Semi-volatile gas phase Organic Compounds and Organic aerosol species measurements at Centreville, AL during SOAS

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Abstract

A Thermal-Desorption Proton-Transfer-Reaction Mass-Spectrometer (TD-PTR-MS) with different sampling systems (multi-stage denuder for gas phase and impact on a collector for aerosol phase) has been deployed in summer 2013 during the Southern Oxidant and Aerosol Study (SOAS) at the SEARCH ground site, Centreville, Alabama for *in-situ* gas phase and aerosol measurements on an hourly time resolution. A bunch of DB-1 column (0.53 mm x 5.0 μm) is used in the denuder for capturing the bulk of SVOCs and a collection-thermal-desorption (CTD) cell is used for collecting aerosol particles. Several hundreds semivolatile organic compounds (SVOCs) in gas phase and aerosol phases have been detected. The high mass resolution capabilities of ~5000, low detection limit (<0.05 pptv for gas species, <0.01 ng m^{-3} for aerosol species) and good physical.

and chemical characterization of SVOCs with the TD-PTR-MS allows constraining both, the quantity and the chemical composition. The SEARCH site was highly impacted by Biogenic Volatile Organic Compounds (BVOCs) and occasionally influenced by anthropogenic pollution. BVOCs and their oxidation products are capable of partitioning into the particle phase, so their simultaneous quantification in both phases has been used to determine the gas/particle-phase partitioning. Our results show the expected diurnal variation based on the changes of air temperature for many species. The results from this study give valuable insights into sources and processing of Secondary Organic Aerosols (SOAs) that can be used to improve parameterization algorithms in regional and global climate models.

Introduction

Semivolatile compounds often partition into different phases, and their simultaneous determination in multiple phases offers a chance to obtain more information about their distribution and fate in the environment. The quantification of semivolatiles in gas phase is an ongoing challenge. Recently, the Thermal desorption Aerosol Gas chromatograph (TAG) method (Williams et al., 2010) has been successfully applied to determine the gas/particle-phase partitioning of semivolatile compounds. In this method, the gas-phase portion of the semivolatiles were measured only on a relative scale and could not be quantified due to the lack of quantitative gas phase measurements. The measurements of gas- and particle-phase concentrations of semivolatile organic compounds is necessary to gain a better understanding of VOC reaction pathways in the atmosphere and derive accurate partitioning parameters for ambient aerosol mixtures. In this study, a sampler box containing multi-denuders in series was developed which was interfaced with TD-PTR-MS to quantify semivolatiles in an ambient aerosol mixture. The instrument was deployed in summer 2013 during the Southern Oxidant and Aerosol Study (SOAS) at the SEARCH ground site, Centreville, Alabama for *in-situ* gas phase and aerosol measurements on an hourly time resolution.
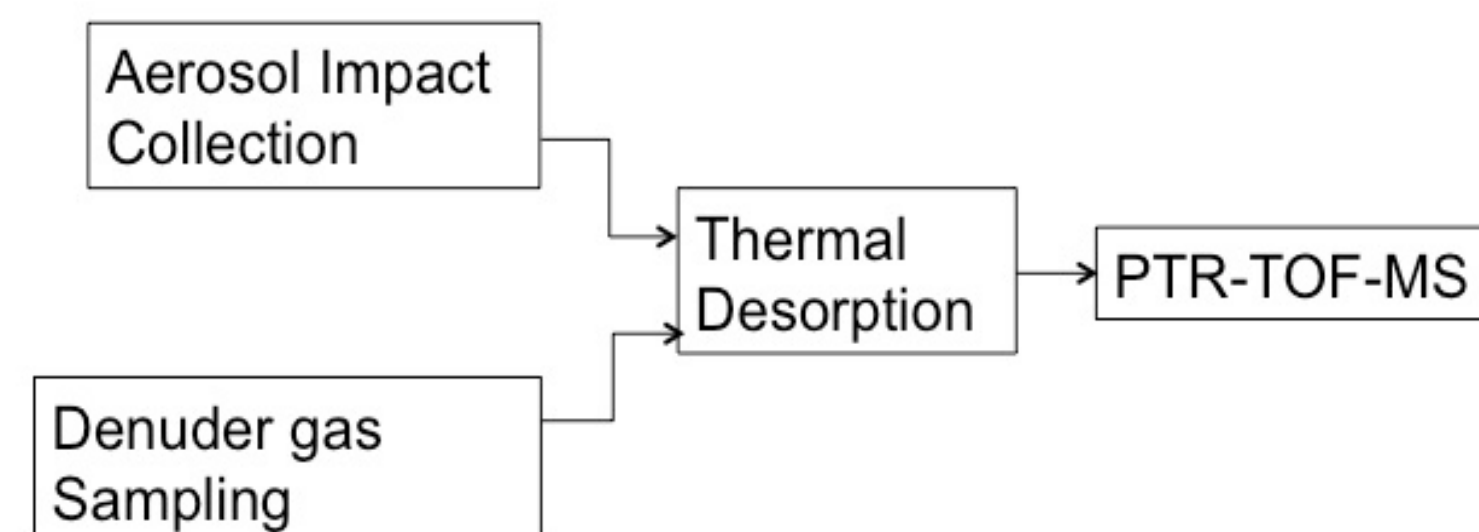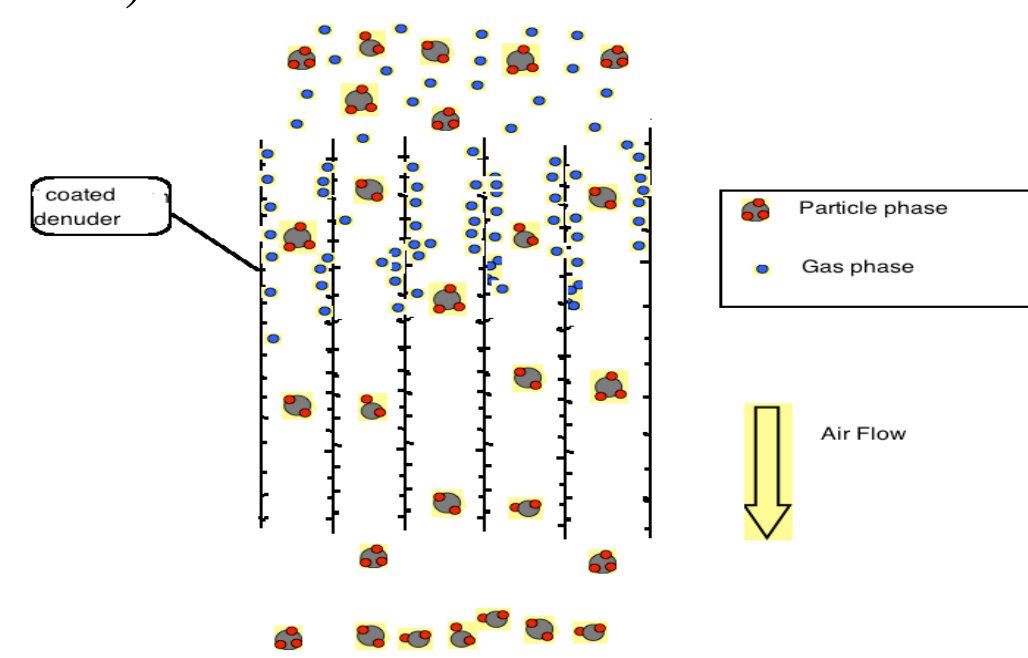
Instrumentation

Aerosol Impact Collection → Thermal Desorption → PTR-TOF-MS

Denuder gas Sampling →

Figure 1: Schematic of the instrument for collecting and measuring SVOCs

Gas Sampling
Three denuders in series:
1st denuder (DB-1) for semivolatile compounds
2nd denuder (DB-1) for recovering any left-over semivolatiles
3rd denuder (Carbon) for VOCs

Gas Desorption
=> With N$_2$ in the opposite direction of the sample collection flow
=> Heated denuders up to 200°C sequentially and stepwise

Aerosol Collection
=> By impaction onto a collection surface in Collection-Thermal-Desorption (CTD) cell using a sonic jet impactor.

Aerosol Desorption
=> Thermally desorbed the CTD cell by ramping the temperature up to 350°C in steps of 50°C

Compound detection
Compounds were detected at their protonated mass by Proton Transfer Reaction-Mass Spectrometer (PTR-MS) using a soft ionization technique. The instrument is equipped with a time of flight mass-spectrometer (TOF) which features high mass resolution capabilities of ~5000.
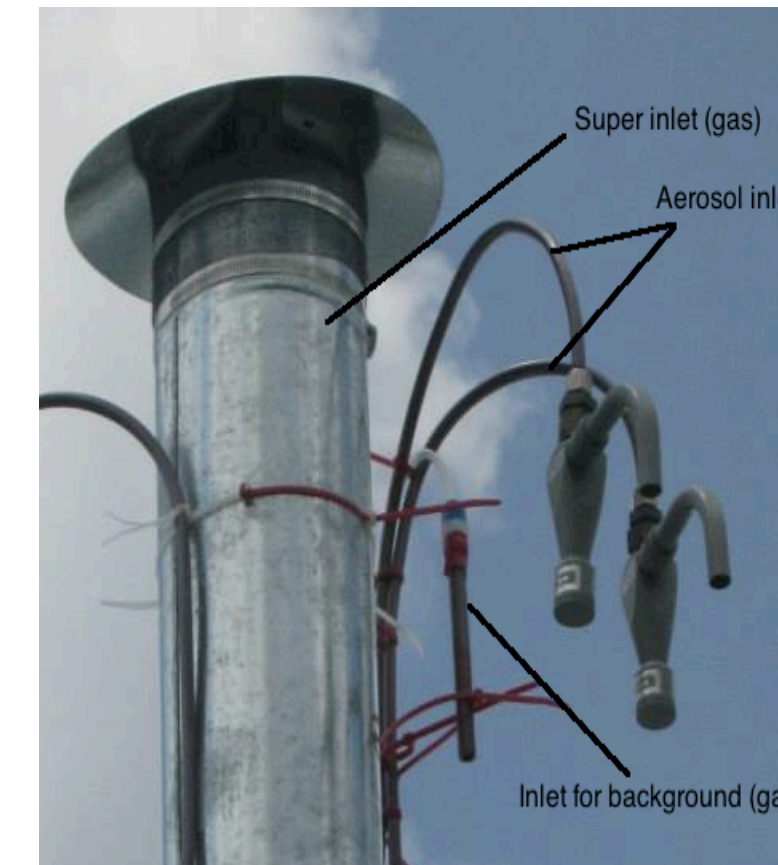
Data analysis
Data were processed in IDL software considering the following items: (a) time to mass conversion, (b) peak detection, (c) homogenization, (d) integration and correction of overlapping signals, (e) mass scale re-calibration and peak identification.

Field campaign
SOAS (Southern Oxidant and Aerosol Study) Campaign
Site : SEARCH ground site, Centreville, Alabama, US
Duration: June 1 to July 15 2013
The site is highly impacted by BVOCs and occasionally influenced by Anthropogenic pollution

Williams, B.J., Goldstein, A.H., Kreisberg, N.M., hering, S.V., In situ measurements of gas/particle-phase transitions for atmospheric semivolatile organic compounds, Proc. Nat. Acad. Sci., 107, 6676-6681, 2010.

Instrumental set-up at SOAS

Sampling inlet

Instrumental set-up (Inside the trailer)

Sampling and measurement frequency

=> Sampling time: ~40 min (Aerosol), ~30 min(Gas).
=> Measurement frequency: Alternate filter and without filter sampling (Aerosol), One background in 9 hour cycle (Gas).
=> Filer samples were collected by passing airstream through a Teflon membrane filter (Zefluor 2.0 μm, Pall Corp.)
=> Background air samples were collected by passing ambient outside air through Platinum catalyst operated at 500°C.
=> Data from 16 June to 15 July has been used for all of the presented results
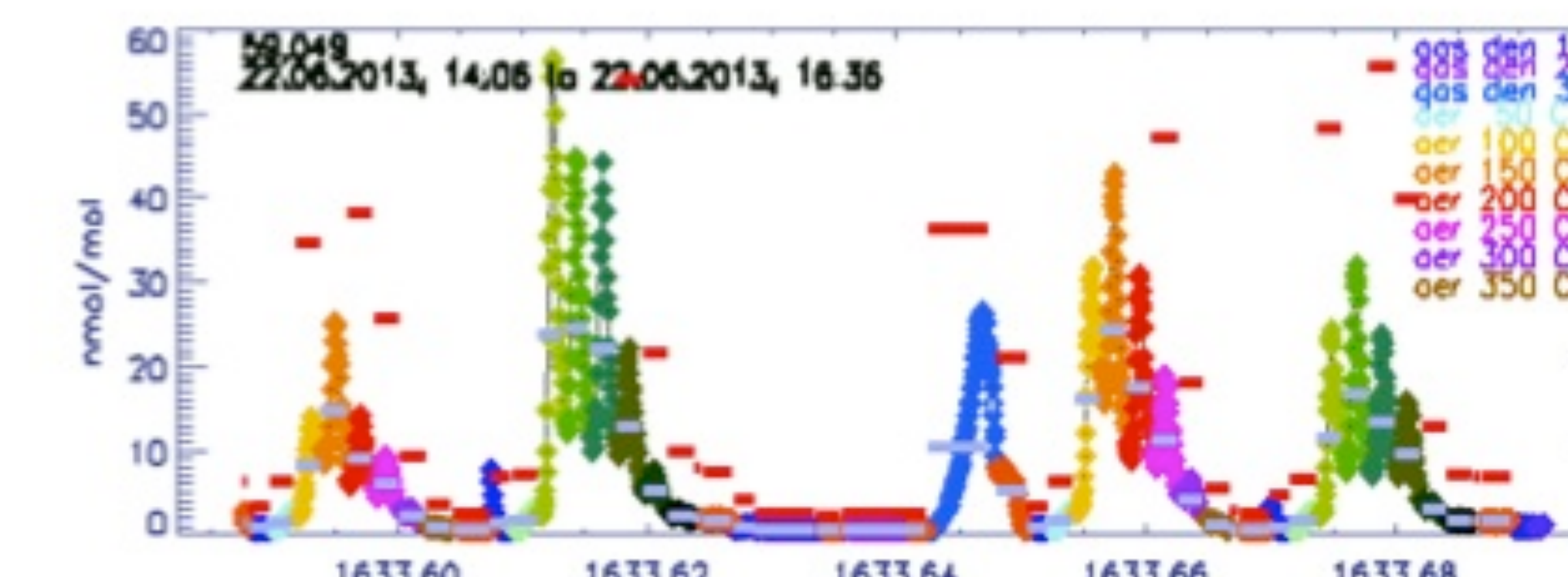
Results

Recovery test of semivolatile gas in DB-1/DB-1/Carbon denuders
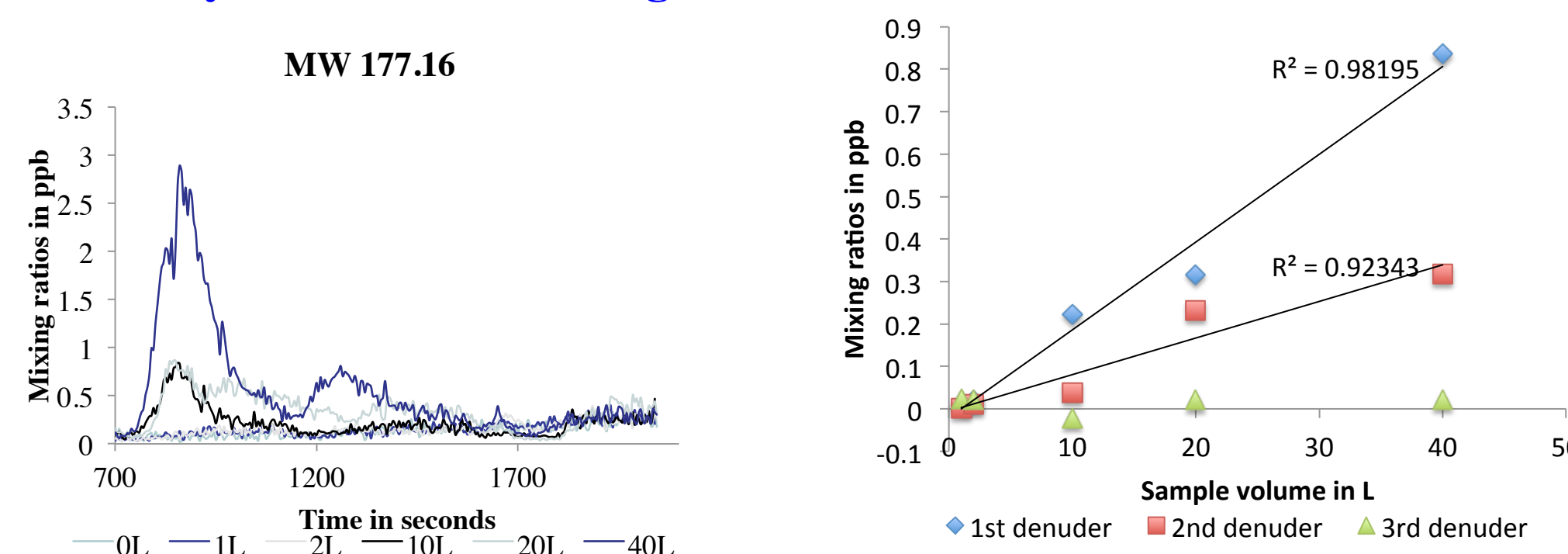
=> 30L sampling was chosen because of improving the limit of detection
=> DB-1 denuders was used in both 1st and 2nd denuders for higher recoveries of semivolatiles

Gas molecules retained (%) whether in DB-1 or C denuder

m/z	DB-1(%)	C (%)	Probable compounds	m/z	DB-1(%)	C(%)	Probable compounds
33.033		83	CH4OH+	135.08		74	C4H10O3N2H+, C9H10OH+
42.034		95	C2H3NH+	137.13	58		C10H16H+
45.033		66	C2H4OH+	139.11	86		C9H14OH+
59.049		96	C3H6OH+	145.12		71	C8H16O2H+
61.028		76	C2H4O2H+	147.07	58		C5H10O3N2H+, C10H10OH+
69.071		95	C5H8H+	148.04		68	C8H5O2NH+
71.084		81	C5H10H+	151.11	86		C10H14OH+
73.029		95	C3H4O2H+	153.12	79		C10H16OH+
81.07	61		C6H8H+	155.07	95		C8H10O3H+, C3H10O5N2H+
83.05		63	C5H6OH+	159.13		60	C9H18O2H+
83.085	63		C6H10H+	163.04		76	C9H6O3H+,
85.029		54	C4H4O2H+	165.08	66		C10H12O2H+, C5H12O4N2H+
87.044		69	C4H6O2H+	167.1		76	C10H14O2H+, C5H14O4N2H+
89.059	87		C4H8O2H+	169.05	93		C8H4O4H+, C3H8O6N2H+
101.06	56		C5H8O2H+	173.14		62	C10H20O2H+
103.07		65	C5H10O2H+	179.08	70		C14H10H+
107.05	93		C8H12H+	181.12	83		C11H16O2H+, C6H16O4N2H+
109.1	90		C8H12H+	201.17	86		C12H14O2H+
111.12	79		C8H14H+	203.17	96		C15H22H+, C10H22O2N2H+
115.07	53		C6H10O2H+	205.18	97		C15H24H+, C10H24O2N2H+
117.09	51		C6H12O2H+	219.16	94		C15H22OH+, C10H22O3N2H+
121.06	86		C8H8OH+, C3H8O3N2H+	221.18	94		C15H24OH+, C10H24O3N2H+
123.04	97		C7H6O2H+	243.21	72		C15H30O2H+
127.07	89		C7H10O2H+	255.21	91		C16H30O2H+
129.13	67		C8H16OH+	257.24	90		C16H32O2H+
133.1			C10H12H+, C5H12O2N2H+	273.24			C20H32H+, C15H32O2N2H+

Aerosol concentration of some selected mass

| m/z	Aerosol conc ng-m^{-3}	Probable Compounds	m/z	Aerosol conc ng-m^{-3}	Probable Compounds
45.033	27.7 ± 31.3	C2H4OH+	107.049	1.7 ± 1.7	C7H6OH+
59.049	32.3 ± 24.0	C3H6OH+	107.083	1.1 ± 1.3	C3H10O2N2H+, C8H10H+
61.028	32.3 ± 30.7	C2H4O2H+	109.028	1.9 ± 1.9	C6H4O2H+
69.035	2.62 ± 2.04	C4H4OH+	109.063	1.3 ± 2.7	C2H8O3N2H+, C7H8OH+
71.05	6.2 ± 6.2	C4H6OH+	111.045	17.0 ± 16.3	C6H6O2H+
73.029	3.7 ± 9.1	C3H4O2H+	113.023	16.3 ± 18.6	C5H4O3H+
79.054	1.8 ± 2.1	CH6O2N2H+, C6H6H+	123.042	2.6 ± 3.3	C2H6O4N2H+, C7H6O2H+
80.053	1.3 ± 1.2	C5H5NH+	125.023	6.9 ± 7.1	C6H4O3H+
81.035	1.6 ± 1.2	C5H4OH+	127.073	3.7 ± 5.5	C7H10O2H+
83.05	24.5 ± 28.0	C5H6OH+	137.057	2.0 ± 3.1	C3H8O4N2H+, C8H8O2H+
83.085	3.2 ± 3.8	C6H10H+	139.037	2.1 ± 3.9	C2H6O5N2H+, C7H6O3H+
85.029	1.8 ± 3.7	C4H4O2H+	139.068	2.2 ± 4.2	C3H10O4N2H+, C8H10O2H+
85.064	1.8 ± 3.0	C5H8OH+	141.052	2.2 ± 3.7	C2H8O5N2H+, C7H8O3H+
87.044	1.8 ± 4.4	C4H6O2H+	147.045	1.3 ± 1.5	C4H6O4N2H+, C9H6O2H+
95.032	2.5 ± 1.5	CH5O4NH+	147.073	1.3 ± 1.9	C5H10O3N2H+, C10H10OH+
97.028	29.9 ± 21.0	C5H4O2H+	149.025	5.6 ± 13.8	C8H4O3H+, C7H4O2N2H+
98.025	11.4 ± 6.9	C4H3O2NH+	161.059	1.2 ± 1.6	C5H8O4N2H+, C10H8O2H+
99.007	64.7 ± 40.4	C4H2O3H+	163.039	5.2 ± 5.4	C4H6O5N2H+, C9H6O3H+
101.02	1.4 ± 4.8	C4H4O3H+	177.048	1.0 ± 1.2	C5H8O5N2H+, C10H8O3H+

Diurnal variation of some selected VOCs concentration
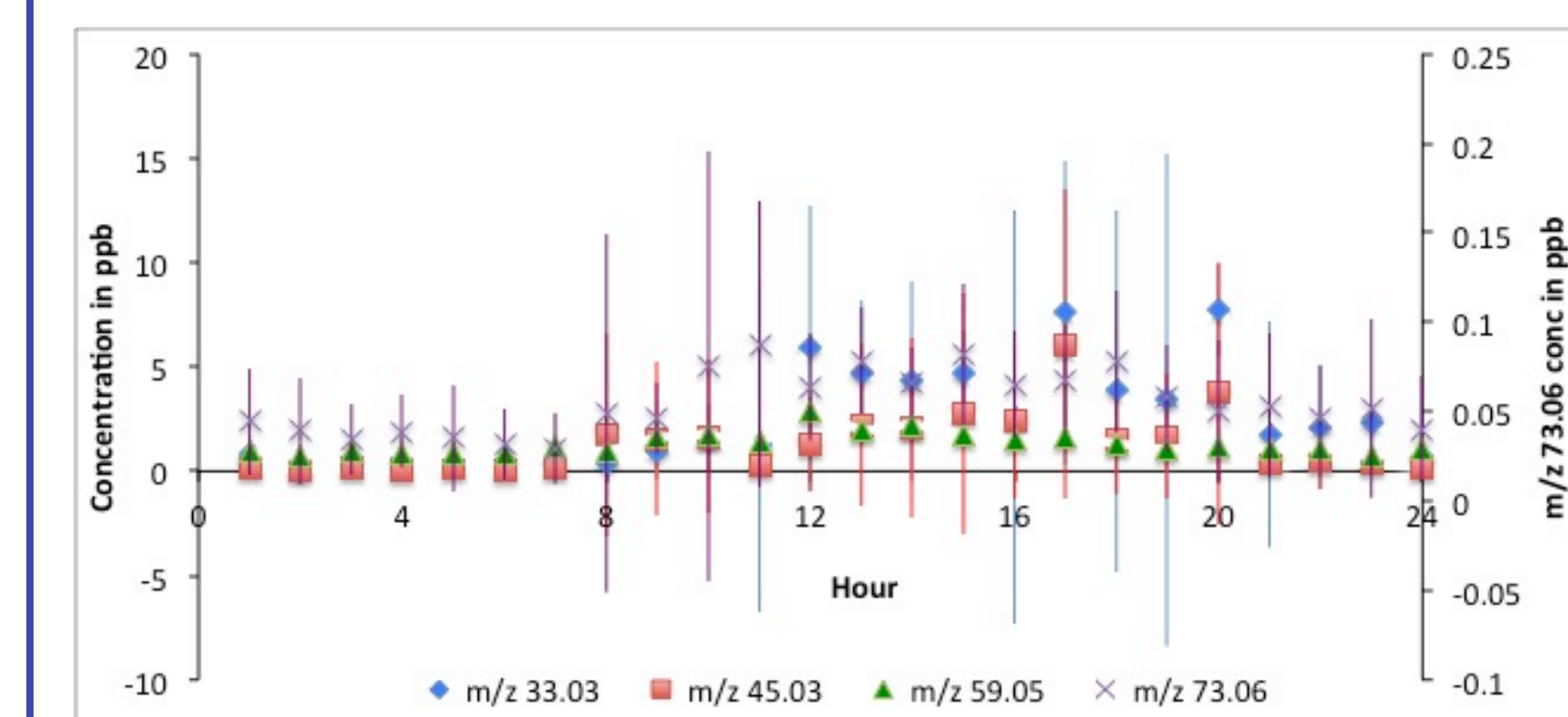
=> m/z 33.03(CH$_4$O, methanol), m/z 45.03 (C$_2$H$_4$O, acetaldehyde), m/z 59.05 (C$_3$H$_6$O, acetone), m/z 73.06 (C$_4$H$_8$O, MEK) with direct emission sources show large variability; produced/emitted at day time and deposited at night time.

=> Comparison with other group:

	Methanol (ppb)	Acetaldehyde (ppb)	Acetone (ppb)	MEK (ppb)
NOAA/CIRES/UC Berkeley	6.9 ± 3.6	1.9 ± 0.6	1.9 ± 0.6	0.2 ± 0.1
This study	2.4 ± 4.9	1.3 ± 3.3	1.3 ± 1.0	0.1 ± 0.1

### Diurnal variation of Isoprene and it's oxidation products
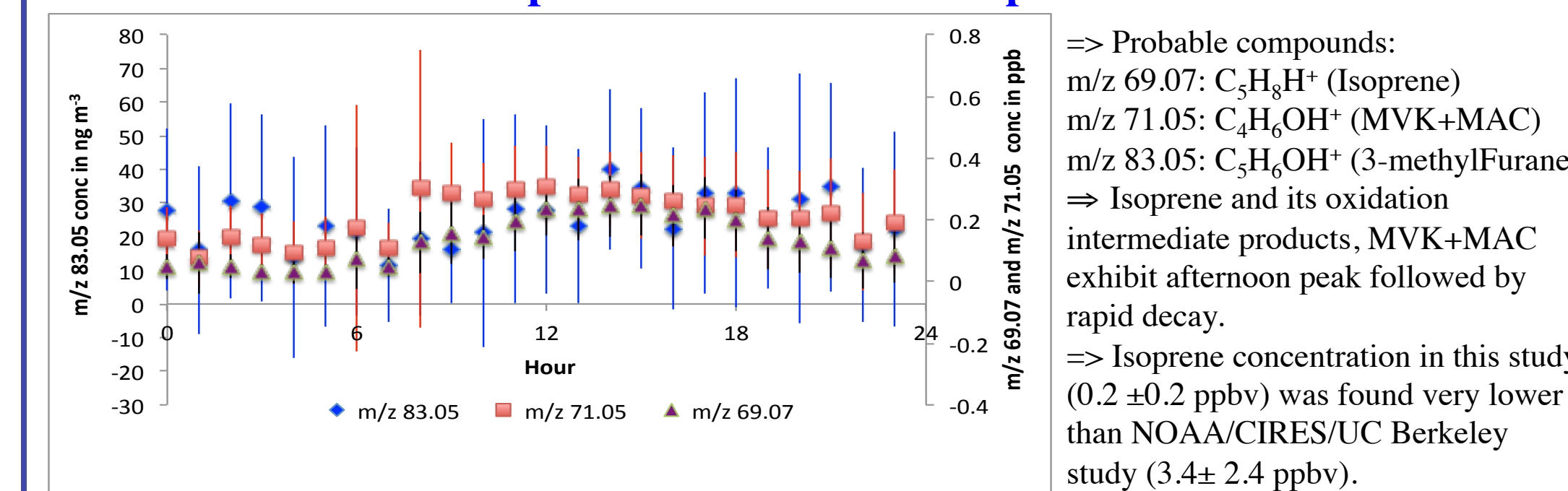
=> Probable compounds:
m/z 69.07: C$_5$H$_8$H$^+$ (Isoprene)
m/z 71.05: C$_4$H$_6$OH$^+$ (MVK+MAC)
m/z 83.05: C$_5$H$_6$OH$^+$ (3-methylFurane)
=> Isoprene and its oxidation intermediate products, MVK+MAC exhibit afternoon peak followed by rapid decay.
=> Isoprene concentration in this study (0.2 ±0.2 ppbv) was found very lower than NOAA/CIRES/UC Berkeley study (3.4± 2.4 ppbv).
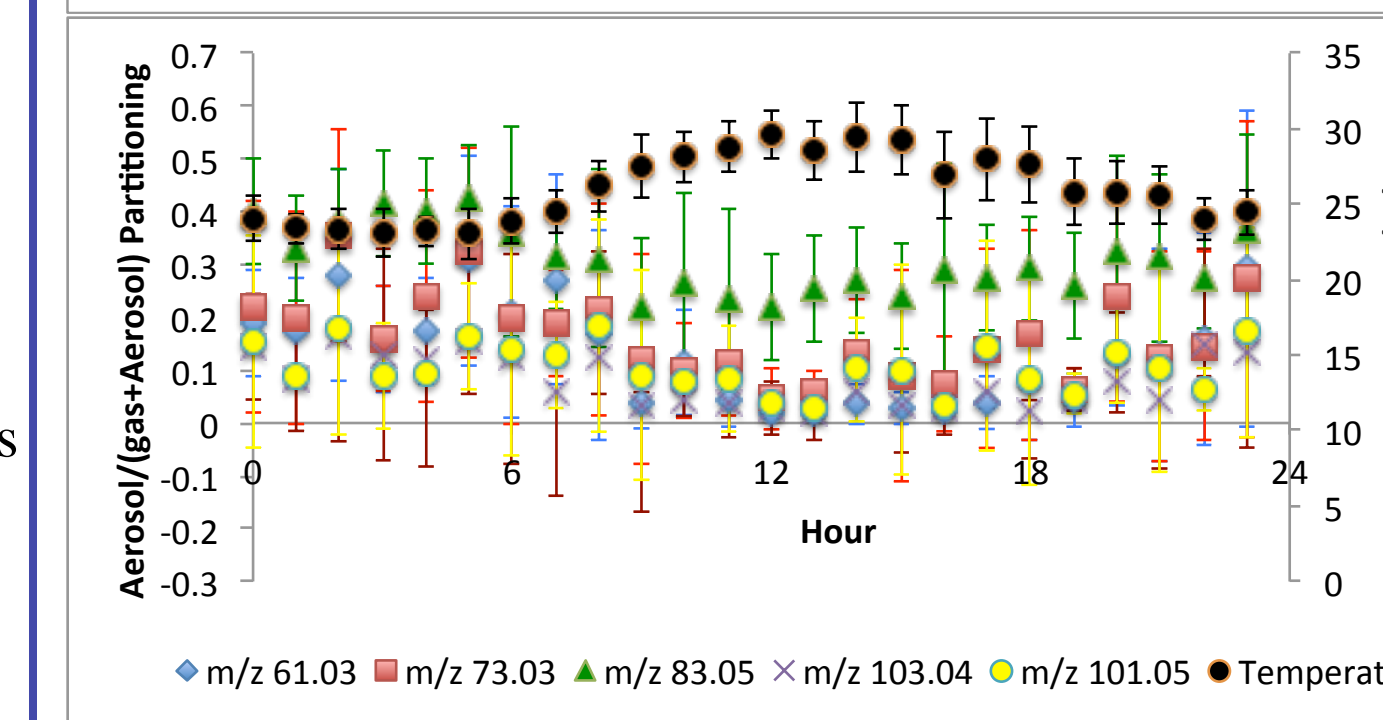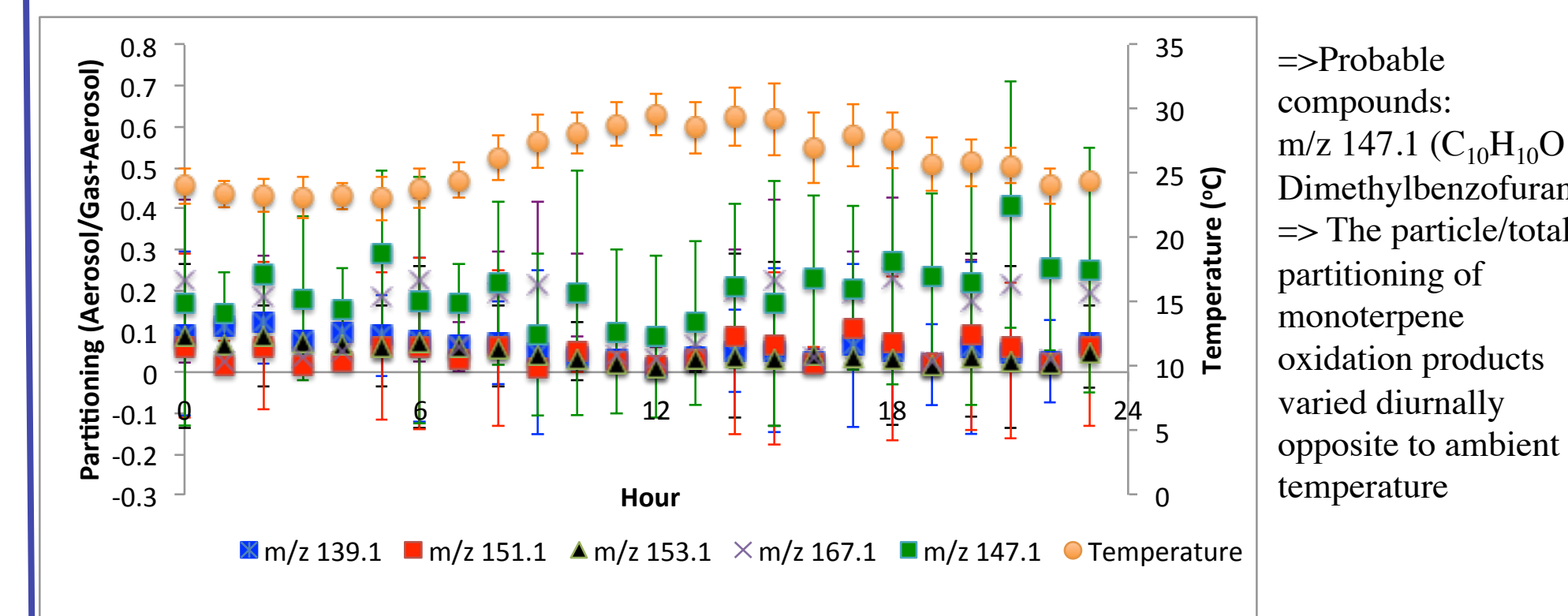
=> Probable compounds:
m/z 61.03: C$_2$H$_4$O$_2$H$^+$ (Glycolaldehyde)
m/z 73.03: C$_3$H$_4$O$_2$H$^+$ (Methylglyoxal)
m/z 103.04: C$_4$H$_6$O$_3$H$^+$ (MAE)
m/z 101.05: C$_5$H$_8$O$_2$H$^+$(4-hydroxy-2-methyl-but-2-enal)
=> Partitioning shows a clear diurnal anti-correlation with ambient temperature

### Diurnal variation of Monterpenes and it's oxidation products
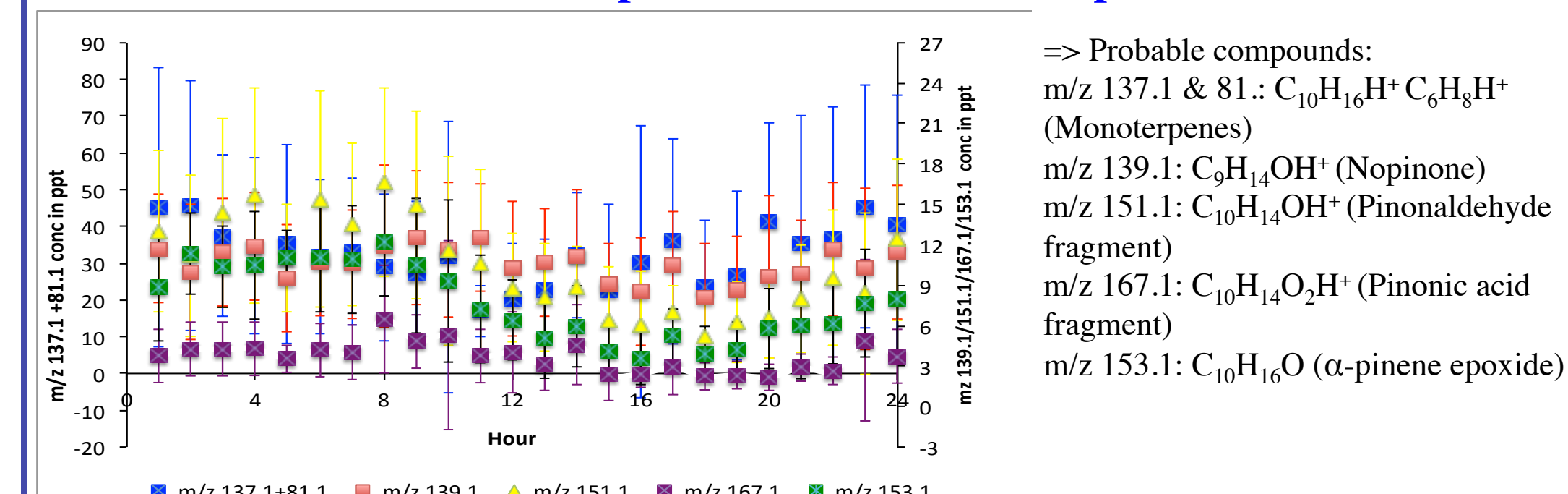
=> Probable compounds:
m/z 137.1 & 81 : C$_{10}$H$_{16}$H$^+$ C$_6$H$_8$H$^+$ (Monoterpenes)
m/z 139.1: C$_9$H$_{14}$OH$^+$ (Nopinone)
m/z 151.1: C$_{10}$H$_{14}$OH$^+$ (Pinonaldehyde fragment)
m/z 167.1: C$_{10}$H$_{14}$O$_2$H$^+$ (Pinonic acid fragment)
m/z 153.1: C$_{10}$H$_{16}$O (α-pinene epoxide)

Nopinone (C$_9$H$_{14}$O) has a longer OH lifetime, allowing it to build up during day.
Pinonaldehyde (C$_{10}$H$_{14}$O) & α-pinene epoxide (C$_{10}$H$_{16}$O) have relatively short photolysis life time, allowing it to increase in rate of the loss relative to that of production during day light hours.
Pinonic acid (C$_{10}$H$_{14}$O$_5$) is produced during the day from freshly emitted monoterpenes and decrease its concentration afternoon because of increased oxidation by OH.

=>Probable compounds:
m/z 147.1 (C$_{10}$H$_{10}$O, Dimethylbenzofurane)
=> The particle/total partitioning of monoterpene oxidation products varied diurnally opposite to ambient temperature

Partitioning (aerosol/gas+aerosol) averages of selected compounds

m/z	Partitioning	Probable Compounds
107.05	0.12 ± 0.13	C7H6OH+
109.03	0.18 ± 0.18	C6H4O2H+
109.06	0.15 ± 0.23	C7H8OH+, C2H8O3N2H+
111.05	0.41 ± 0.29	C6H6O2H+
113.02	0.40 ± 0.26	C5H4O3H+
119.03	0.29 ± 0.27	C9H4OH+
121.06	0.10 ± 0.19	C8H8OH+, C3H8O3N2H+
123.04	0.12 ± 0.21	C7H6O2H+, C2H6O4N2H+
125.02	0.44 ± 0.31	C6H4O3H+
127.04	0.61 ± 0.33	C6H6O2N2H+
127.07	0.33 ± 0.22	C7H10O2H+
133.06	0.11 ± 0.14	C3H8O4N2H+, C8H8O3H+
133.1	0.07 ± 0.08	C10H12H+, C5H12O2N2H+
135.08	0.11 ± 0.13	C9H10OH+, C4H10O3N2H+
137.06	0.11 ± 0.14	C8H8O2H+, C3H8O4N2H+
139.11	0.05 ± 0.16	C9H14OH+
140.04	0.59 ± 0.43	C6H5O3NH+
141.05	0.35 ± 0.24	C7H8O3H+, C2H8O5N2H+
143.07	0.15 ± 0.20	C7H10O3H+, C9H6N2H+, C6H10O2N2H+
145.1	0.06 ± 0.11	C8H16O2H+
146.06	0.57 ± 0.40	C9H7ONH+
147.05	0.39 ± 0.34	C9H6O2H+, C4H6O4N2H+
147.07	0.39 ± 0.28	C10H10OH+, C5H10O3N2H+
148.04	0.19 ± 0.29	C8H5O2NH+
149.03	0.29 ± 0.38	C8H4O3H+, C7H4O2N2H+
151.03	0.12 ± 0.22	C8H6O3H+, C7H6O2N2H+
151.1	0.05 ± 0.16	C10H14OH+
153.05	0.17 ± 0.22	C8H8O3H+, C3H8O5N2H+, C10H4N2H+
153.1	0.05 ± 0.16	C10H16OH+
155.06	0.27 ± 0.36	C7H7O3H+, C11H7NH+
155.07	0.19 ± 0.21	C8H10O3H+, C3H10O5N2H+
159.1	0.06 ± 0.16	C9H18O2H+
161.06	0.22 ± 0.22	C10H8O2H+, C5H8O4N2H+
163.04	0.46 ± 0.32	C9H6O3H+, C4H6O5N2H+
165.08	0.09 ± 0.15	C10H12H+, C5H12O4N2H+
166.03	0.28 ± 0.26	C4H7O6NH+, C7H3O4NH+, C3H3O7NH+
167.05	0.12 ± 0.23	C5H6O6H+, C11H6N2H+, C12H6OH+, C9H10O3H+
167.1	0.07 ± 0.17	C10H14O2H+, C5H14O4N2H+
169.05	0.11 ± 0.19	C8H8O4H+, C3H8O6N2H+
173.1	0.11 ± 0.19	C10H20O2H+
177.05	0.24 ± 0.26	C10H8O3H+, C5H8O5N2H+
179.08	0.09 ± 0.17	C14H10H+, C9H10O2N2H+, C7H14O5H+
181.12	0.10 ± 0.16	C11H16O2H+, C6H16O4N2H+, C7H16O5H+
183.08	0.07 ± 0.17	C13H10OH+, C8H10O3N2H+, C12H10N2H+
255.2	0.05 ± 0.18	C16H30O2H+
257.2	0.18 ± 0.36	C16H32O2H+

Time series of Sesquiterpenes and monoterpenes and their correlation
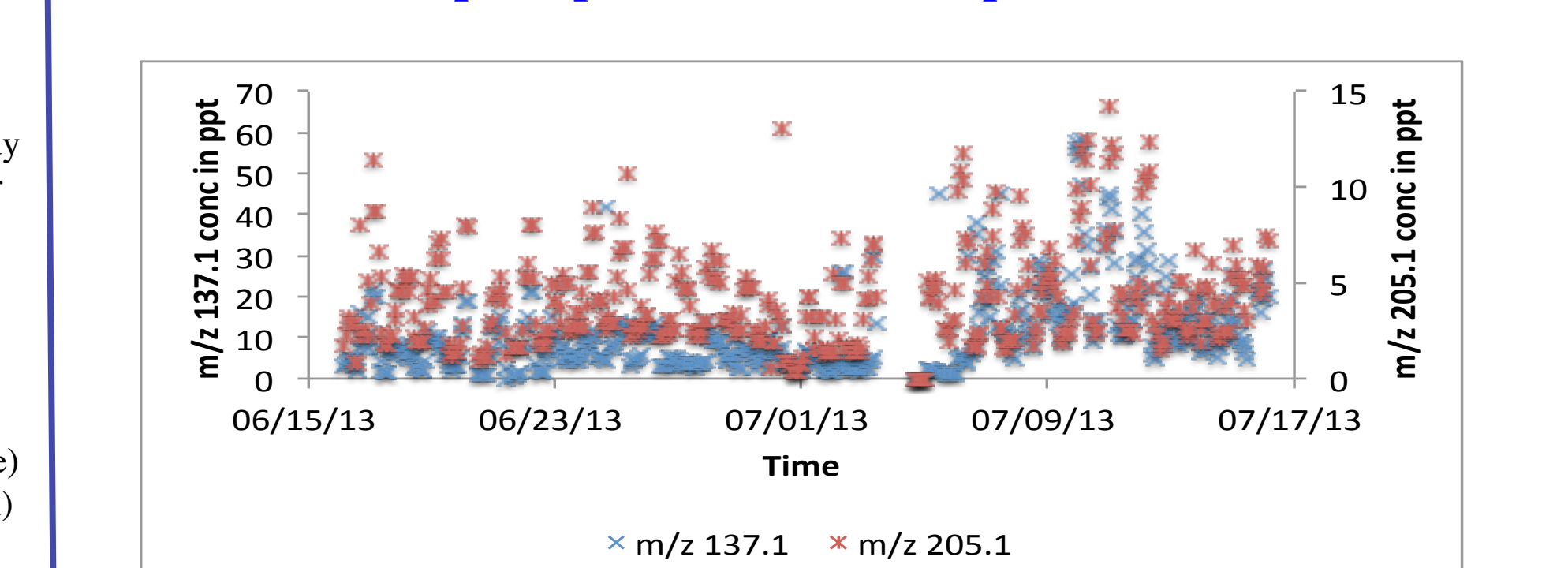
The correlation between Monoterpenes (m/z 137.1) and Sesquiterpenes (m/z 205.1) is significant (r=0.62) suggesting common biogenic source.

Major Findings from the Research

=> Developed a denuder gas sampling system (DB-1-DB-1-C combination) coupled with TD-PTR-MS for collecting and then quantifying SVOCs in gas and aerosol phase separately.
=> Several hundreds of SVOCs have been detected in both gas and aerosol phases.
=> Biogenic VOCs and their oxidation products show the expected diurnal variation.
=> Partitioning of Monoterpenes and isoprene oxidation products show a clear diurnal variation opposite to ambient temperature.