2 sites		TYPE 3 sites		TYPE 4 sites	
Propane	43204	Propane	43204	Isopentane	43221	Propane	43204	Propane	43204
Isopentane	43221	Ethane	43202	Propane	43204	Ethane	43202	Ethane	43202
Ethane	43202	Toluene	45202	Ethane	43202	Isoprene	43243	Isoprene	43243
Toluene	45202	Isopentane	43221	Toluene	45202	Toluene	45202	Isopentane	43221
n-Butane	43212	Isoprene	43243	n-Butane	43212	Isopentane	43221	Toluene	45202
n-Pentane	43220	n-Butane	43212	n-Pentane	43220	1,2,3-Trimethylbenzene	45225	n-Butane	43212
Isoprene	43243	Ethylene	43203	Isobutane	43214	n-Butane	43212	n-Pentane	43220
Isobutane	43214	n-Pentane	43220	2-Methylpentane	43285	n-Pentane	43220	1,2,3-Trimethylbenzene	45225
Ethylene	43203	Isobutane	43214	m/p Xylene	45109	Ethylene	43203	Benzene	45201
m/p Xylene	45109	1,3,5-Trimethylbenzene	45207	Ethylene	43203	Isobutane	43214	Isobutane	43214
2-Methylpentane	43285	2,2,4-Trimethylpentane	43250	n-Hexane	43231	m/p Xylene	45109	2-Methylpentane	43285
n-Hexane	43231	m/p Xylene	45109	2,2,4-Trimethylpentane	43250	2-Methylpentane	43285	m/p Xylene	45109
2,2,4-Trimethylpentane	43250	2-Methylpentane	43285	Isoprene	43243	Benzene	45201	n-Hexane	43231
Propylene	43205	Ethylbenzene	45203	Propylene	43205	n-Hexane	43231	Ethylene	43203
Benzene	45201	n-Hexane	43231	3-Methylpentane	43230	2,2,4-Trimethylpentane	43250	2,2,4-Trimethylpentane	43250
1,2,3-Trimethylbenzene	45225	Benzene	45201	Benzene	45201	Propylene	43205	p-Ethyltoluene	45213
3-Methylpentane	43230	1,2,3-Trimethylbenzene	45225	Methylcyclopentane	43262	m-Ethyltoluene	45212	Propylene	43205
Ethylbenzene	45203	Propylene	43205	3-Methylhexane	43249	3-Methylhexane	43249	3-Methylpentane	43230
3-Methylhexane	43249	Acetylene	43206	n-Heptane	43232	3-Methylpentane	43230	m-Ethyltoluene	45212
Methylcyclopentane	43262	o-Xylene	45204	1,2,4-Trimethylbenzene	45208	p-Ethyltoluene	45213	3-Methylhexane	43249
Acetylene	43206	3-Methylpentane	43230	Acetylene	43206	Acetylene	43206	Ethylbenzene	45203
n-Heptane	43232	n-Undecane	43954	Ethylbenzene	45203	n-Heptane	43232	Methylcyclopentane	43262
1,2,4-Trimethylbenzene	45208	n-Heptane	43232	2-Methylhexane	43263	1,2,4-Trimethylbenzene	45208	n-Heptane	43232
o-Xylene	45204	1,2,4-Trimethylbenzene	45208	o-Xylene	45204	Methylcyclopentane	43262	Acetylene	43206
m-Ethyltoluene	45212	3-Methylhexane	43249	2,3-Dimethylbutane	43284	o-Xylene	45204	o-Xylene	45204
2-Methylhexane	43263	Methylcyclopentane	43262	Styrene	45220	Ethylbenzene	45203	trans-2-Butene	43216
2,3-Dimethylbutane	43284	n-Decane	43238	1,2,3-Trimethylbenzene	45225	2-Methylhexane	43263	2,3-Dimethylbutane	43284
1,3,5-Trimethylbenzene	45207	m-Ethyltoluene	45212	m-Ethyltoluene	45212	2,3-Dimethylbutane	43284	2-Methylhexane	43263
Methylcyclohexane	43261	2-Methylhexane	43263	Methylcyclohexane	43261	Methylcyclohexane	43261	Cyclohexane	43248
Styrene	45220	Methylcyclohexane	43261	2,3,4-Trimethylpentane	43252	Cyclohexane	43248	2,3,4-Trimethylpentane	43252
n-Undecane	43954	2,3,4-Trimethylpentane	43252	n-Decane	43238	n-Octane	43233	1,2,4-Trimethylbenzene	45208
n-Decane	43238	n-Nonane	43235	trans-2-Pentene	43226	2,3,4-Trimethylpentane	43252	Methylcyclohexane	43261
2,3,4-Trimethylpentane	43252	o-Ethyltoluene	45211	2,3-Dimethylpentane	43291	n-Decane	43238	2,2-Dimethylbutane	43244
p-Ethyltoluene	45213	2,3-Dimethylbutane	43284	n-Octane	43233	n-Nonane	43235	n-Octane	43233
n-Nonane	43235	p-Diethylbenzene	45219	Cyclohexane	43248	Styrene	45220	Cyclopentane	43242
n-Octane	43233	trans-2-Butene	43216	trans-2-Butene	43216	2,3-Dimethylpentane	43291	2,3-Dimethylpentane	43291
2,3-Dimethylpentane	43291	2-Methylheptane	43960	n-Nonane	43235	n-Undecane	43954	3-Methylheptane	43253
Cyclohexane	43248	n-Propylbenzene	45209	n-Undecane	43954	Cyclopentane	43242	n-Nonane	43235
trans-2-Butene	43216	n-Octane	43233	2,2-Dimethylbutane	43244	1-Butene	43280	2,4-Dimethylpentane	43247
trans-2-Pentene	43226	2,3-Dimethylpentane	43291	Cyclopentane	43242	2,2-Dimethylbutane	43244	1-Pentene	43224
Cyclopentane	43242	Styrene	45220	2,4-Dimethylpentane	43247	trans-2-Butene	43216	2-Methylheptane	43960
2,2-Dimethylbutane	43244	2,2-Dimethylbutane	43244	1-Pentene	43224	1,3,5-Trimethylbenzene	45207	Styrene	45220
2,4-Dimethylpentane	43247	Cyclohexane	43248	1,3,5-Trimethylbenzene	45207	3-Methylheptane	43253	o-Ethyltoluene	45211
o-Ethyltoluene	45211	Cyclopentane	43242	3-Methylheptane	43253	1-Pentene	43224	1,3,5-Trimethylbenzene	45207
2-Methylheptane	43960	p-Ethyltoluene	45213	cis-2-Butene	43217	2-Methylheptane	43960	1-Butene	43280
1-Pentene	43224	trans-2-Pentene	43226	1-Butene	43280	2,4-Dimethylpentane	43247	n-Decane	43238
1-Butene	43280	m-Diethylbenzene	45218	p-Ethyltoluene	45213	o-Ethyltoluene	45211	n-Propylbenzene	45209
3-Methylheptane	43253	1-Butene	43280	2-Methylheptane	43960	trans-2-Pentene	43226	trans-2-Pentene	43226
cis-2-Butene	43217	2,4-Dimethylpentane	43247	o-Ethyltoluene	45211	p-Diethylbenzene	45219	cis-2-Butene	43217
p-Diethylbenzene	45219	1-Pentene	43224	cis-2-Pentene	43227	Isopropylbenzene	45210	n-Undecane	43954
n-Propylbenzene	45209	3-Methylheptane	43253	n-Propylbenzene	45209	n-Propylbenzene	45209	m-Diethylbenzene	45218
cis-2-Pentene	43227	Isopropylbenzene	45210	p-Diethylbenzene	45219	cis-2-Butene	43217	p-Diethylbenzene	45219
Isopropylbenzene	45210	cis-2-Butene	43217	Isopropylbenzene	45210	m-Diethylbenzene	45218	cis-2-Pentene	43227
m-Diethylbenzene	45218	cis-2-Pentene	43227	m-Diethylbenzene	45218	cis-2-Pentene	43227	Isopropylbenzene	45210

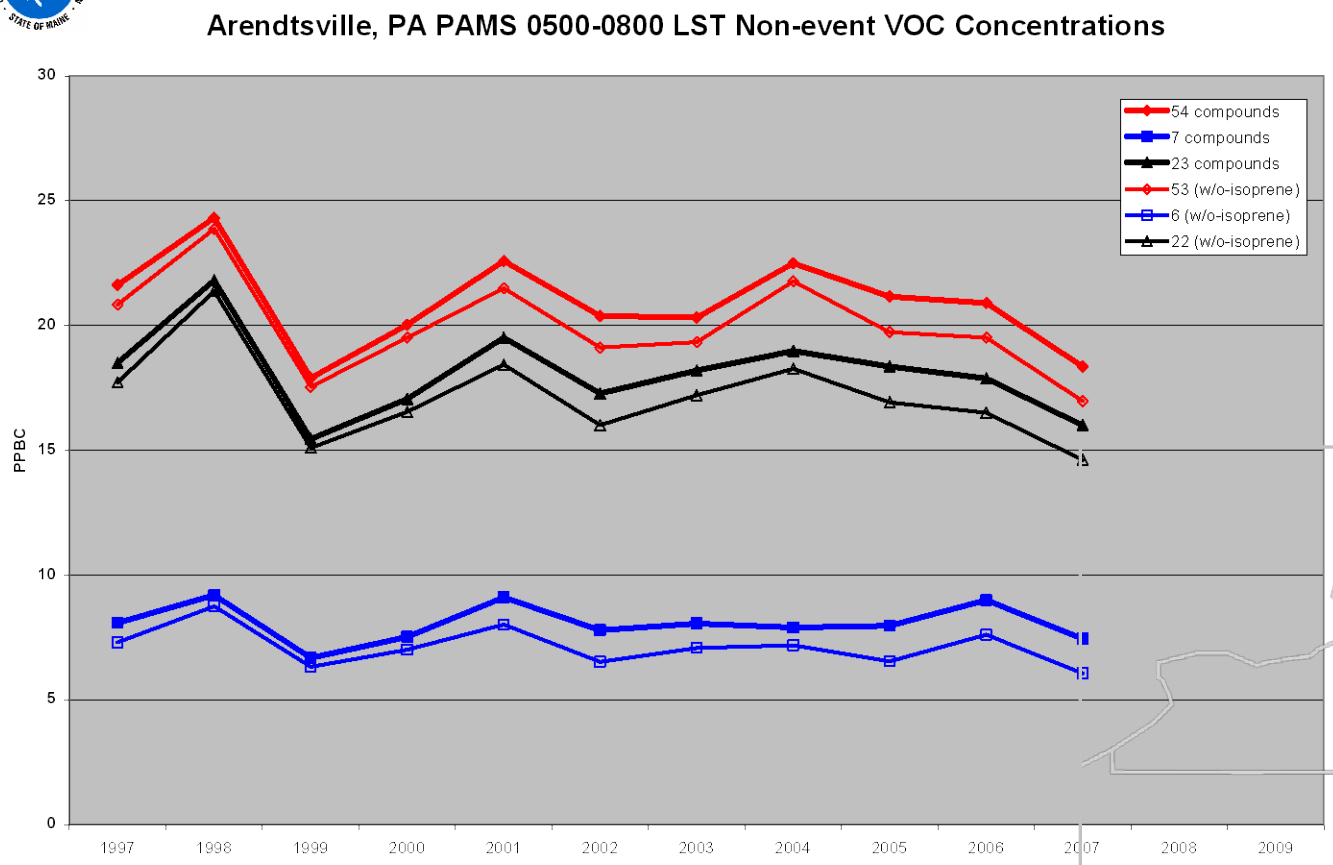
Only in the 23 target compounds list

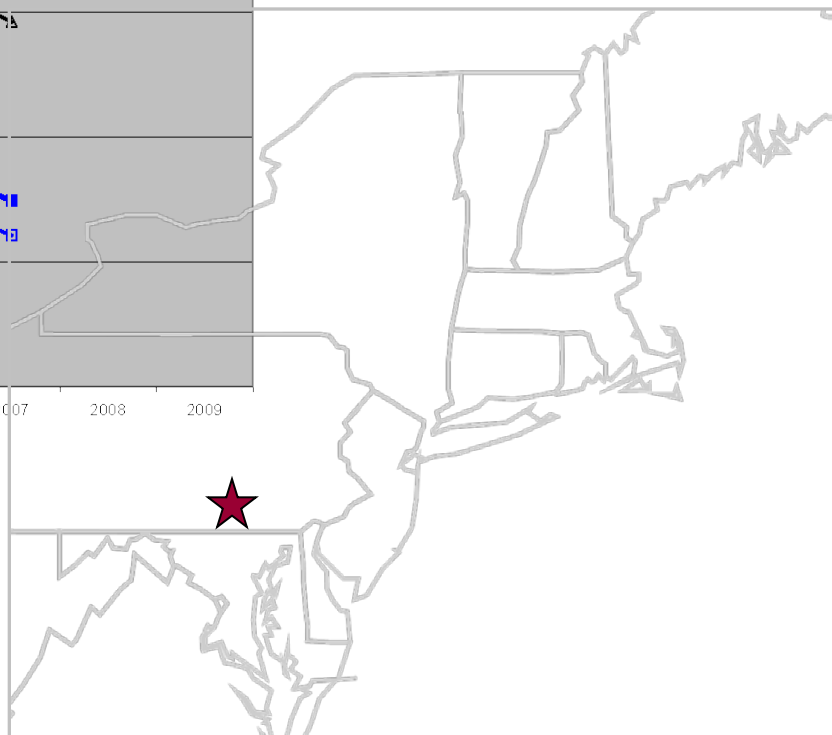
In both the 23 and 7 target compounds lists

Only in the 7 target compounds list

Type 1 (Upwind) Site Trends

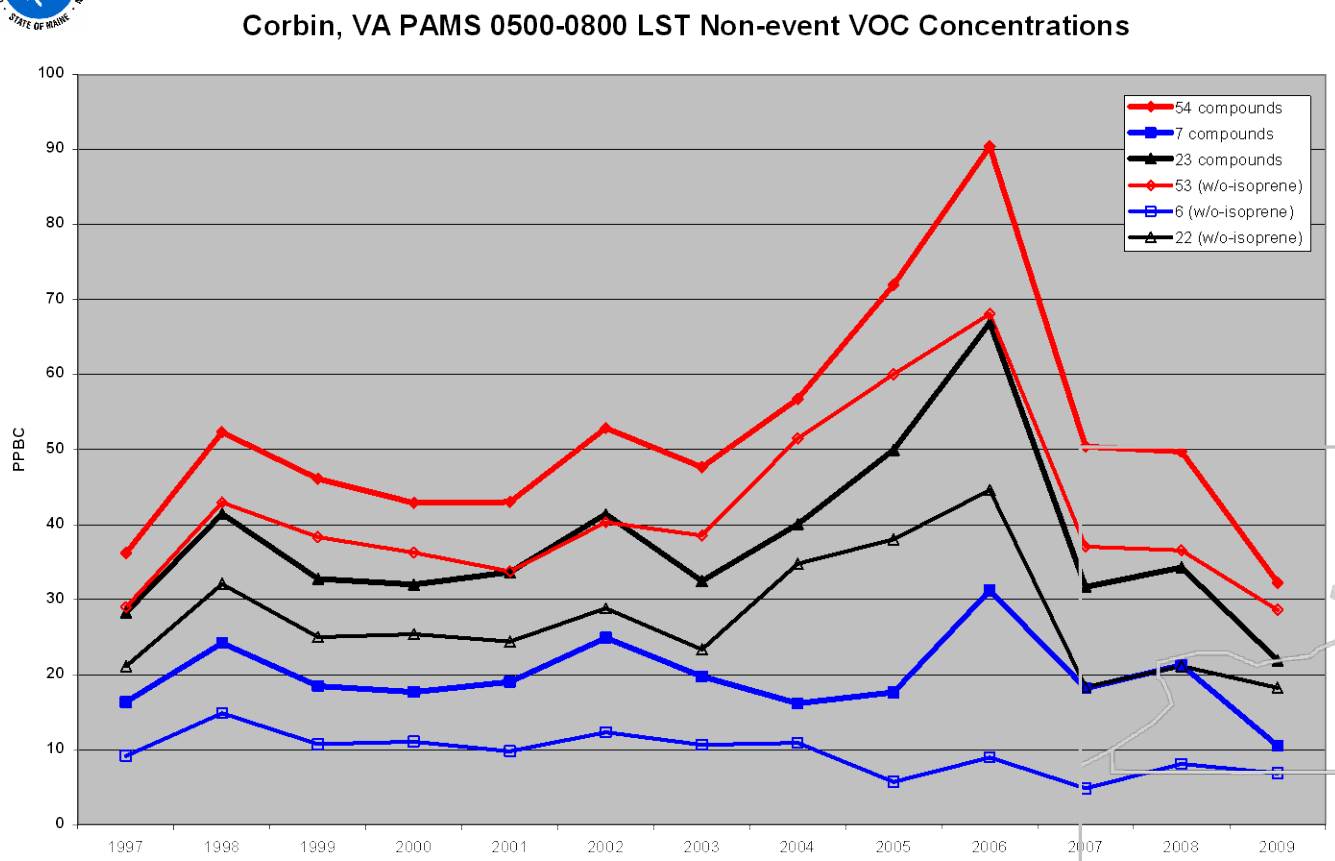
Tom Downs, Maine DEP-BAQ - 11/9/2010

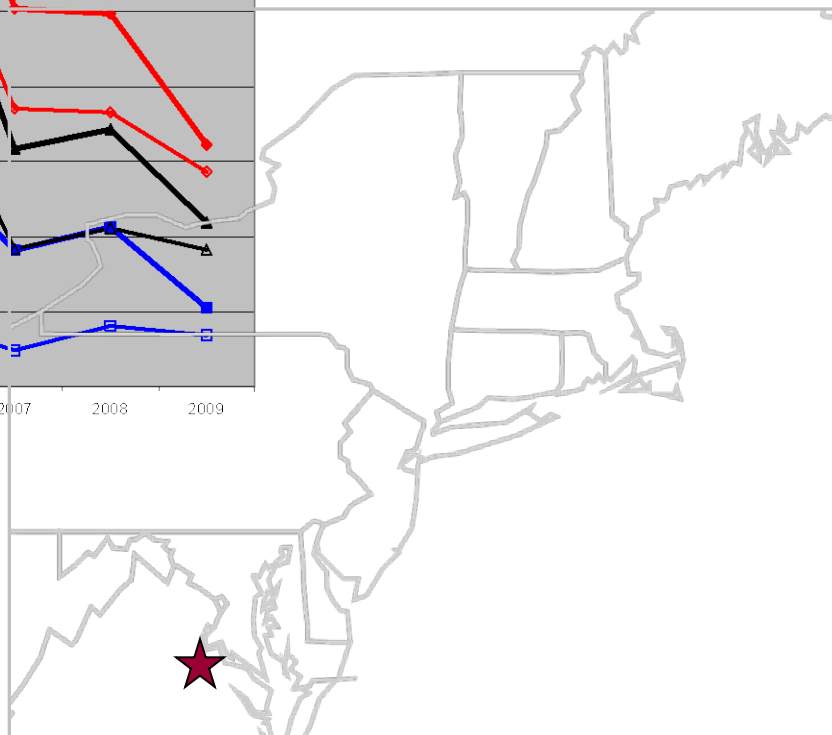




Type 1 (Upwind) Site Trends

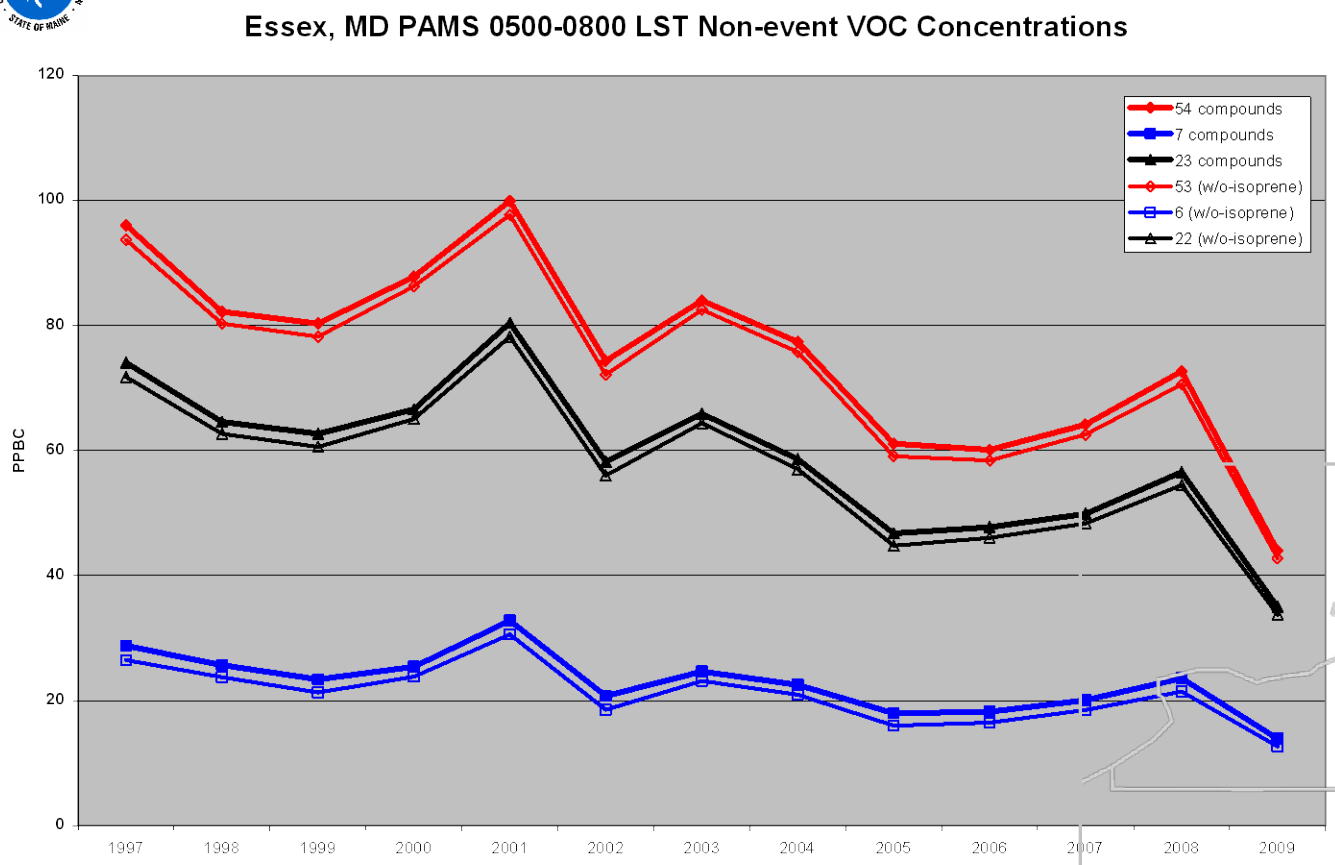
Tom Downs, Maine DEP-BAQ - 11/17/2010

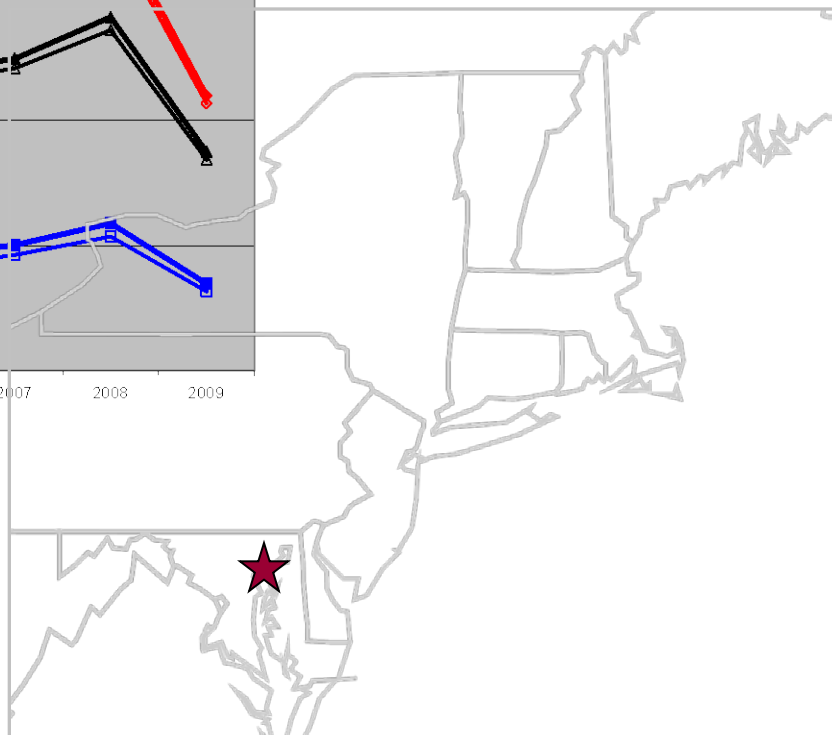




Type 2 (High Emission) Site Trends

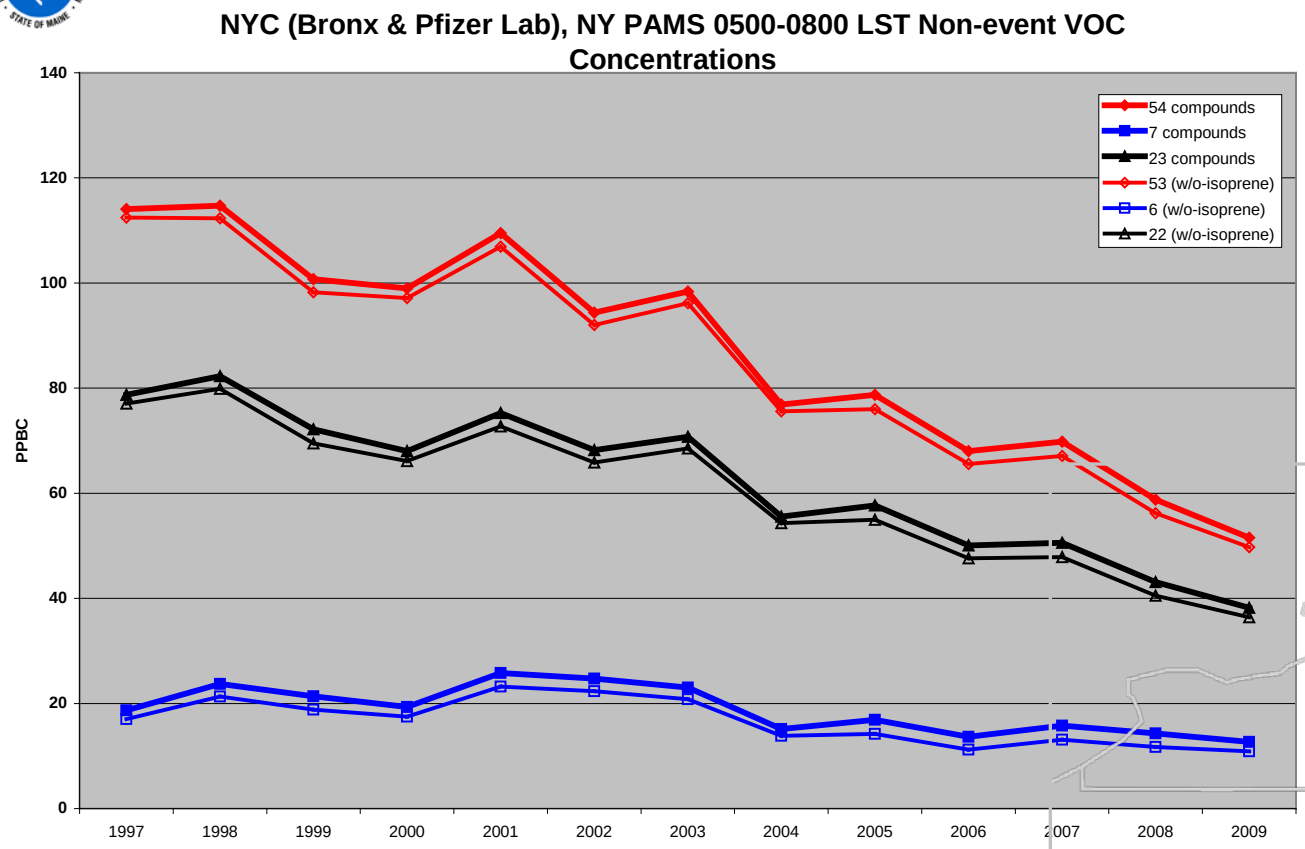
Tom Downs, Maine DEP-BAQ - 11/1/2010

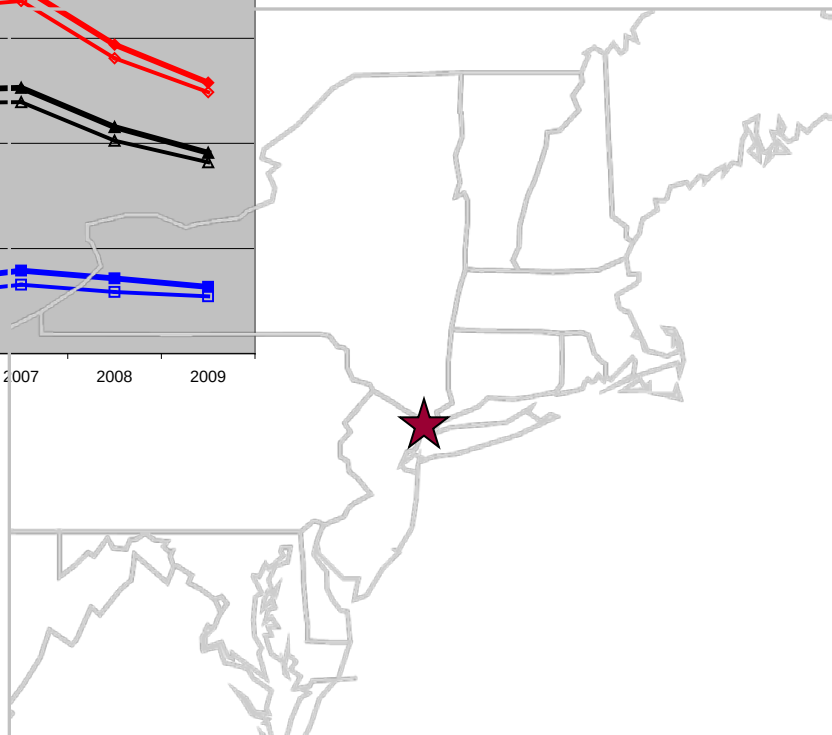




Type 2 (High Emission) Site Trends

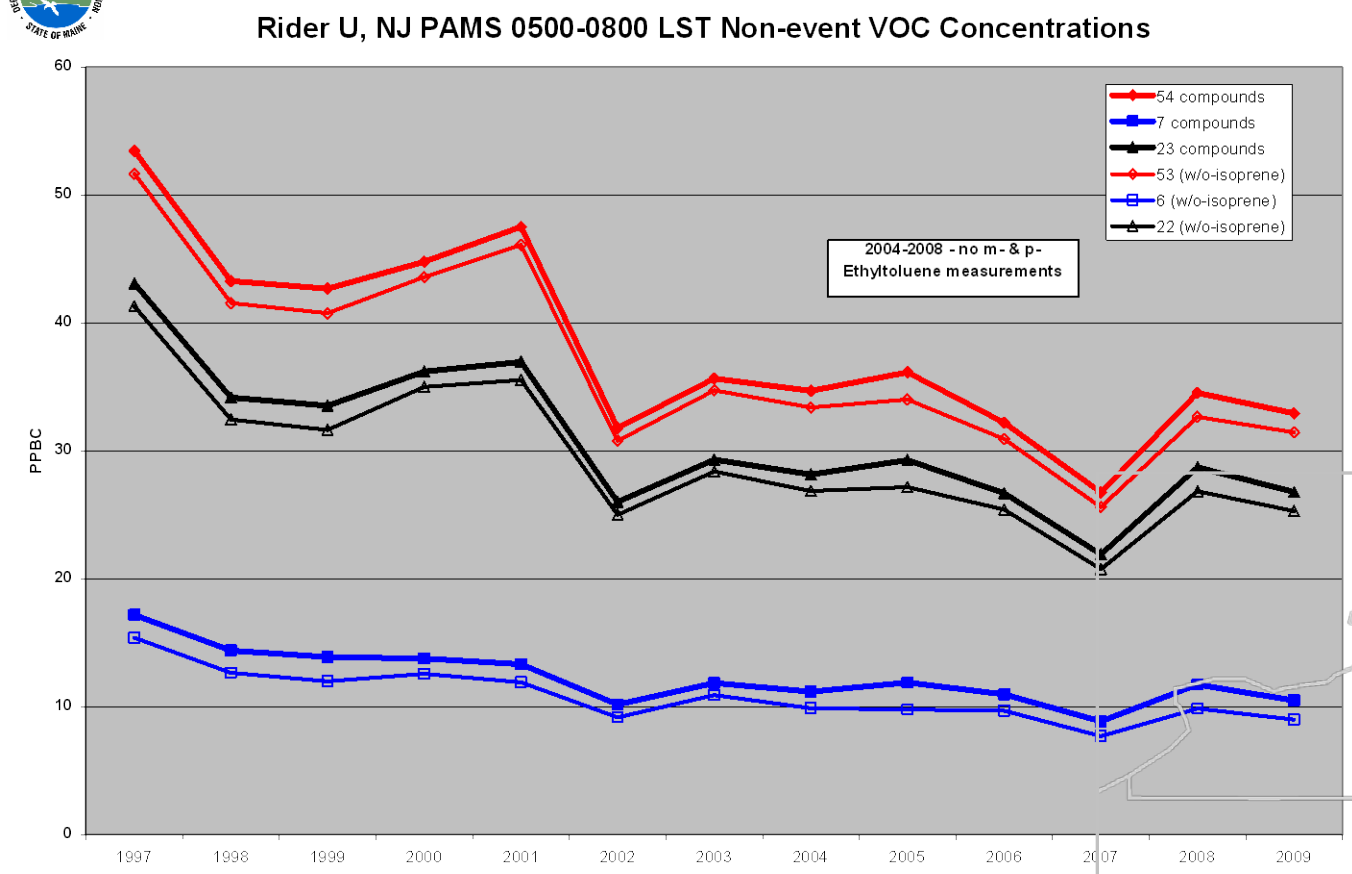
Tom Downs, Maine DEP-BAQ - 10/26/2010

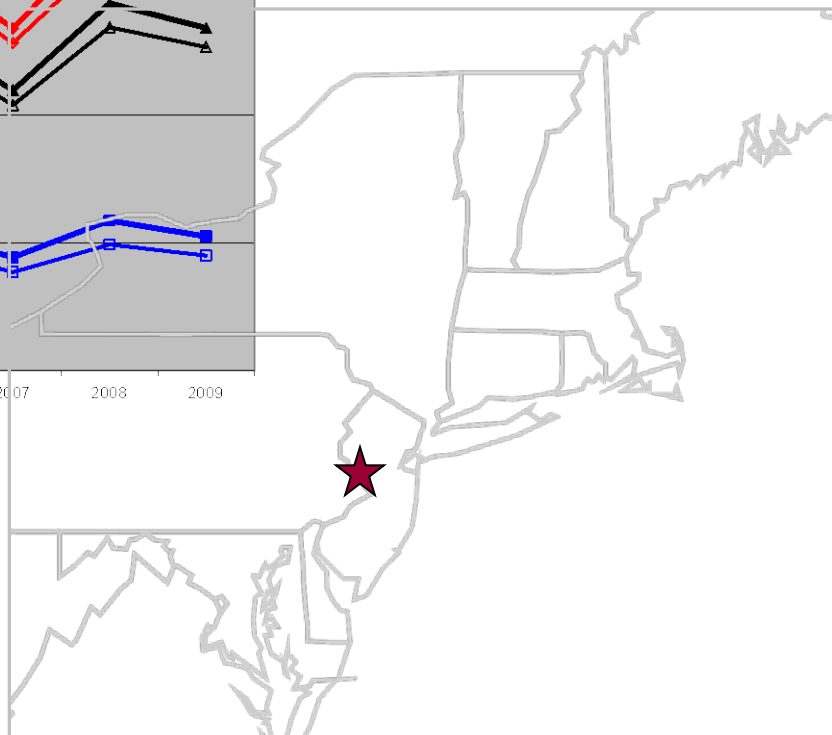




Type 3 (High Ozone) Site Trends

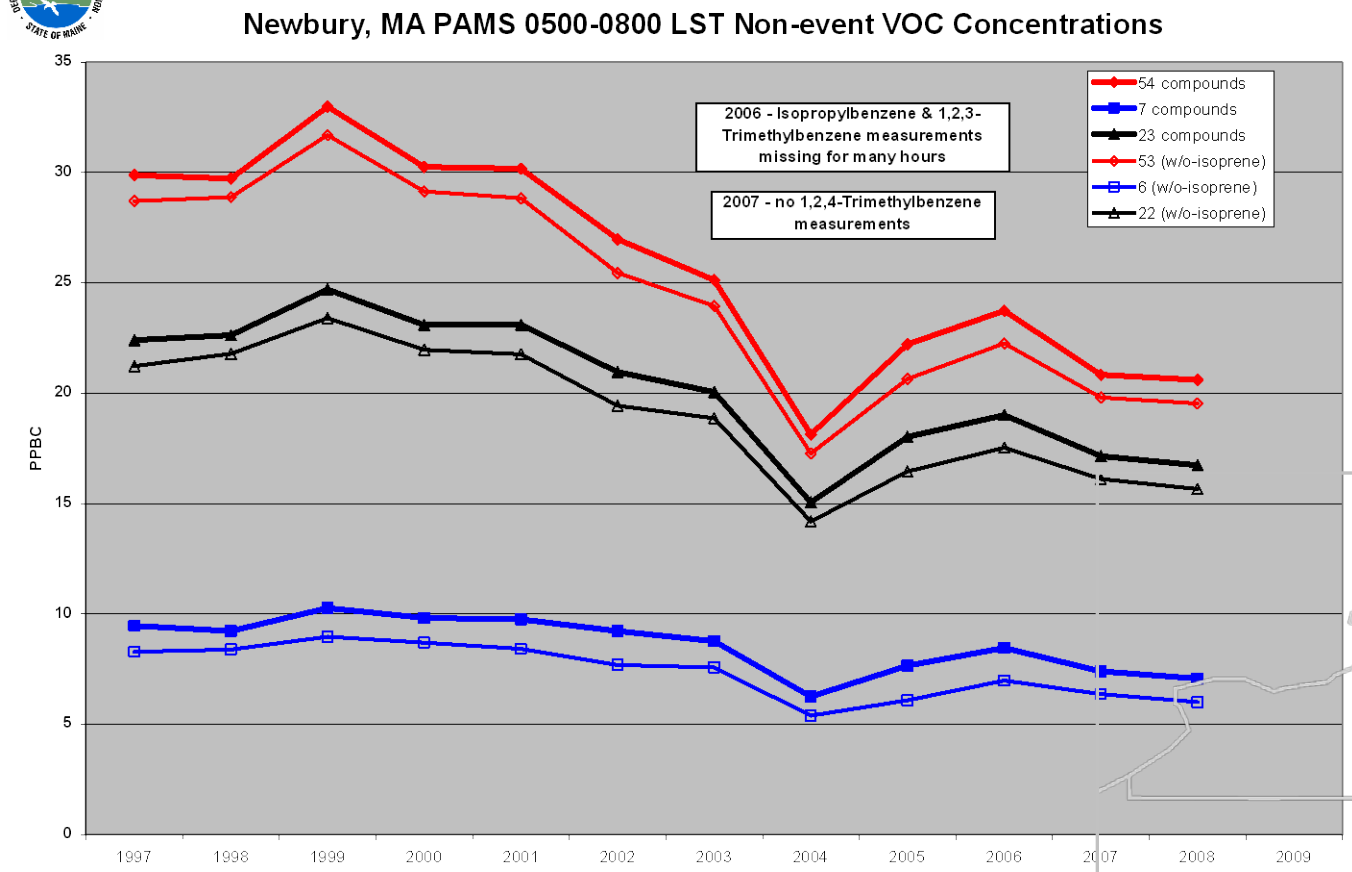
Tom Downs, Maine DEP-BAQ - 9/23/2010

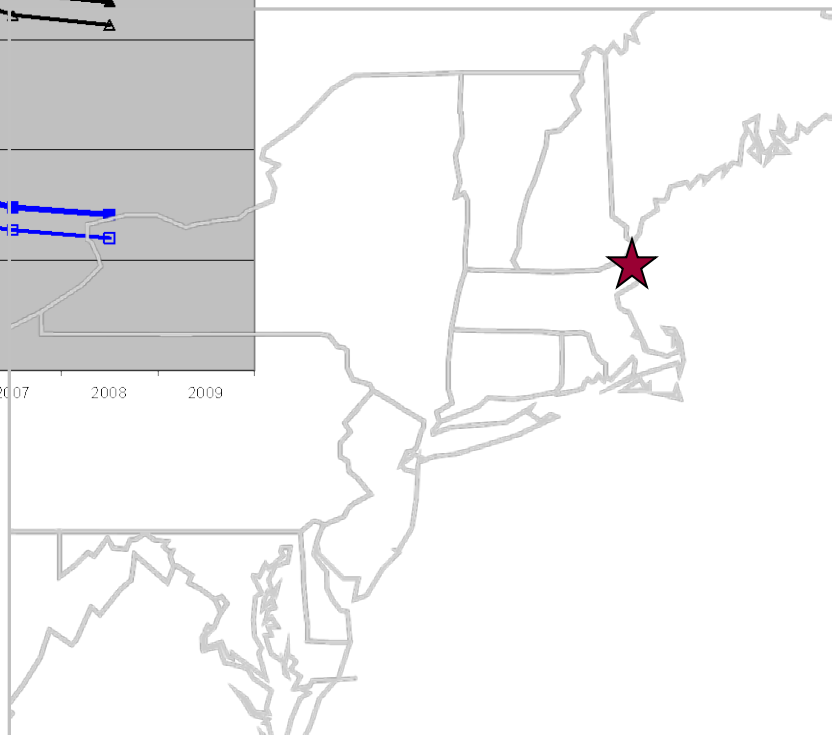




Type 3 (High Ozone) Site Trends

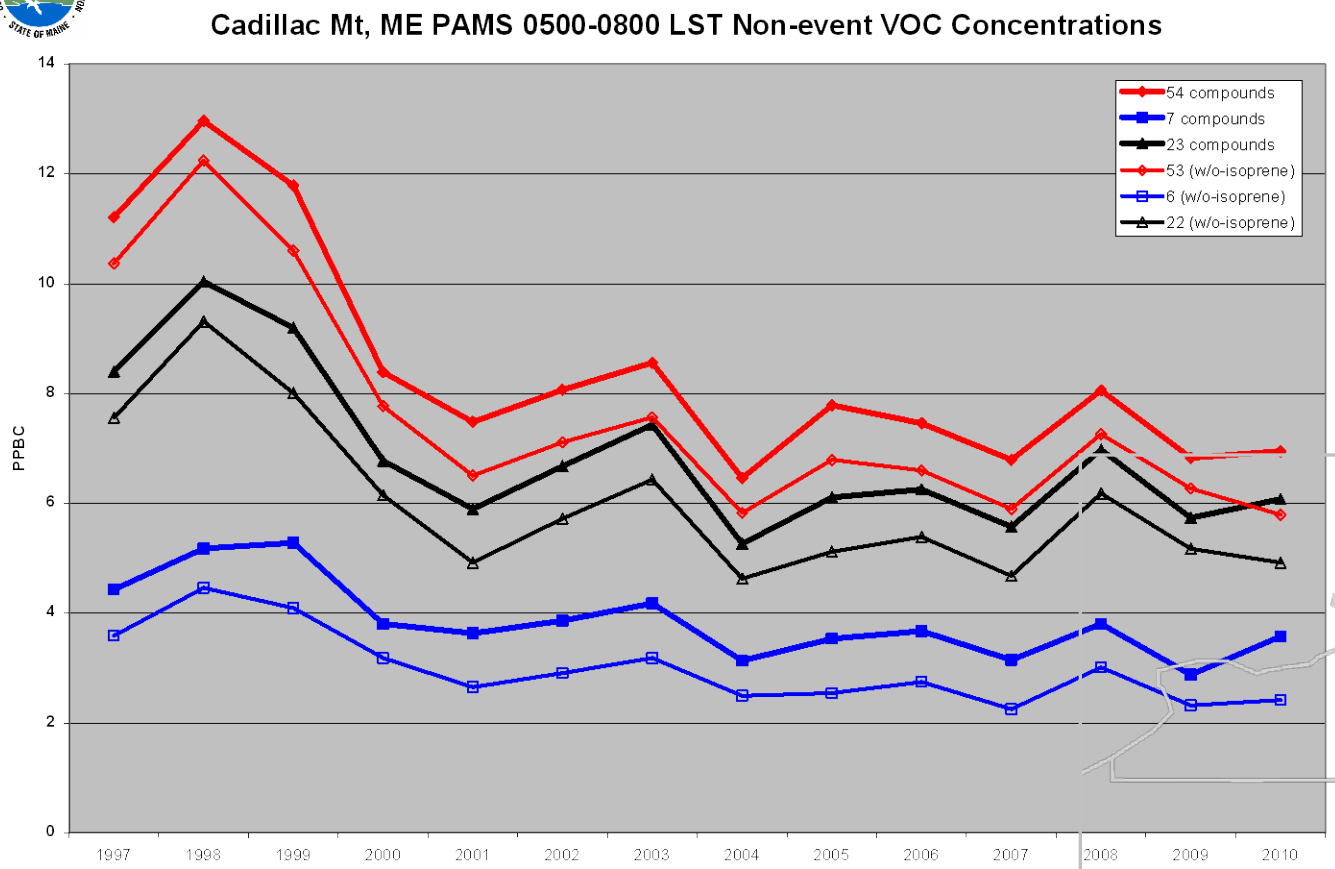
Tom Downs, Maine DEP-BAQ - 9/23/2010

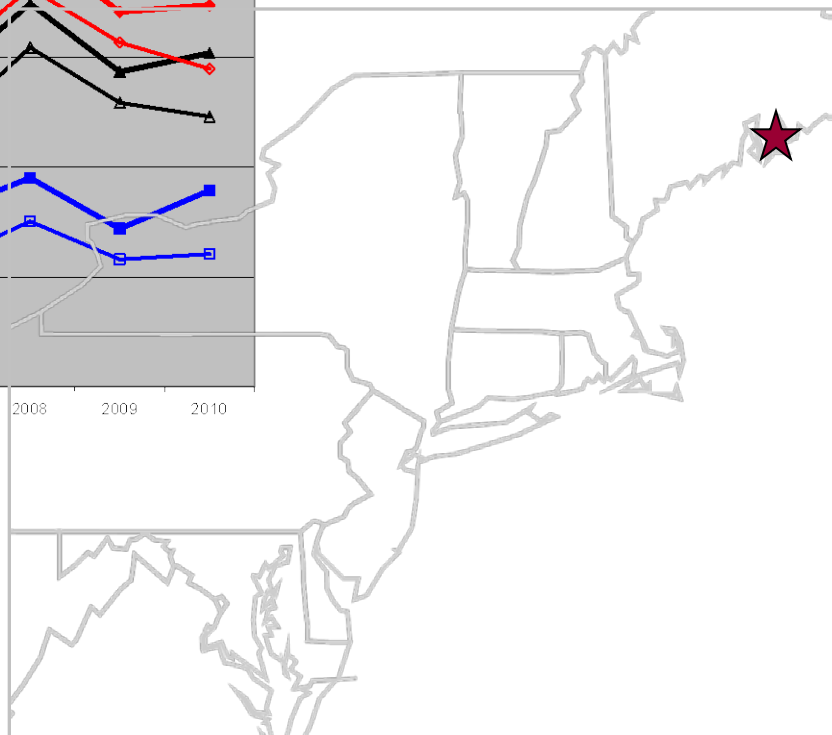




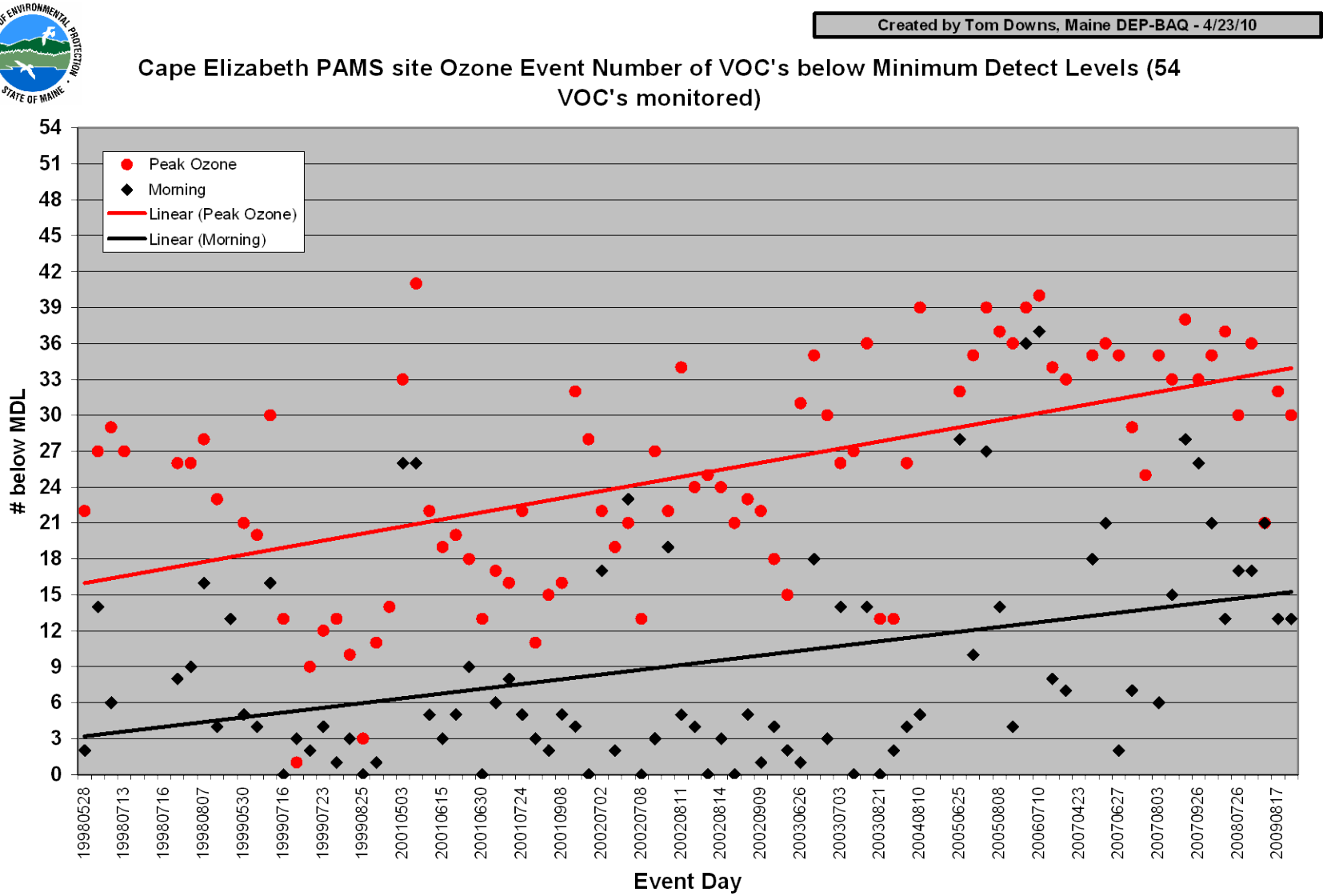
Type 4 (Downwind) Site Trends

Tom Downs, Maine DEP-BAQ - 12/20/2010



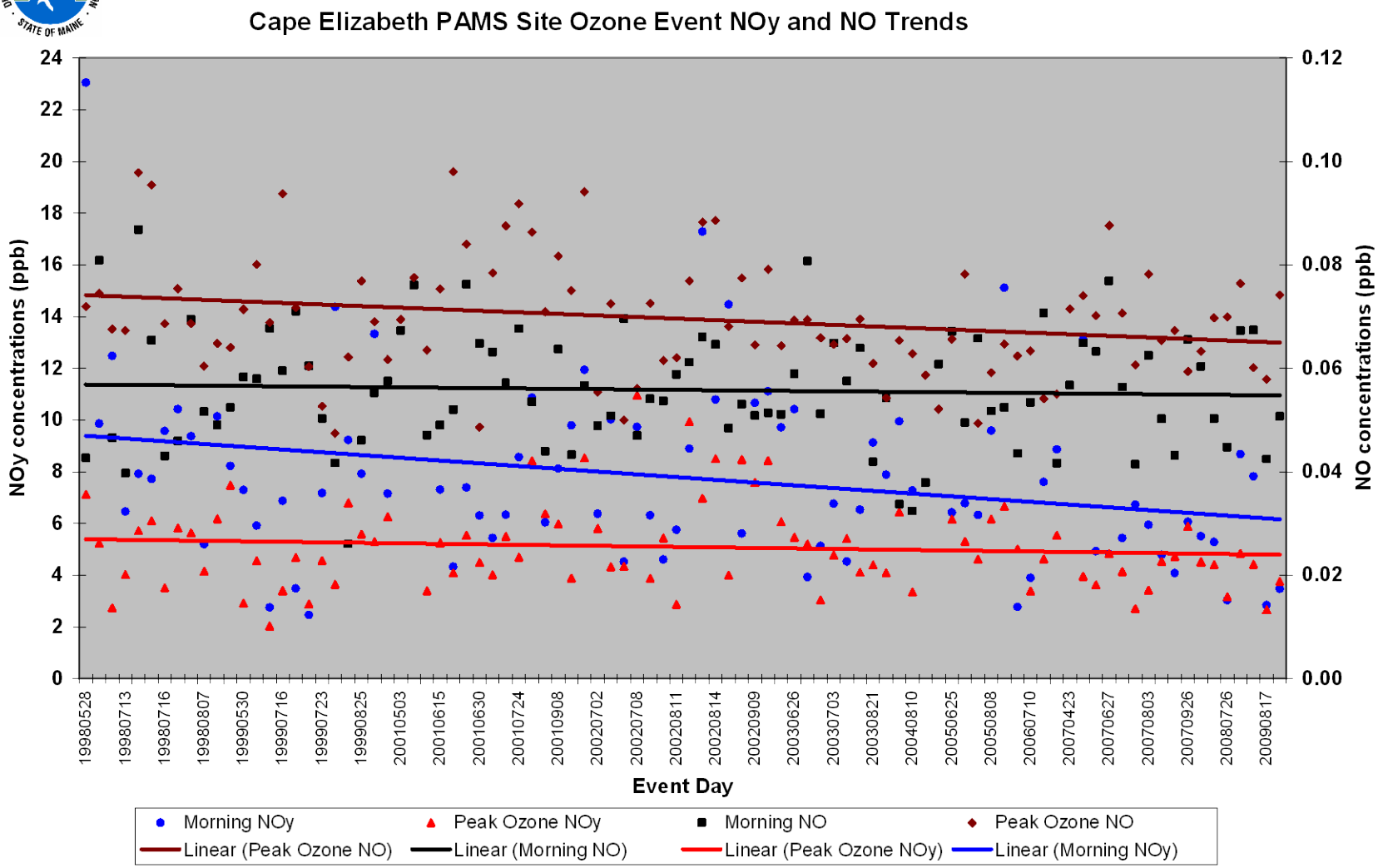


As VOCs Emissions are Reduced, There are More Below Detection Limits



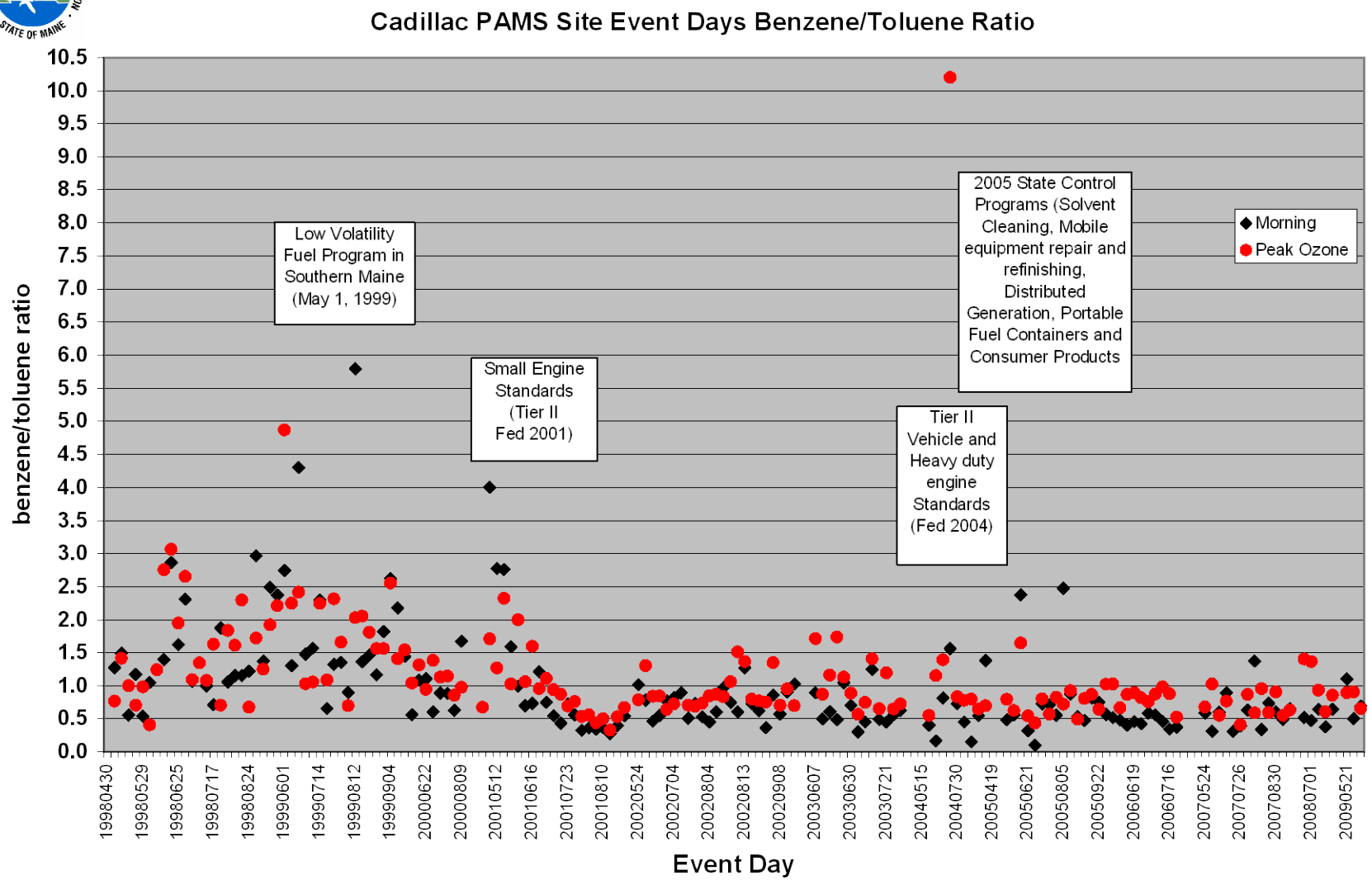
NO/NOy Trends(?)

Created by Tom Downs, Maine DEP-BAQ - 4/23/10



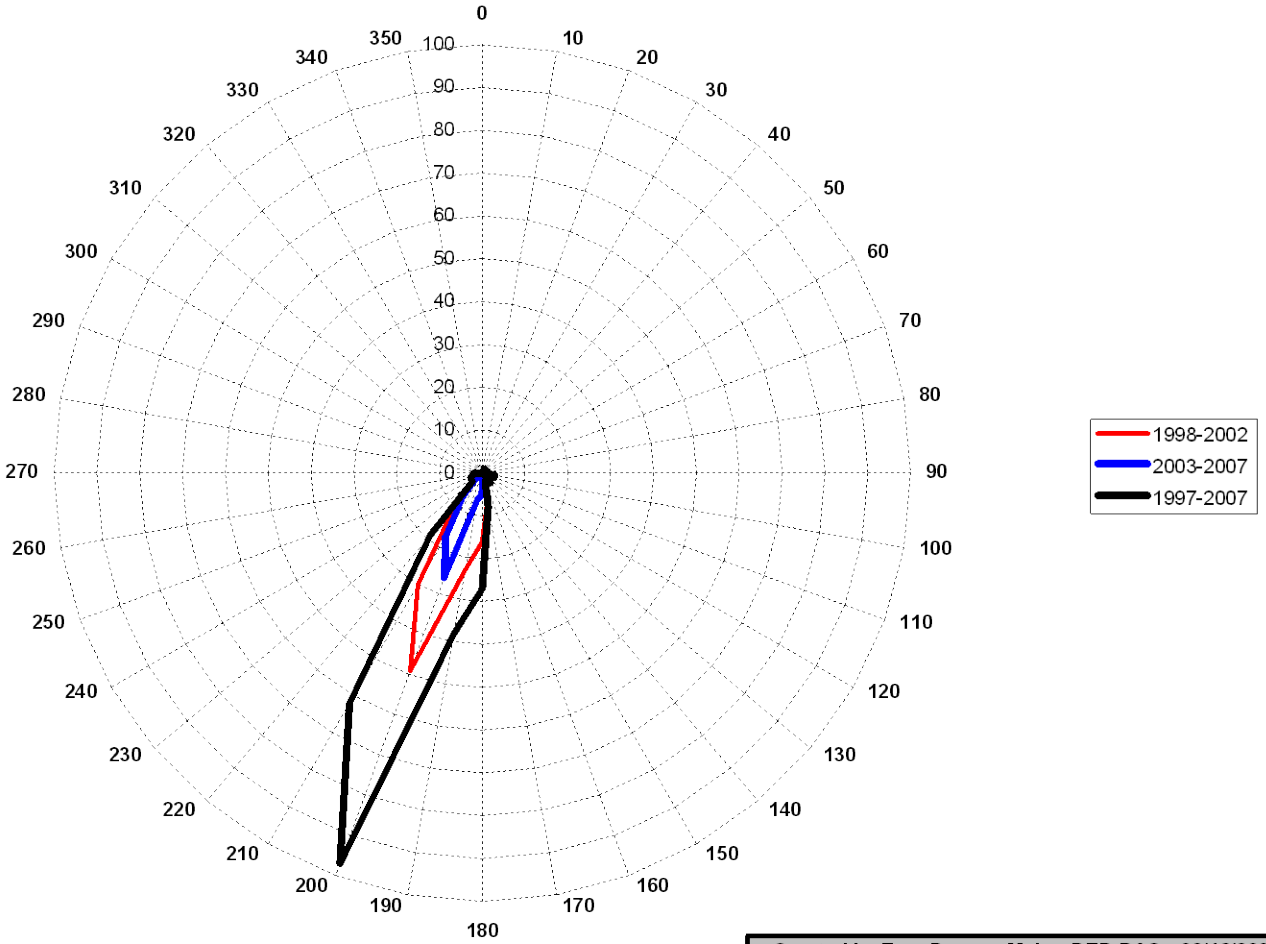
Aging Ratios – Benzene/Toluene

Created by Tom Downs, Maine DEP-BAQ - 4/23/10



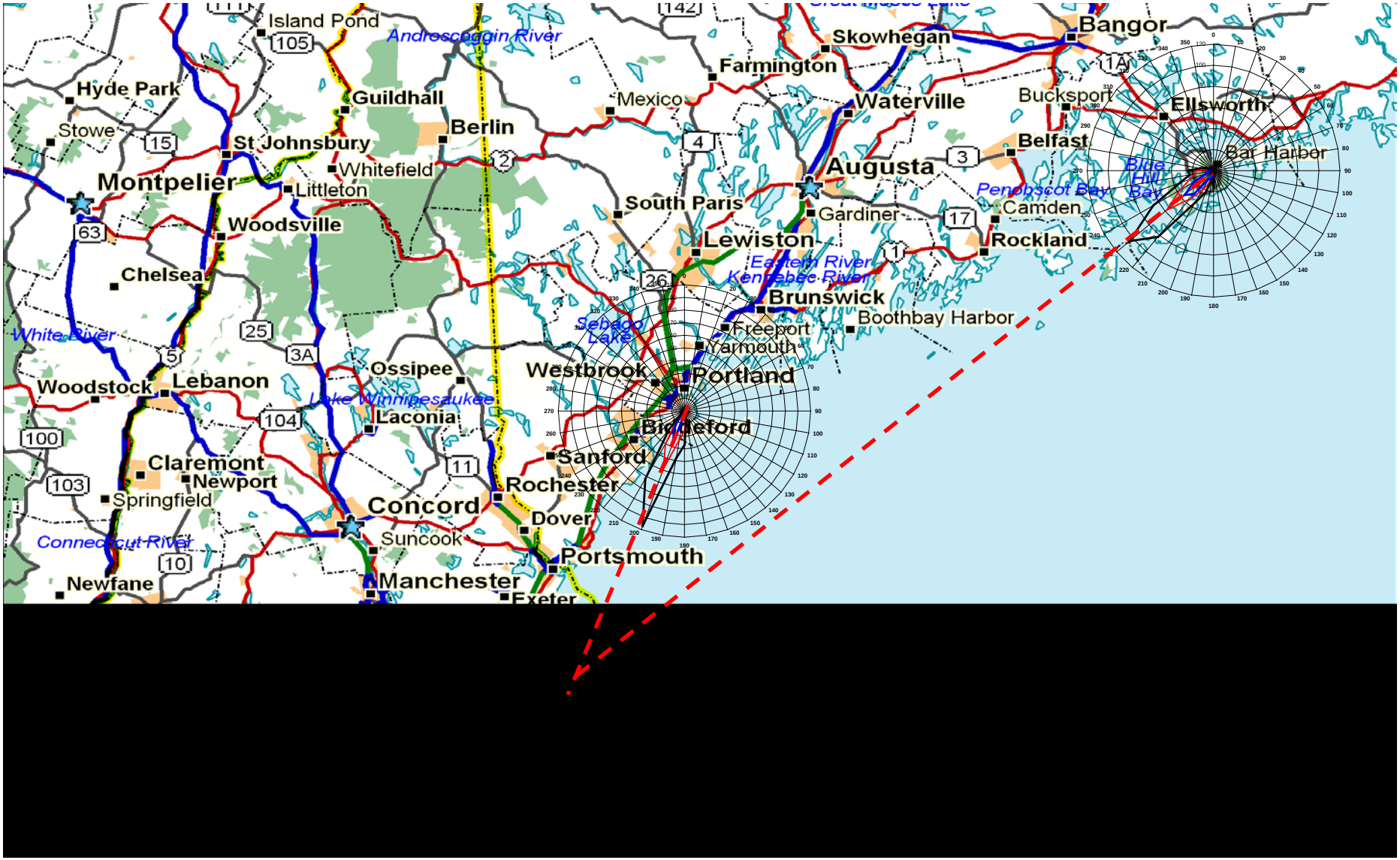
Wind Directions During High Ozone

Cape Elizabeth, ME (1000-1500 LST) Wind Direction Frequency During 1997-2007 Ozone events (8-hr Ozone max > 75 ppb)



Created by Tom Downs, Maine DEP-BAQ - 02/16/2008

Ozone Rose Map Overlay



NESCAUM PAMS Workgroup Data

NESCAUM PAMS ftp data archive:

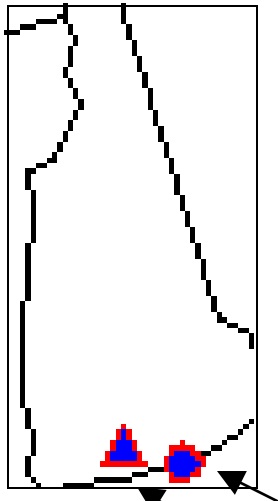
ftp://airbeat.org/PAMS/

Tom Down's (MEDEP) links to his data sets and analyses files :

http://www.maine.gov/dep/ftp/DEP_PAMS/NESCAUM_PAMS_DATA/ and

http://www.maine.gov/dep/ftp/DEP_PAMS/NESCAUM_PAMS_ANALYSES/

New Hampshire Data Analyses



- Trends of all species
- Comparison of PAMS Species with Toxic Thresholds (AALs)
- Trends of most toxic and most reactive species
- Comparisons of Two PAMS sites in close proximity but at different elevations:
  - ground level – Nashua, and at
  - transport level 2300 feet – Miller
- Investigation of photochemical reactivity patterns
- Investigation of role of Isoprene

New Hampshire PAMS Sites

Nashua
Gilson Rd

Miller State Park
(Pack Monadnock Mt)
2288 feet

Nashua AAL Comparison

NASHUA

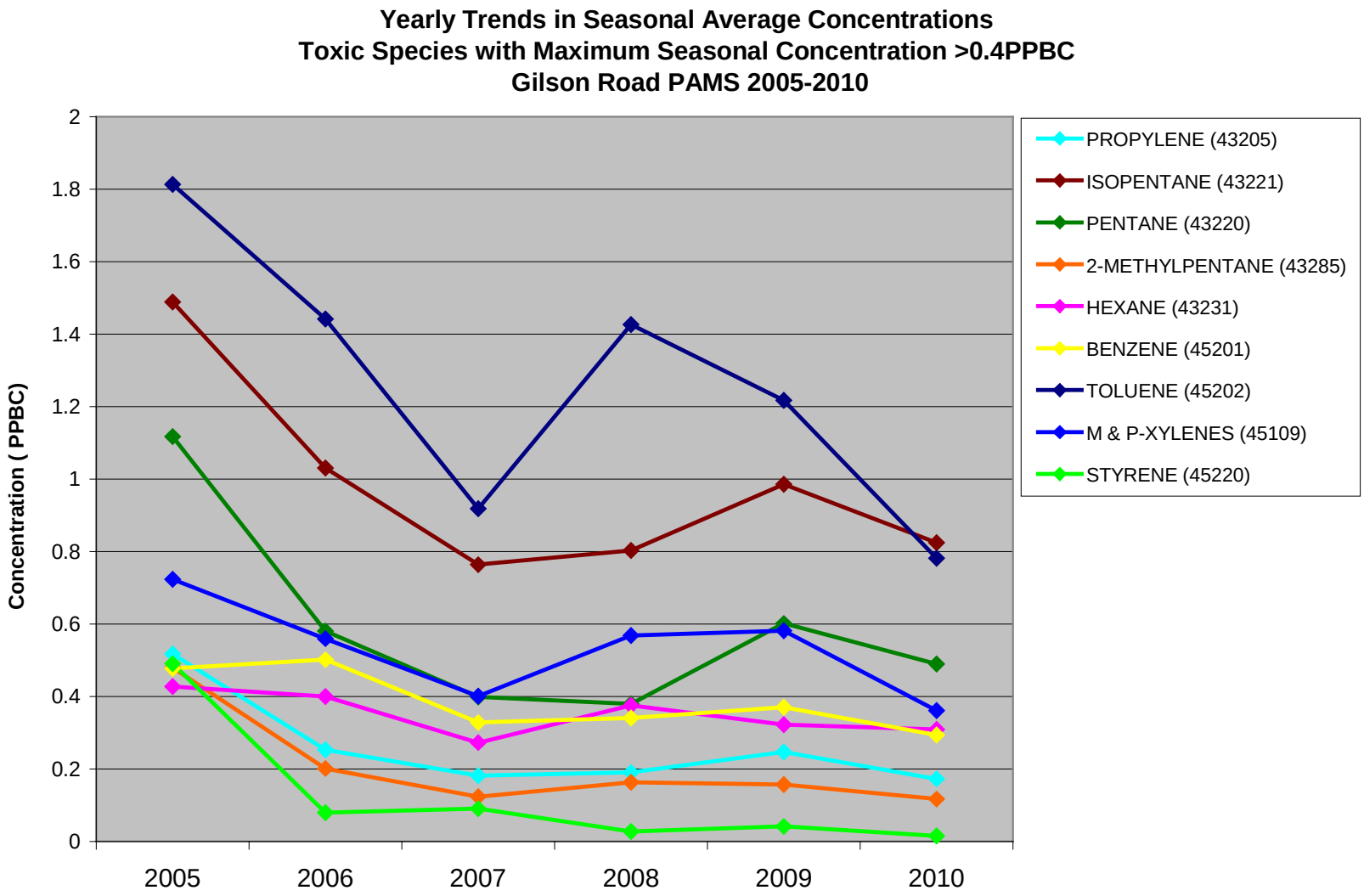
PAMS Parameter	AAL ug/m3	Max 24 Hour Avg. (ug/m3)						Max as % of AAL
		2005	2006	2007	2008	2009	2010	
PROPYLENE (43205)	35,833	0.55	0.34	0.30	0.33	0.35	0.20	0.00%
CYCLOPENTANE (43242)	25,595	0.23	0.23	0.16	0.13	0.15	0.10	0.00%
ISOPENTANE (43221)	36,875	2.04	2.50	1.56	1.41	1.23	1.13	0.01%
PENTANE (43220)	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%

Miller AAL Comparison

MILLER

PAMS Parameter	AAL ug/m3	Max 24 Hour Avg. (ug/m3)					Max as % of AAL
		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 of Most Common Toxic Species (Nashua)



REACTIVITY OF IDENTIFIED HYDROCARBONS

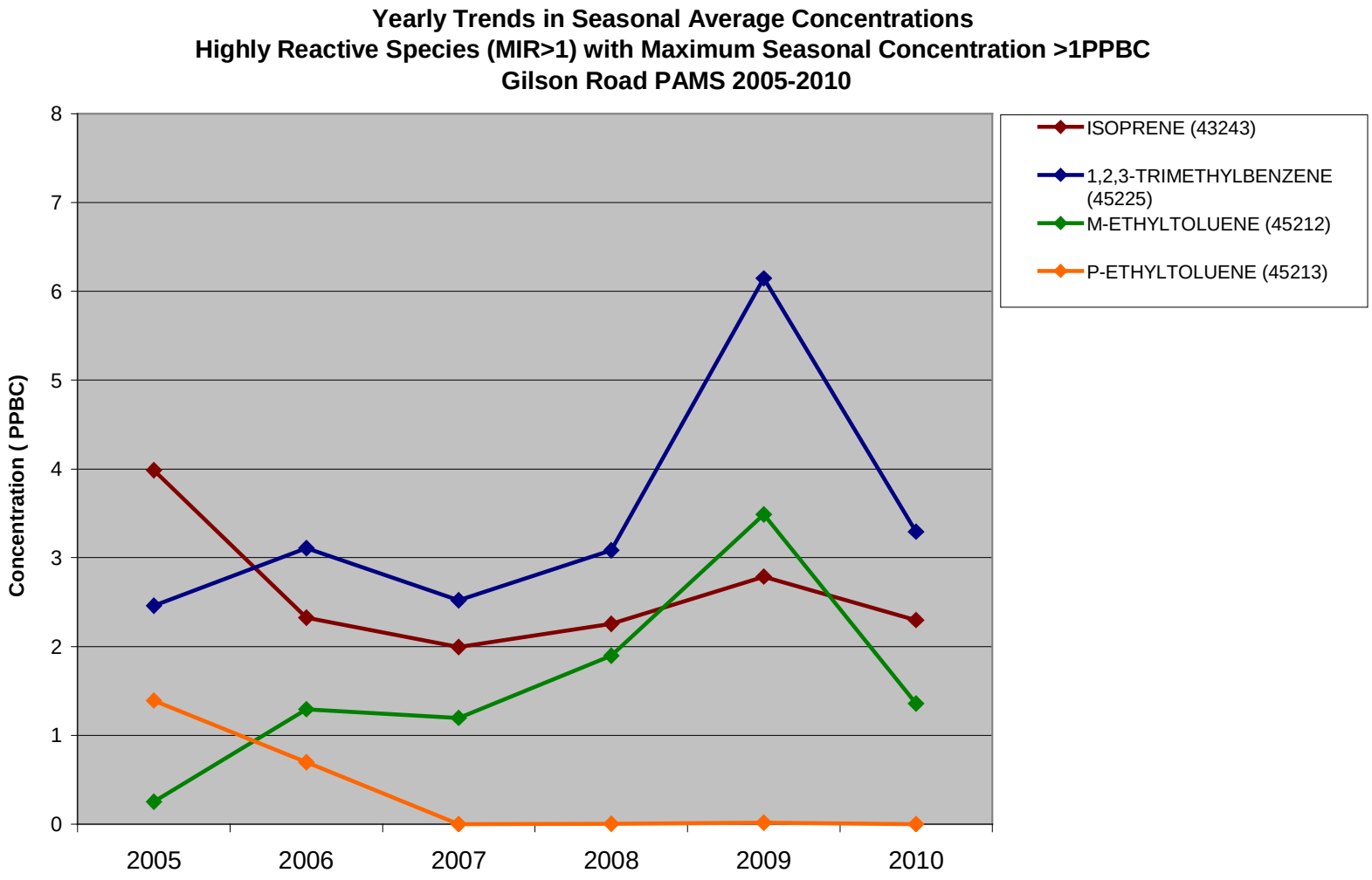
- Incremental reactivity is the change in ozone caused by adding a small amount of test VOC to the emission in an episode, divided by the amount of test VOC added:

  g ozone/g C or moles ozone/mole C

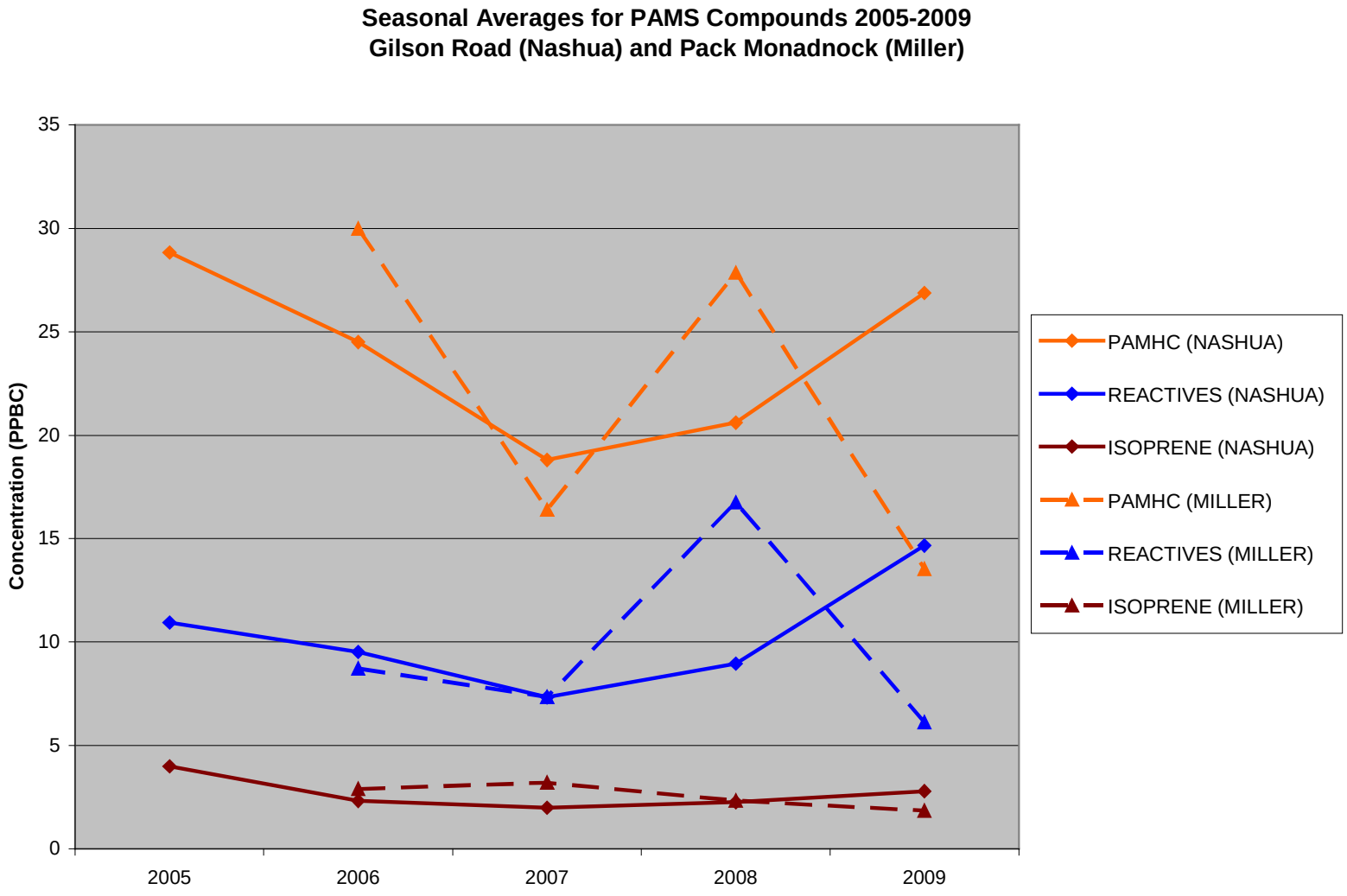
- Most useful in a relative rather than absolute manner.
- Uncertainty associated with MIR scale values and the notion that total reactivity equals the sum of individual species incremental reactivities is unverified.
- (MIR scale values for >C4 aldehydes not yet available.)

Maximum Incremental Reactivity (MIR)[a]			
Species Name	**AIRS No.**	**g Ozone/ g C**	**mol Ozone/ mol C[b]**
Acetylene	43206	0.5	0.14
Ethene	**43203**	**7.4**	**2.16**
Ethane	43202	0.25	0.08
Propene	**43205**	**9.4**	**2.75**
Propane	43204	0.48	0.15

Trends of Most Photochemically Reactive Species (Nashua)

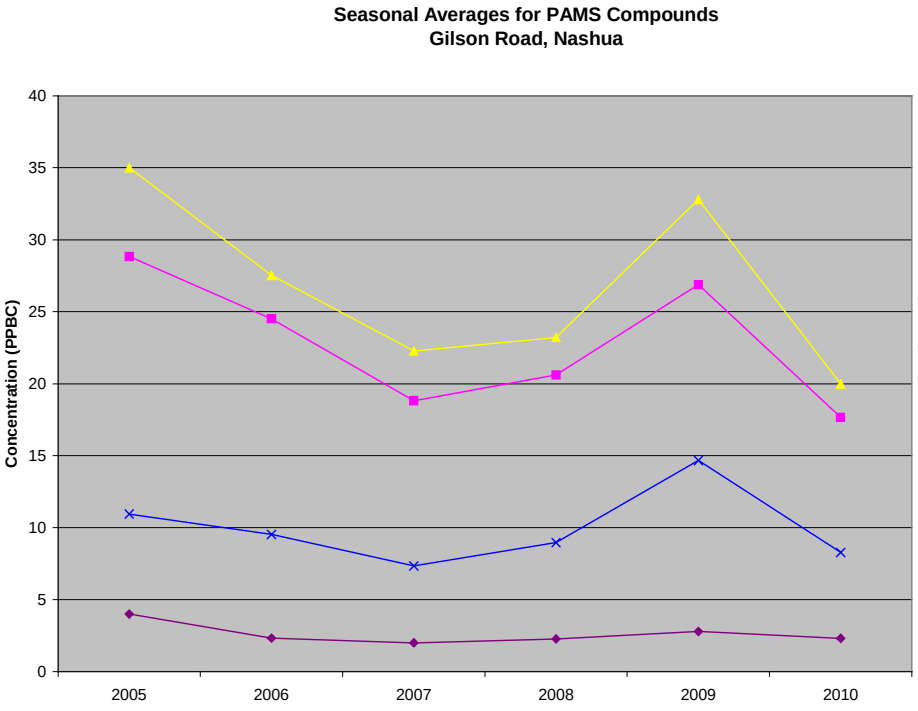


Reactivity Trends for Key PAMS Species Groupings

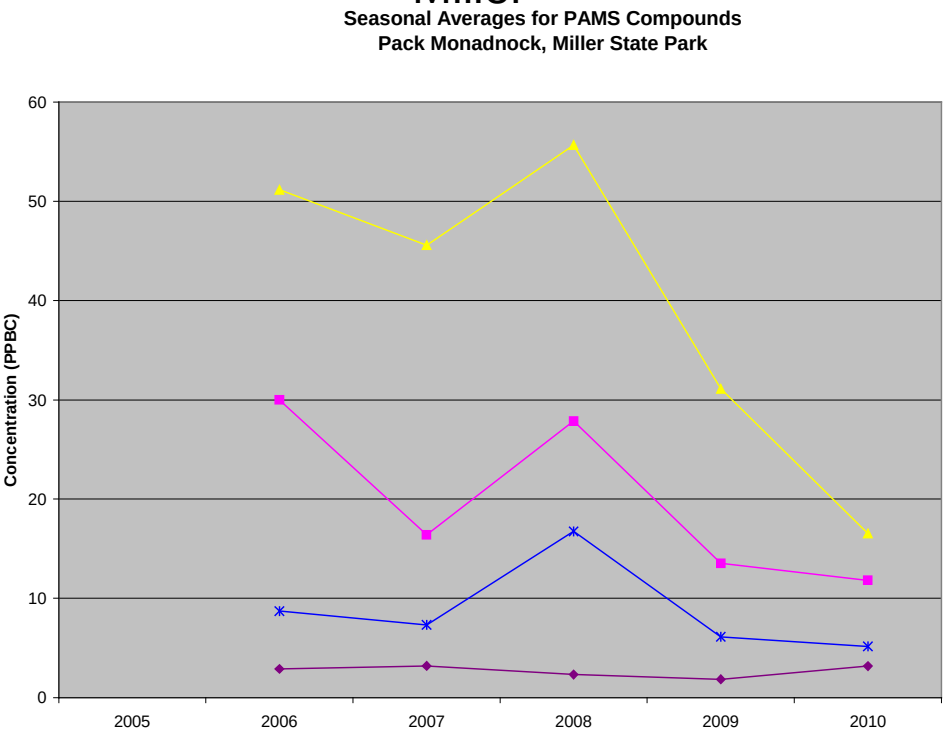


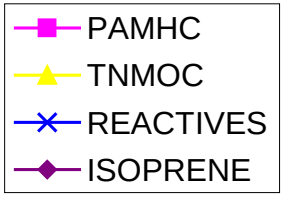
Concentration Trends for Key PAMS Species Groupings

Nashua



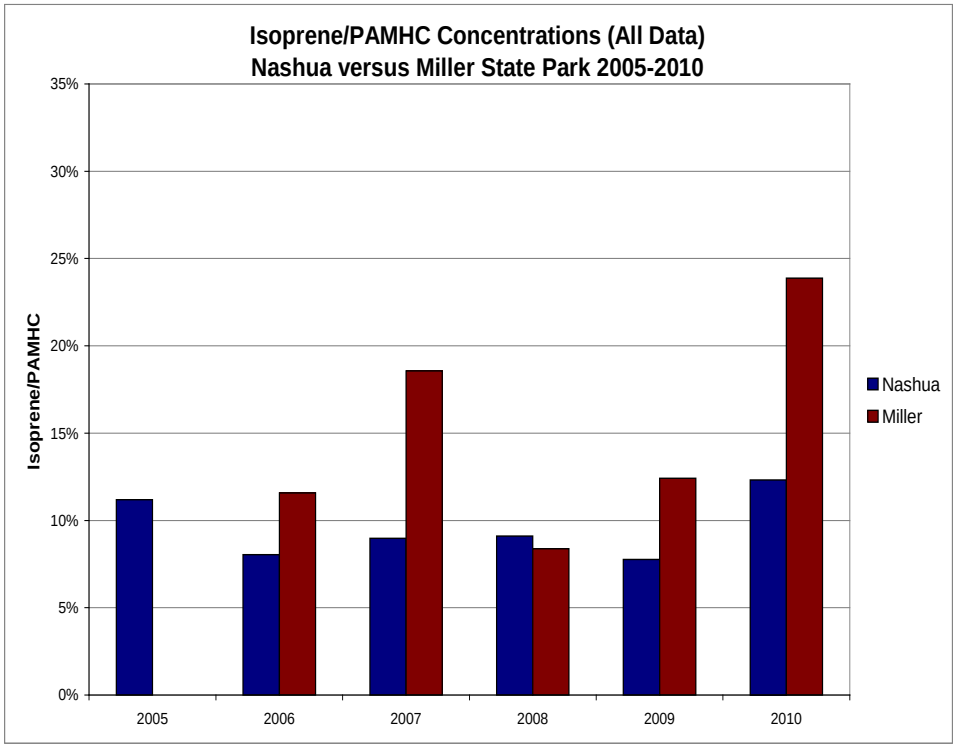
Miller



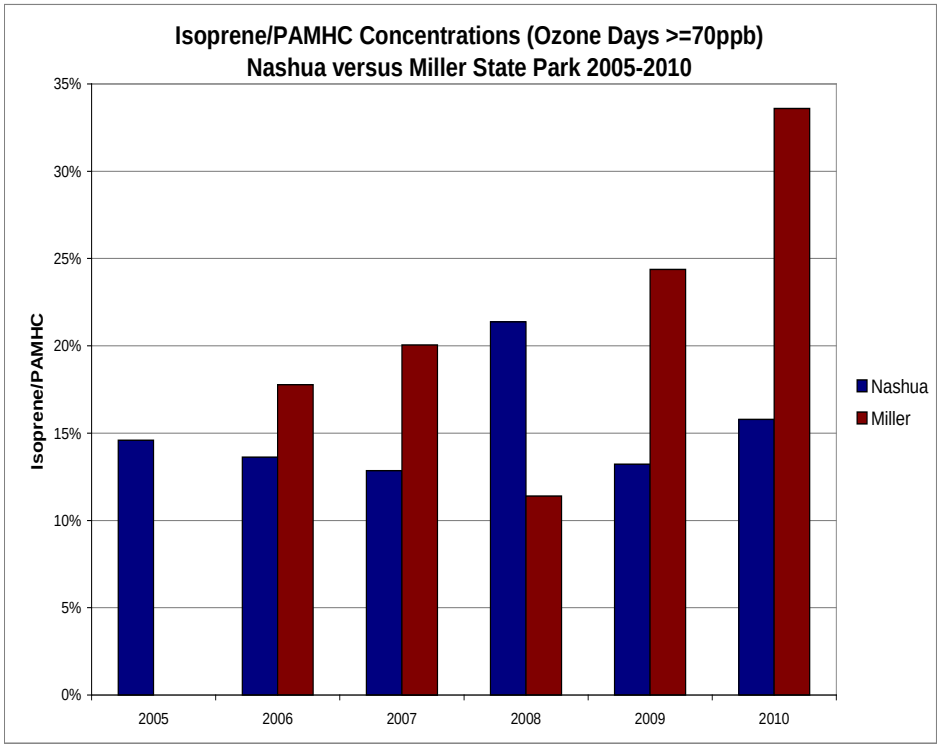


Isoprene as Percent of PAMs HC

All Days



Days with >70ppb Ozone

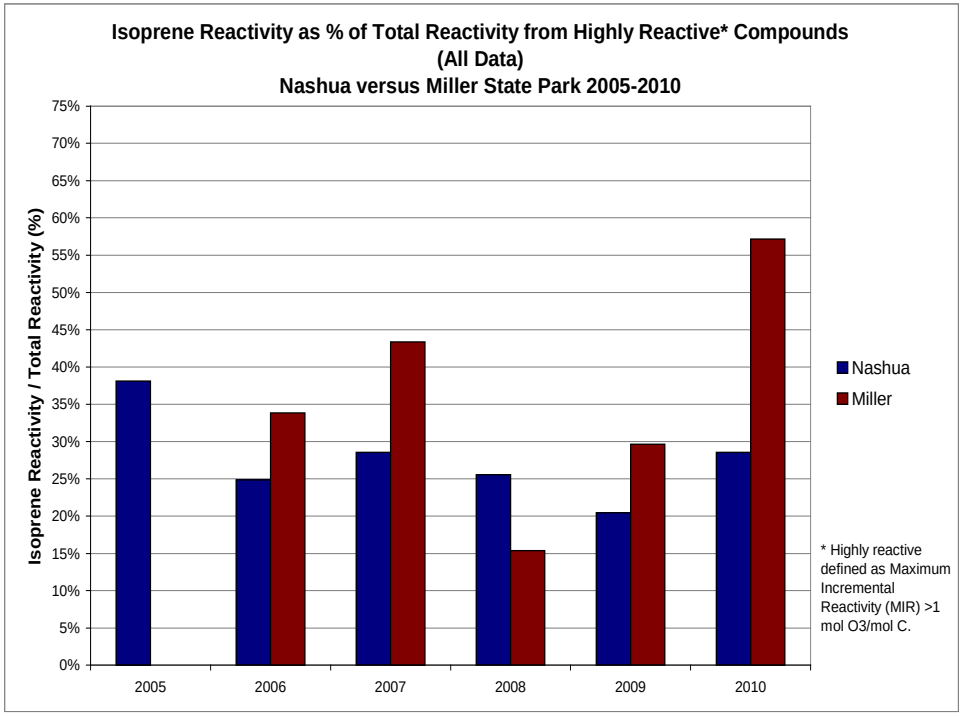


NASHUA

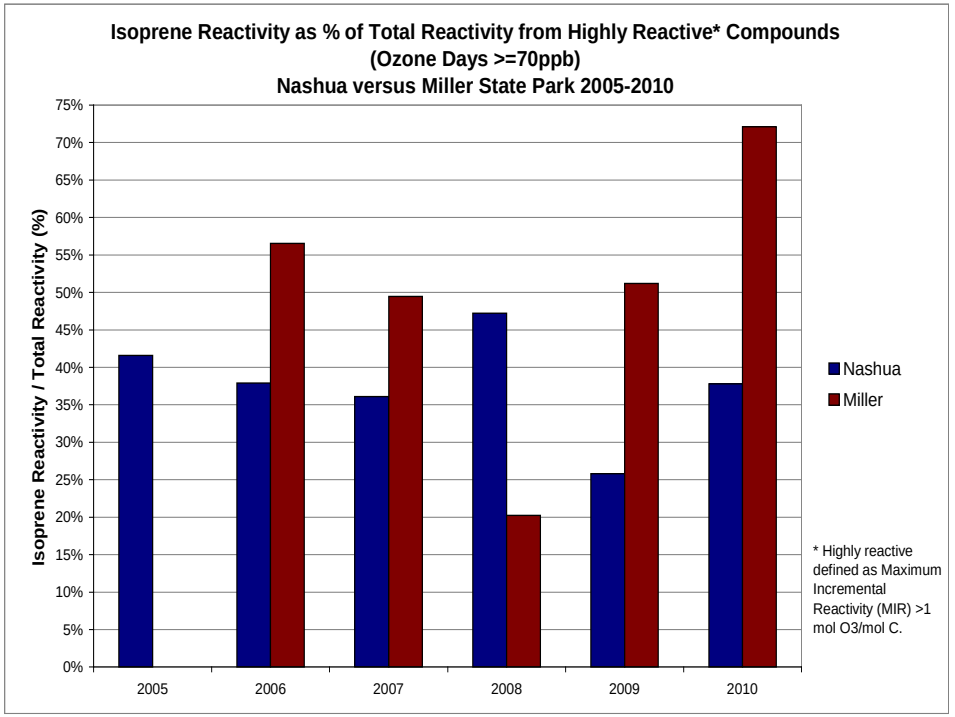
MILLER

Isoprene as Percent of Relative Atmospheric Photochemical Reactivity

All Days



Days with >70ppb Ozone



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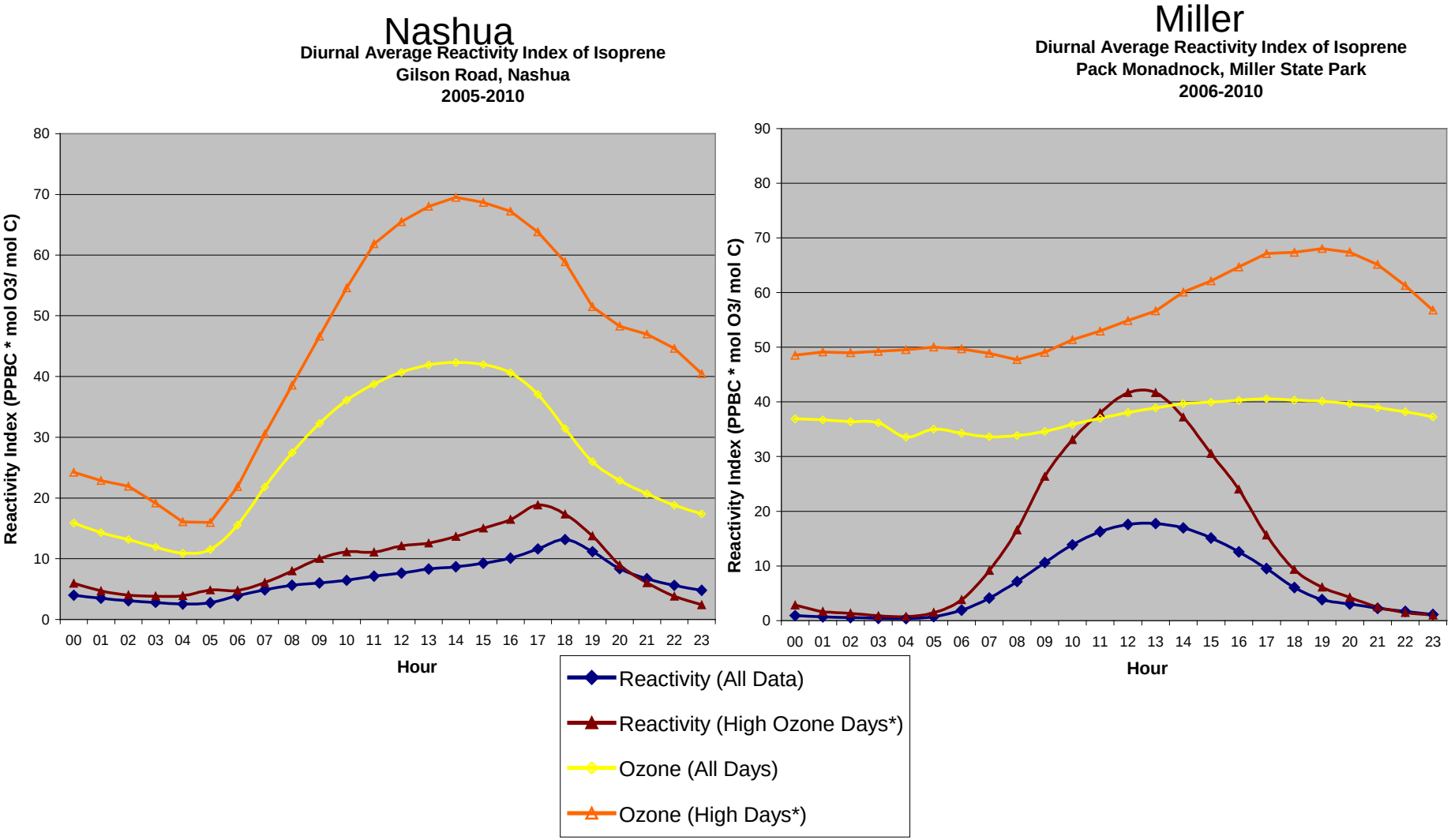
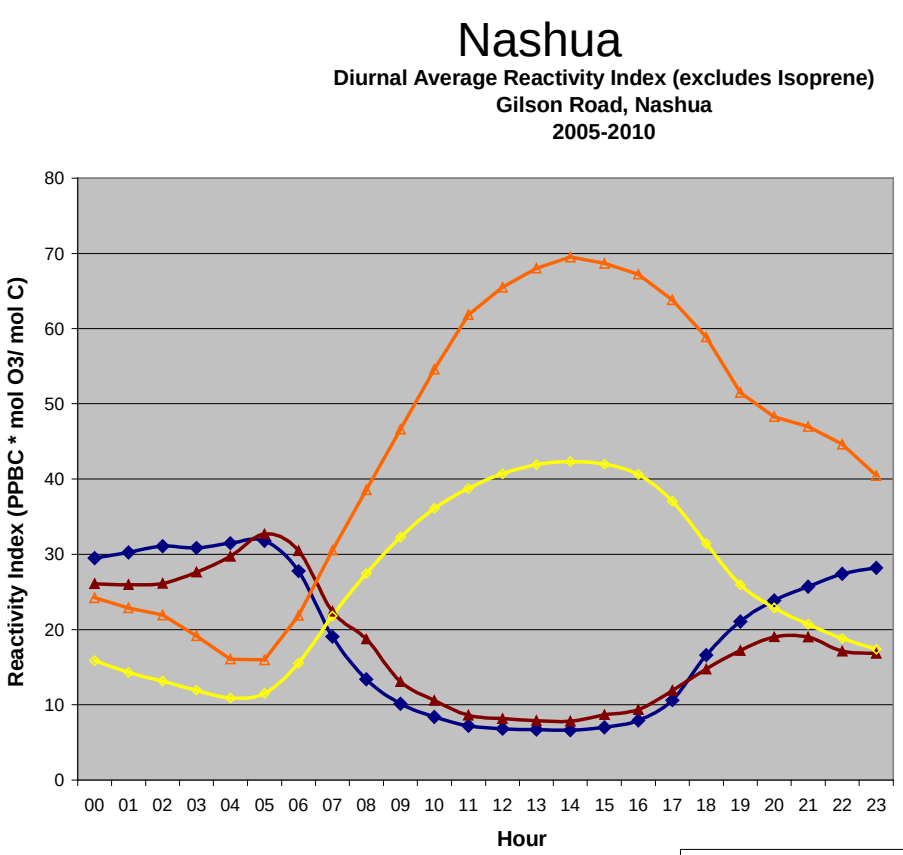
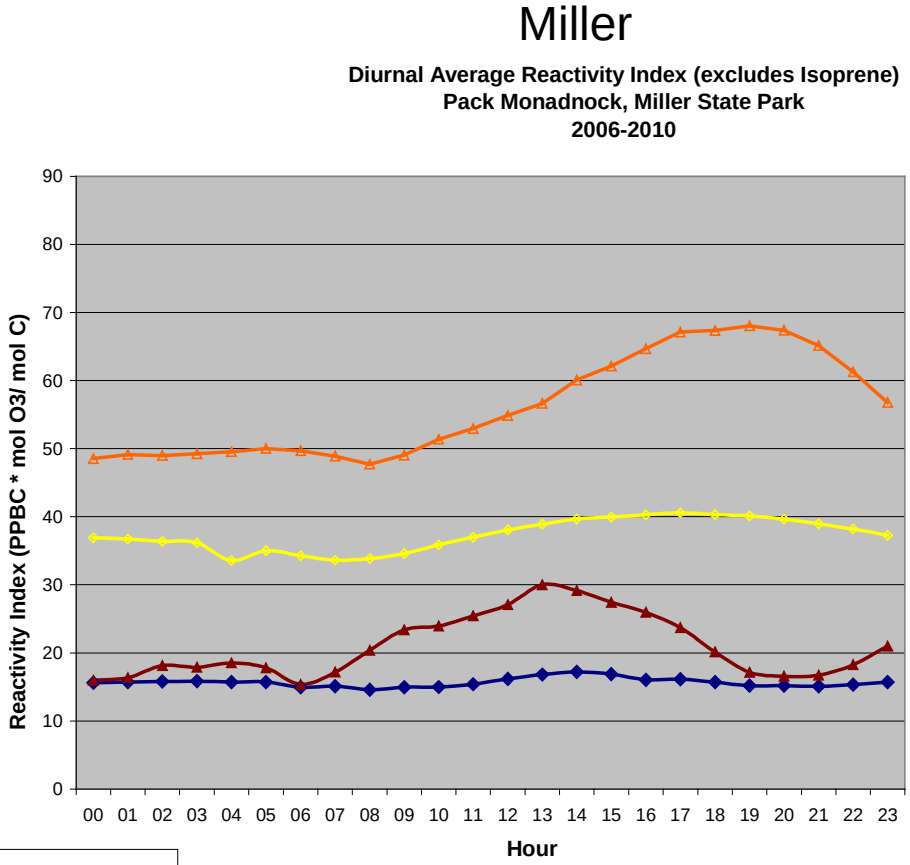
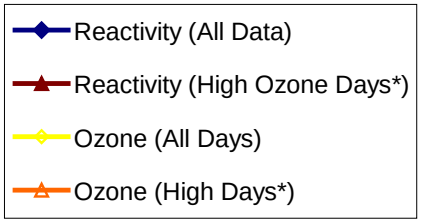
Diurnal Reactivity Trends for Isoprene



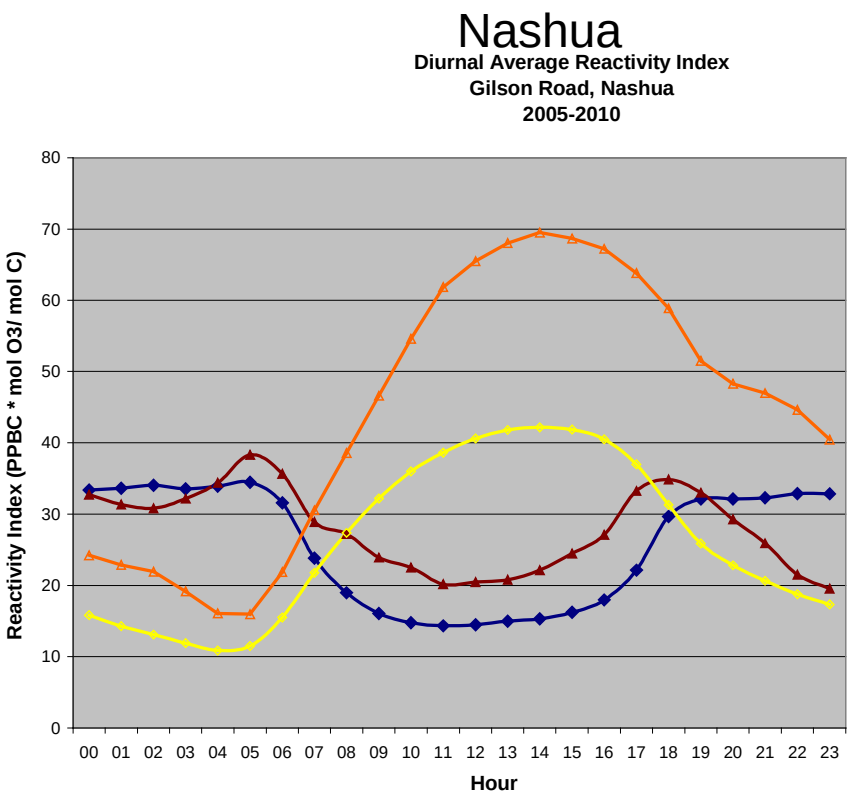
Diurnal Reactivity Trends for All PAMS Species Except Isoprene

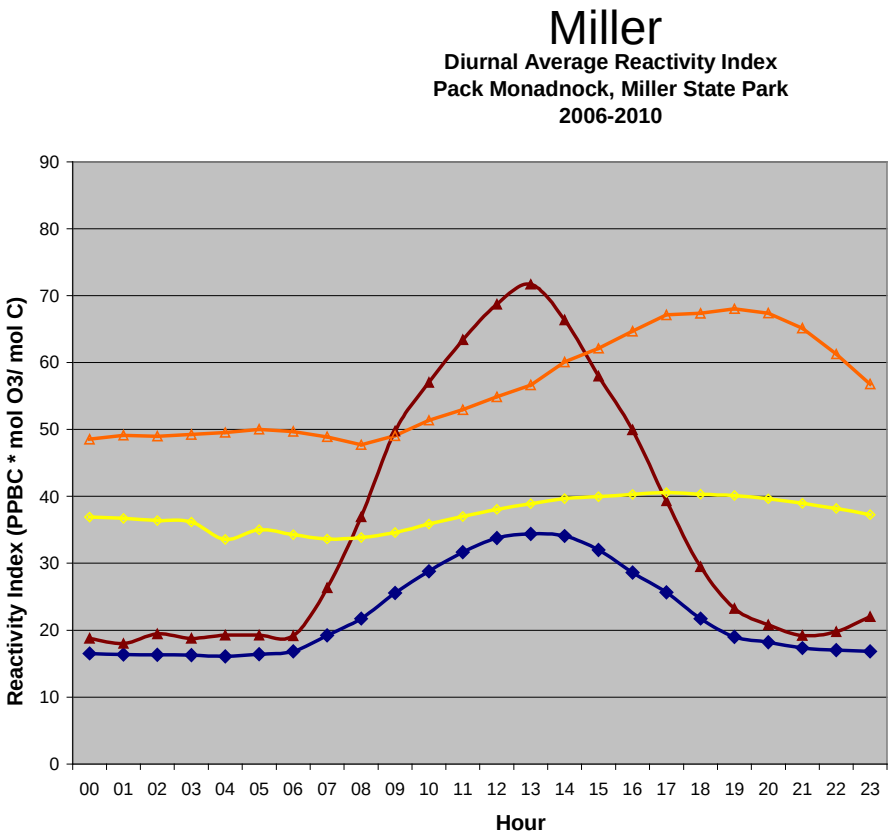






Total Diurnal Reactivity Trends for All PAMS Species

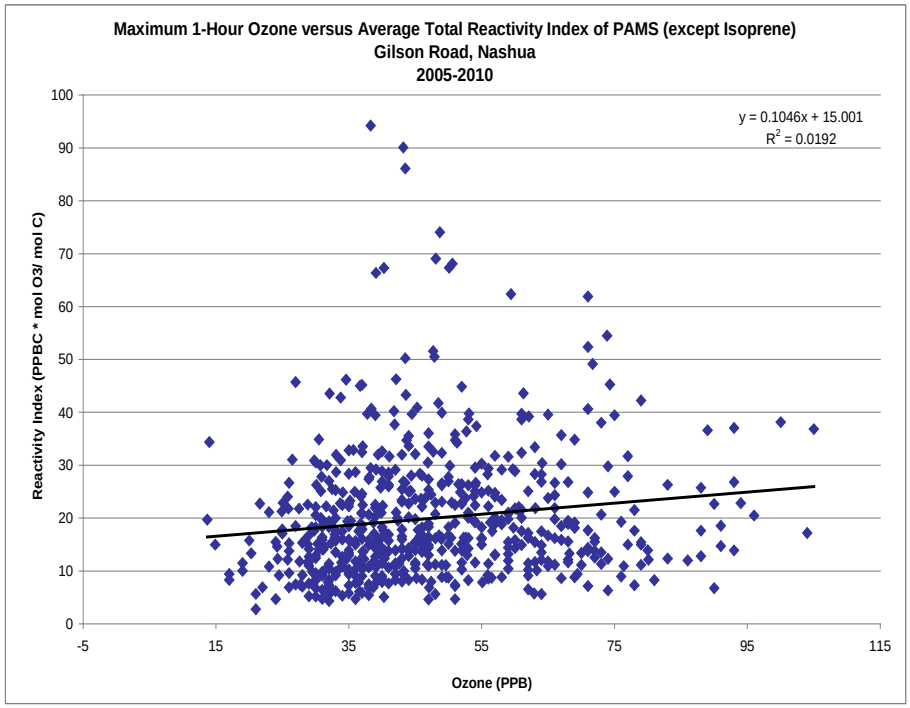




- Reactivity (All Data)
- Reactivity (High Ozone Days*)
- Ozone (All Days)
- Ozone (High Days*)

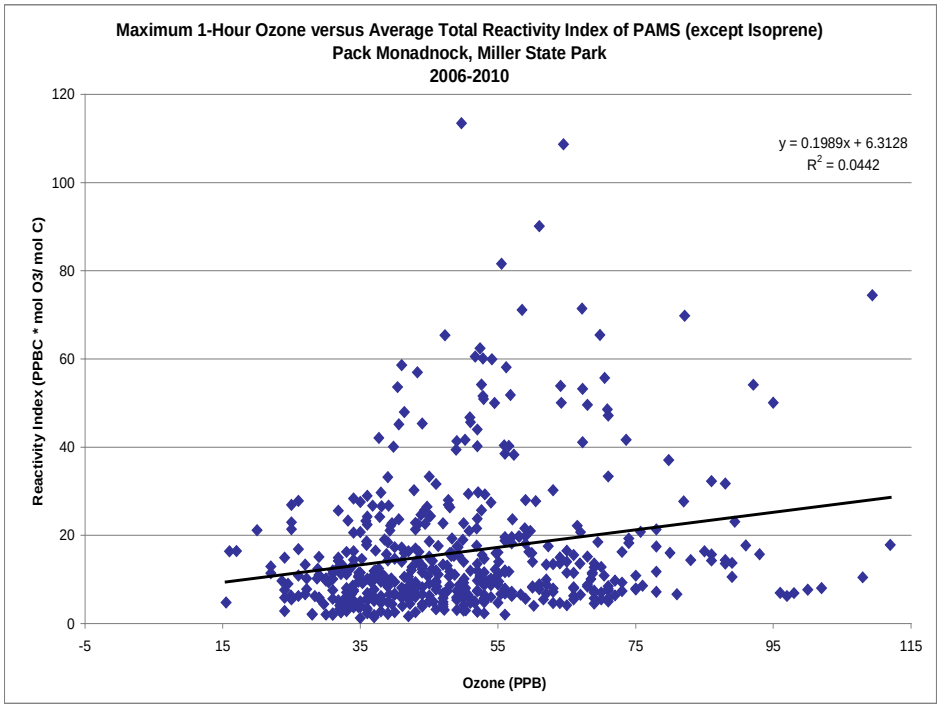
Correlations for Atmospheric Photochemical Reactivity to Ozone

Nashua



$R^2 = 0.02$

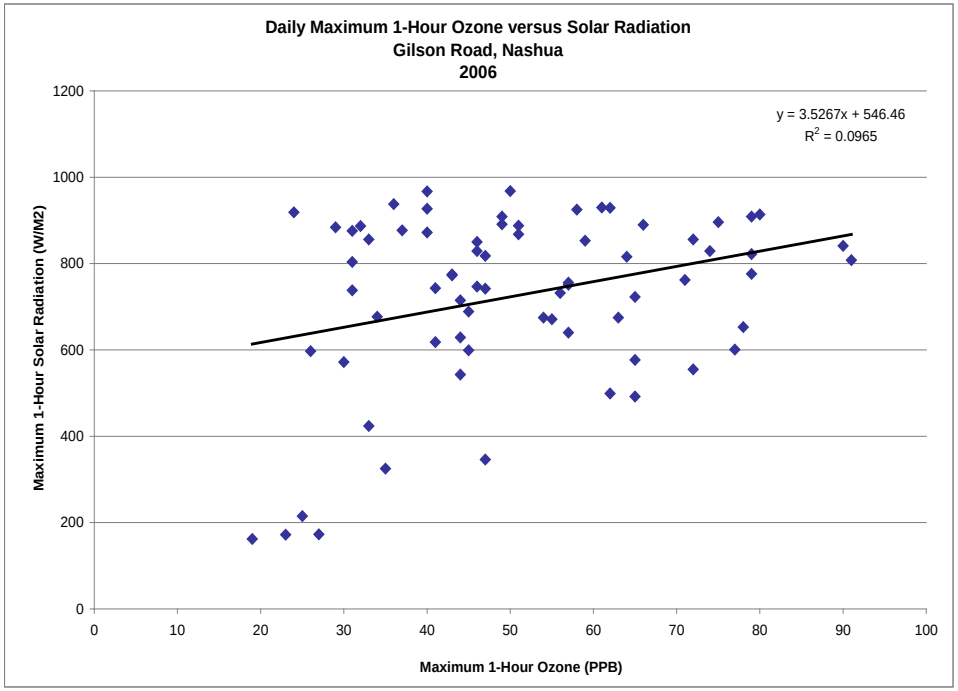
Miller



$R^2 = 0.04$

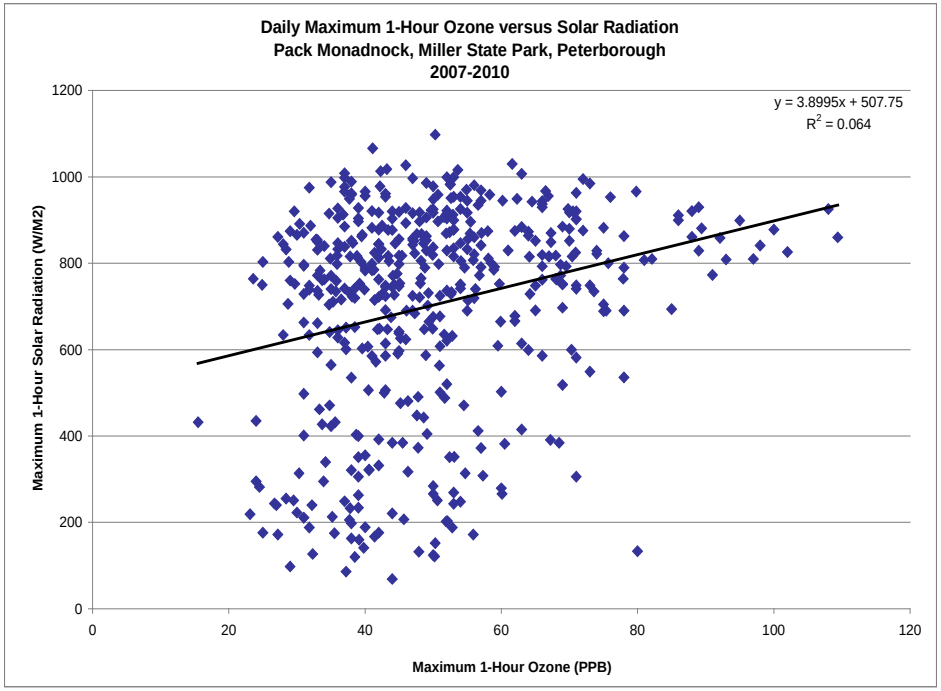
Correlations for Solar Radiation to Ozone

Nashua



$R^2 = 0.10$

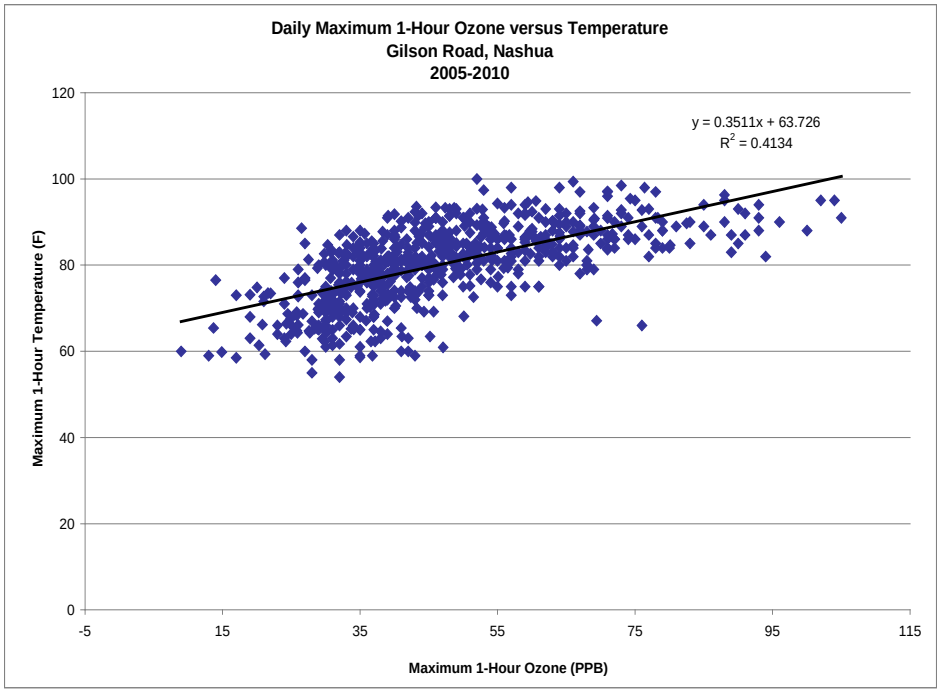
Miller



$R^2 = 0.06$

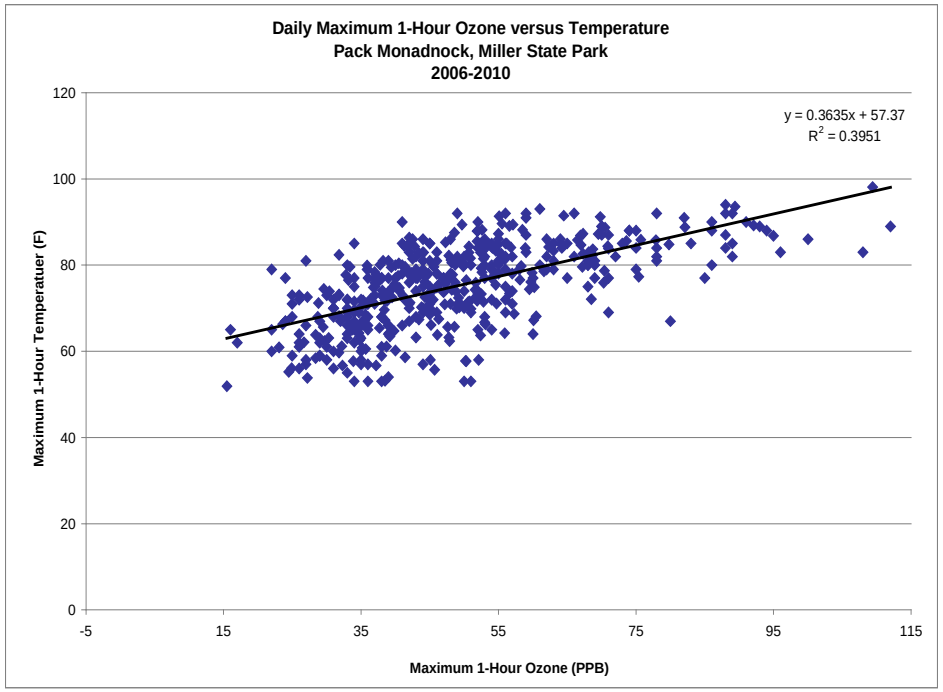
Correlations for Max Temperature to Ozone

Nashua



$R^2 = 0.41$

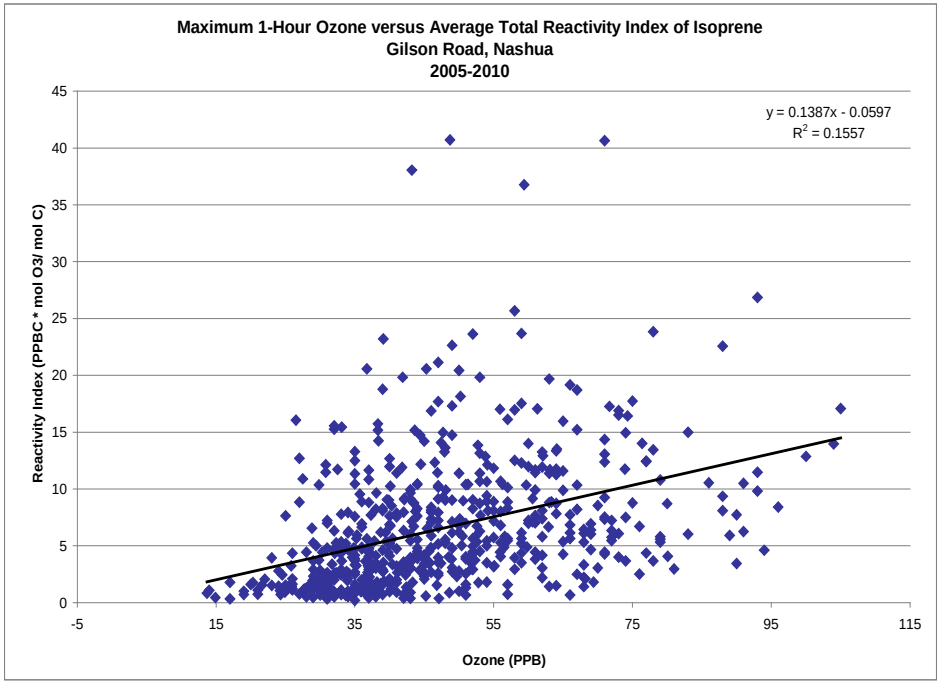
Miller



$R^2 = 0.40$

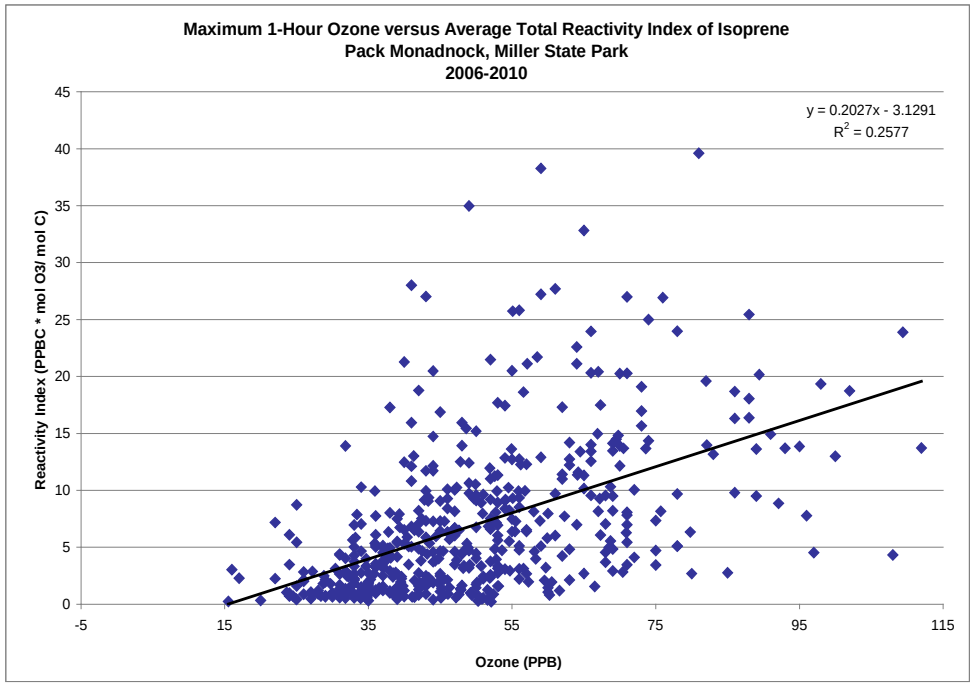
Correlations for Isoprene to Ozone

Nashua



$R^2 = 0.16$

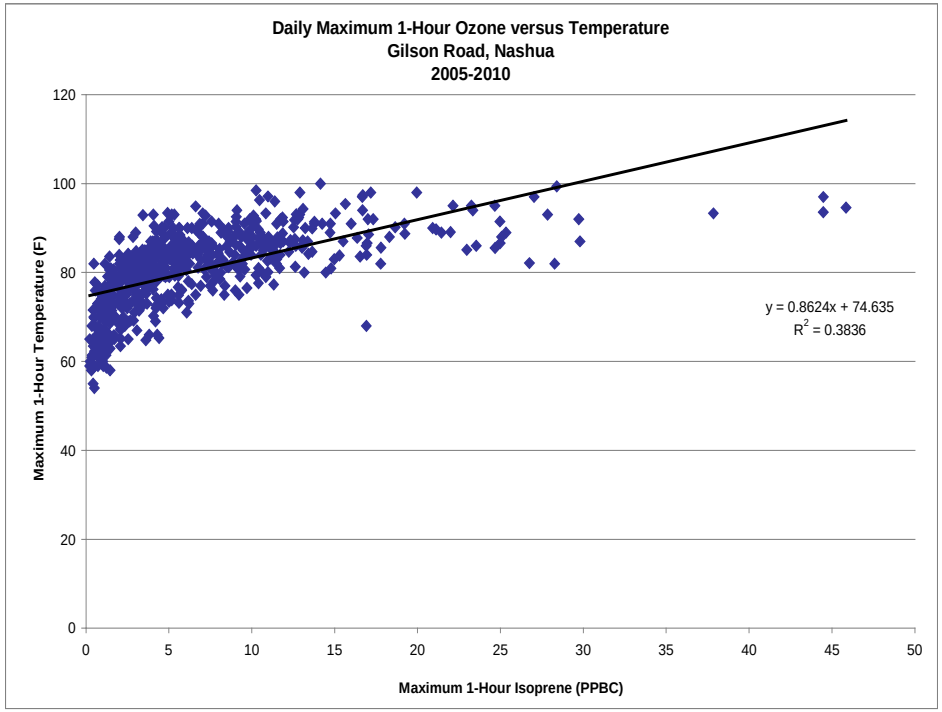
Miller



$R^2 = 0.26$

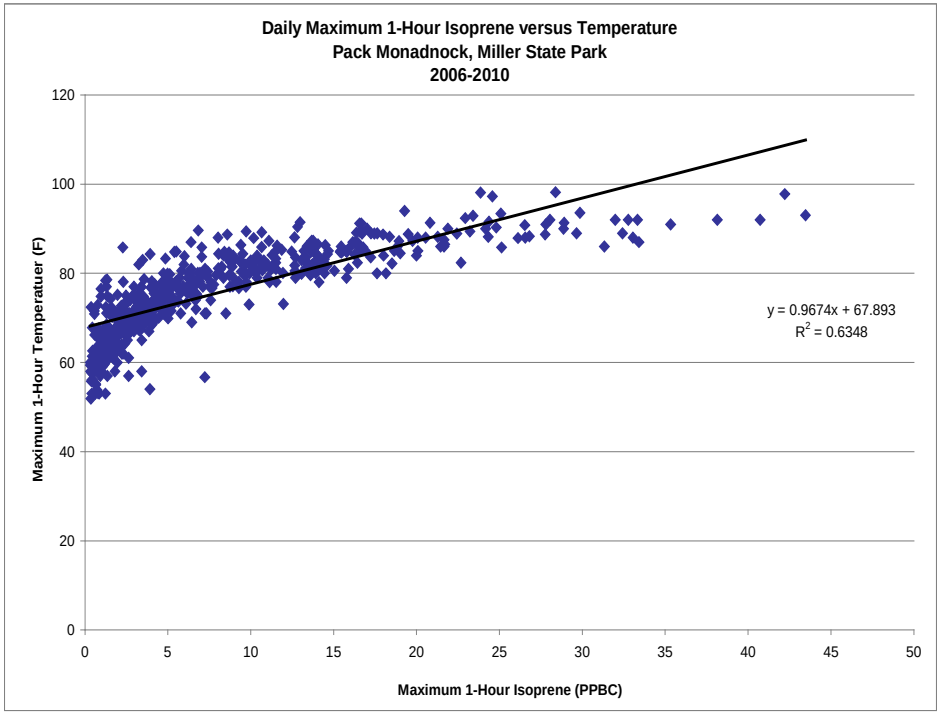
Correlations for Isoprene to Temperature

Nashua



$R^2 = 0.38$

Miller



$R^2 = 0.63$

High-Low Elevation Concentrations

Equal	Low Elevation Preference	High Elevation Preference	No Preference
Ethane	Propane	n-Butane	Isopentane
	Isobutane	2 and 3 Methylpentane	n-Butane
	n-Hexane	Isoprene	Ethylbenzene
	1,2,3-Trimethylbenzene	1,2,4-Trimethylbenzene	Acetylene
	mE-Toluene	Unidentified VOCs	
	o-Xylene	Undecane	
	Benzene	n-decane	
	Toluene	pE-Toluene	
	m&p-Xylene	n-Pentane	

Summary

- Decreasing trends for most anthropogenic PAMS species in most OTR locations.
- As PAMS species decrease, there are an increasing number of non-detects.
  - Need for more sensitive and less expensive analytical techniques.
- Carbonyl data is questionable in quality for most locations and species. Further, current techniques are expensive and often sampled infrequently
  - Need for more sensitive and less expensive analytical techniques.
- Aging ratio techniques are questionable in value as currently applied.
- Wind direction frequency plots and diurnal plots can be useful
- Appears to be more VOCs at higher elevations in New England than at ground level – mostly unknowns.