

Long-term study of VOCs measured with PTR-MS at a rural site in New Hampshire with urban influences

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Abstract. A long-term, high time-resolution volatile organic compound (VOC) data set from a ground site that experiences urban, rural, and marine influences in the Northeastern United States is presented. A proton-transfer-reaction mass spectrometer (PTR-MS) was used to quantify 15 VOCs: a marine tracer dimethyl sulfide (DMS), a biomass burning tracer acetonitrile, biogenic compounds (monoterpenes, isoprene), oxygenated VOCs (OVOCs: methyl vinyl ketone (MVK) plus methacrolein (MACR), methanol, acetone, methyl ethyl ketone (MEK), acetaldehyde, and acetic acid), and aromatic compounds (benzene, toluene, C₈ and C₉ aromatics). Time series, overall and seasonal medians, with 10th and 90th percentiles, seasonal mean diurnal profiles, and inter-annual comparisons of mean summer and winter diurnal profiles are shown. Methanol and acetone exhibit the highest overall median mixing ratios 1.44 and 1.02 ppbv, respectively. Comparing the mean diurnal profiles of less well understood compounds (e.g., MEK) with better known compounds (e.g., isoprene, monoterpenes, and MVK + MACR) that undergo various controls on their atmospheric mixing ratios provides insight into possible sources of the lesser known compounds. The constant diurnal value of ~ 0.7 for the toluene:benzene ratio in winter, may possibly indicate the influence of wood-based heating systems in this region. Methanol exhibits an initial early morning release in summer unlike any other OVOC (or isoprene) and a dramatic late afternoon mixing ratio increase in spring. Although several of the OVOCs appear to have biogenic sources, differences in features observed between isoprene, methanol, acetone, acetaldehyde, and MEK suggest they are produced or emitted in unique ways.

1 Introduction

Volatile organic compounds (VOCs) are emitted into the atmosphere from both natural and anthropogenic sources and have lifetimes ranging from minutes to months. This diverse group of compounds is of interest in the troposphere because of their role in ozone (O₃) production, aerosol formation and controls on regional air quality. While long-term records of VOCs exist (e.g., Penkett et al., 1993; Jobson et al., 1994; Goldstein et al., 1995; Thijssse et al., 1999; Solberg et al., 2001; Gautrois et al., 2003; Yang et al., 2005; Reiss, 2006; Simmonds et al., 2006; Lee et al., 2006; Qin et al., 2007; Sive et al., 2007; Nguyen et al., 2009), the measurements rely on conventional methods such as gas chromatography with hourly time resolution at best. Although these records provide a wealth of information, proton transfer reaction-mass spectrometry (PTR-MS) offers greatly improved time resolution. However, the current literature has little to offer in terms of seasonal comparisons based on this technique (Schade and Goldstein, 2006; Filella and Peñuelas, 2006) and is devoid of inter-annual comparisons.

A PTR-MS was used to quantify a suite of VOCs at Thompson Farm in southeastern New Hampshire, from 24 July to 31 August 2004 and from 1 June 2005 to 31 May 2008. The results presented here encompass four summers, and three falls, winters and springs. The summary provided here terminates 31 May 2008, but these measurements are ongoing. These data are available upon request. This long-term data set permits inter-annual comparisons and defines seasonal and diurnal characteristics of the analytes at a mid-latitude site.

The compounds reported here (Table 1) broadly fall into three categories: biogenic (monoterpenes, isoprene and its oxidation products methyl vinyl ketone (MVK) and methacrolein (MACR)), oxygenated VOCs (OVOCs: methanol, acetone, methyl ethyl ketone (MEK), acetaldehyde, and acetic acid), and aromatic (benzene, toluene, C₈



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Table 1. List of reported compounds along with their protonated m/z , limits of detection (LOD), and type as discussed in the text.

Compound	Protonated m/z	LOD (ppb)	Group
Methanol	33	0.240	Oxygenated
Acetonitrile	42	0.020	Biomass Burning
Acetaldehyde	45	0.050	Oxygenated
Acetone	59	0.020	Oxygenated
Acetic Acid	61	0.080	Oxygenated
DMS	63	0.025	Marine Tracer
Isoprene	69	0.020	Biogenic
Methyl vinyl ketone (MVK)	71	0.020	Oxygenated
Methacrolein (MACR)	71	0.020	Oxygenated
Methyl ethyl ketone (MEK)	73	0.015	Oxygenated
Benzene	79	0.020	Aromatic
Toluene	93	0.015	Aromatic
C ₈ Aromatics	107	0.025	Aromatic
C ₉ Aromatics	121	0.025	Aromatic
Monoterpenes	137	0.050	Biogenic

and C₉ aromatics). In addition, dimethyl sulfide (DMS) released by phytoplankton (Bates et al., 1992) in the Gulf of Maine is a marine tracer, while acetonitrile is a biomass burning tracer (Lobert et al., 1990; Holzinger et al., 1999; Bange and Williams, 2000). The complete time series are presented here, along with median annual and seasonal mixing ratios, mean diurnal characteristics of the data, and inter-annual variability of the mean diurnal cycles in summer and winter.

2 Methods

2.1 Field site description

The University of New Hampshire Observing Station at Thompson Farm (TF) (43.11° N, 70.95° W, elevation 24 m) is located in Durham, a rural area in southeastern New Hampshire (Fig. 1). TF is 24 km from the Gulf of Maine and 5 km northwest of Great Bay, NH, and is located on an active corn (through 2005) and alfalfa (2006 to present) farm surrounded by a mixed forest. Located near the coasts of Maine and New Hampshire, TF is a unique sampling location, where air masses that have been influenced by a variety of different source regions, including coastal marine, the forested sub-Arctic, the industrialized Midwestern US, the metropolitan East coast and the open North Atlantic Ocean, are periodically encountered.

Ambient air at TF is analyzed onsite for numerous species including CO, O₃, SO₂, NO and NO_y, as well as VOCs. Additionally, meteorological parameters such as wind speed, wind direction and temperature are also monitored. Details and a record of these measurements are reported at the AIRMAP website (<http://airmap.unh.edu/>).

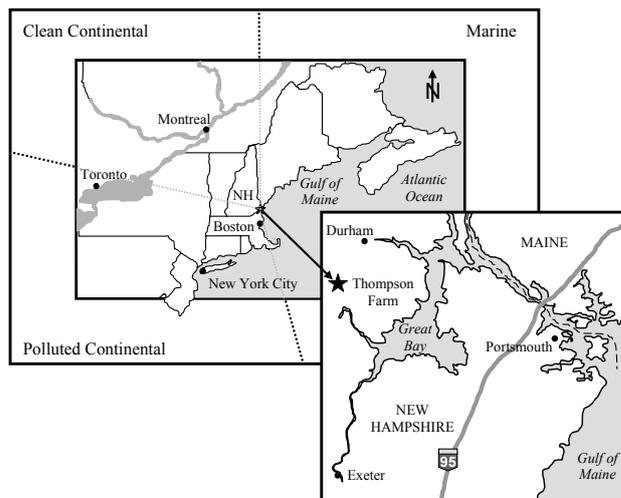


Fig. 1. Thompson Farm (TF) in Durham, NH is located in New England region of United States. This location is influenced by polluted continental air masses from the south and west, clean continental air masses from the north, and marine air masses from the east (main map). TF is located approximately 20 km west of Portsmouth on the sea coast of NH and the Interstate 95 corridor (inset).

2.2 Instrument operation

A PTR-MS obtained from Ionicon Analytik, Innsbruck, Austria was used for high frequency measurements of several groups of non-methane hydrocarbons (NMHCs), certain individual OVOCs, DMS, and acetonitrile at TF (Table 1). PTR-MS employs chemical ionization by reaction of H₃O⁺ reagent ions for soft ionization of gas phase compounds having a proton affinity greater than that of water; ionization occurs via proton transfer from the H₃O⁺ and the resulting ion is detected using a quadrupole mass spectrometer (Lindinger et al., 1998). The instrument and its operation have been described in great detail in a recent review (de Gouw and Warneke, 2007) and will not be described here further. Specifics on the operational parameters of the PTR-MS at TF may be found in Talbot et al. (2005) and Ambrose et al. (2007).

The PTR-MS sampled ambient air that was continuously drawn down a PFA Teflon-lined manifold from the top of a 12 m tower (Talbot et al., 2005). A sub-stream of air off the main sample line was sent directly to the PTR-MS at 1000 standard cubic centimeters per minute. The PTR-MS was operated with the drift tube set to an E/N of 140 Townsend while continuously stepping through a series of 30 m/z channels. Of the 30 channels monitored, 6 were used for diagnostic purposes while the other 24 corresponded to the VOCs of interest. The dwell time for each of the 24 channels ranged from 2–20 s, yielding a total measurement cycle of ~6 min.

The background signal was obtained every 2.5 h through 2006 and then every 12 h from 2006-present because of the

system stability. The system is zeroed for 4 cycles by diverting the flow of ambient air through a heated catalytic converter (0.5% Pd on alumina at 450°C) to oxidize the VOCs and determine system background signals (Talbot et al., 2005; Ambrose et al., 2007). Following a linear interpolation, the background was subtracted from the ambient signal. Ambient mixing ratios for most species were then determined by converting the raw PTR-MS signal in Hz to mixing ratio in ppbv or parts per trillion by volume (pptv) using experimentally determined calibration factors. Limits of detection (LOD) were determined based on a signal to noise ratio of 2 as described by Karl et al. (2003) and are reported in Table 1.

Calibrations for the PTR-MS system were conducted using three different high-pressure cylinders containing synthetic blends of selected NMHCs, OVOCs and acetonitrile at the part per billion by volume (ppbv) level (Apel-Riemer Environmental, Inc., Denver, CO). Each of the cylinders used in the calibrations had an absolute accuracy of $< \pm 5\%$ for all gases. Using methods similar to those described by Apel et al. (1998), standards were diluted to atmospheric mixing ratios (ppbv to pptv levels) with catalytic converter prepared zero air adjusted to maintain the humidity of the sampled air. Calibrations were conducted periodically (manual calibrations were performed seasonally in 2004, 2005, and 2006 (ranging from every 4 to 12 weeks), daily single point calibrations and bi-weekly multi-point calibrations began in July 2007) to monitor PTR-MS performance, quantify the mixing ratios of target gases and to confirm calibration factors.

Acetic acid calibration factors were determined using a permeation calibration system similar to that described in Talbot et al. (1999) and tubes obtained from Kin-Tek Laboratories, Inc. (La Marque, TX). A dilution flow of VOC-free air, generated by passing ambient air through the catalytic converter, was used to dilute and vary the acetic acid mixing ratios to construct a multipoint calibration curve.

DMS mixing ratios were calculated based on the ion-molecule reaction kinetics of the reagent gas and the ion transmission through the quadrupole. To verify the accuracy of the calculated DMS mixing ratios, inter-calibrations were conducted using both canister samples and an automated in situ gas chromatographic system (Sive et al., 2005) using whole air standards from D. Blake (University of California, Irvine).

Table 1 lists the 15 compounds/groups of compounds of interest to this study and their corresponding protonated m/z measured by PTR-MS. Several isobaric species should be noted: mixing ratios reported for m/z 71 are the sum of MVK and MACR; m/z 107 includes, among others, the three isomers of xylene and ethylbenzene and is collectively referred to as C_8 aromatics. Similarly, m/z 121 includes the trimethylbenzenes and propylbenzenes and is summarized as C_9 aromatics. Finally, total monoterpenes are measured at m/z 137; for most monoterpenes $>99\%$ of the signal can be attributed to the $C_{10}H_{16}H^+$ ion (Tani et al., 2003; Lee et al., 2005).

From 24 July 2004 until 8 November 2005, measurements were conducted at TF using a standard sensitivity PTR-MS, after which time it was replaced with a high sensitivity PTR-MS. The difference between these two instruments is that the high sensitivity instrument consists of an additional vacuum chamber and turbomolecular pump located between the drift tube and the quadrupole (de Gouw and Warneke, 2007). A number of rigorous validation experiments were used to ensure coherence between the two instruments; both instruments were collocated and shared a common inlet and operated using the same conditional parameters. The agreement between the two instruments during these experiments validates our ability to meaningfully compare the data sets generated by each and view the analysis of these measurements as one contiguous data set (e.g., White et al., 2008a).

2.3 Deposition velocity calculations

Following the method in Talbot et al. (2005) deposition velocities from the mean summer diurnal curves have been calculated. The calculation is simply: $[(\text{depletion rate} - \text{pptv h}^{-1}) \times (\text{height of the layer below the nocturnal inversion} - m)] / [\text{mean mixing ratio} - \text{pptv}]$. The units are then converted to cm s^{-1} . Here the height of the layer below the inversion is assumed to be 125 m (the upper limit of the 70–125 m range given in Talbot et al., 2005) and the interval used for the depletion in all cases was from 2200 to 04:00 EST. As shown by Talbot et al. (2005) nocturnal inversions are common at TF (occurring nearly 50% of the time in warm months) and the strong diurnal cycles observed here reflect the prevalence of those inversions. Another site they evaluated in this region showed weaker diurnal curves, attributed to the lower frequency of nocturnal inversions at that site.

Based on these results, we applied this calculation to the mean summer diurnal curves in order to compare the loss rate between the affected species reported here. However, the reader is strongly cautioned that these deposition velocities are not true dry deposition velocities and should not be interpreted as such. The nocturnal depletion observed for certain species (not all species are depleted at night) is due to a combination (Talbot et al., 2005) of dry deposition, wet removal (i.e., loss of soluble species to dew), chemical loss, and dilution by vertical mixing (Hurst et al., 2001). It is not possible within the framework of mean seasonal diurnal behavior to determine the relative contribution of each process for each species to the overall loss observed. Indeed by including all data in the calculation (both nights with and without a nocturnal inversion) the deposition velocities reported here are significantly lower than those reported by Talbot et al. (2005) (see Table 5 in that reference compared with Table 3 here). Again, here the intention is to describe mean behavior and to compare species in a consistent manner.

When there is a nocturnal inversion vertical mixing is anticipated to be limited, but when there is no inversion, dilution via vertical mixing may be the dominant nighttime

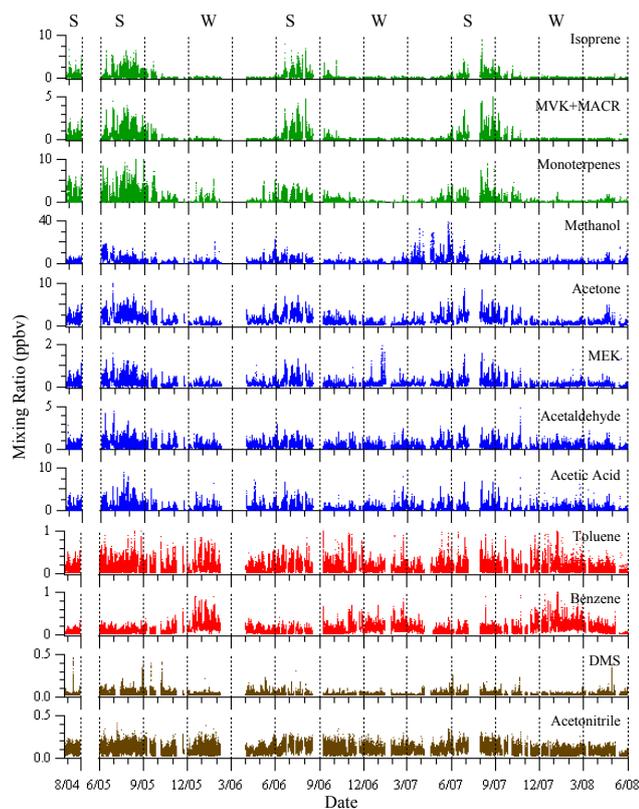


Fig. 2. Time series of measured compounds. Initial sampling conducted in summer 2004 (Jul–Aug). Continuous sampling followed from 1 June 2005 to 31 May 2008. Summers denoted with S, winters with W. Biogenic species shown in green, OVOCs in blue, aromatics in red, with DMS (marine) and acetonitrile (biomass burning) in brown. MVK+MACR are OVOCs, but they are principally oxidation products of isoprene, hence they are included with biogenics.

removal process. However, on average, for the species discussed here nocturnal depletion is followed by a rapid increase in mixing ratios after sunrise. This suggests that for these species, vertical mixing is not the dominant loss process on average in summer, since the mixing ratios in the remnant layer are higher than those near the surface. The mean influence of chemical loss is discussed in Sect. 4.1.3. We will use the term deposition velocity throughout the discussion, but one is advised to bear the preceding caveats in mind.

3 Results – time series and statistics

The time series plots (Fig. 2) and overall and seasonal statistics (Table 2) reveal the range of mixing ratios and seasonal variability observed at TF. Note, only values above the LOD (Table 1) are included in the statistical calculations shown in Table 2. Methanol (1.44 ppbv) and acetone (1.02 ppbv) ex-

hibited the highest overall median mixing ratios observed at TF (Table 2), with 90th percentile mixing ratios of 4.56 ppbv and 2.87 ppbv respectively.

3.1 Seasonal characteristics

Seasons here are defined as spring (March–May), summer (June–August), fall (September–November), and winter (December–February). As expected, the biogenic compounds showed the strongest seasonal variability (Fig. 2, Table 2) with median mixing ratios exhibiting a summer/winter ratio of ~ 8 for isoprene and MVK+MACR. Isoprene varied between 0.05–0.09 ppbv in three seasons, compared to a median of 0.42 ppbv in summer. MVK+MACR were 0.04–0.06 ppbv in three seasons compared to a median of 0.33 ppbv in summer. Monoterpene median mixing ratios were 5 times higher in summer than winter.

Similar to seasonal behavior exhibited by the biogenic compounds, two OVOCs (MEK and acetaldehyde) had comparable median mixing ratios for three seasons (0.10–0.11 ppbv and 0.31–0.33 ppbv, respectively) with enhanced summer median mixing ratios (0.22 and 0.54 ppbv, respectively). In contrast, two other OVOCs (acetone and methanol) exhibited different seasonal behavior with low winter median mixing ratios (0.57 and 0.97 ppbv, respectively), high summer median mixing ratios (2.11 and 2.69 ppbv, respectively), and median mixing ratios in spring and fall in between these values. The last OVOC in this set (acetic acid) was the only compound reported here to have low fall median mixing ratios (0.28 ppbv) with high summer median mixing ratios (0.62 ppbv) and winter and spring in between (0.39 ppbv for both seasons).

The aromatics, unlike the biogenic compounds and OVOCs, generally did not exhibit strong seasonal variability (Fig. 2, Table 2). Toluene, C₈ and C₉ aromatics were all highest in summer with median mixing ratios 0.14, 0.12, and 0.08 ppbv respectively, but only by factors of ~ 1.1 – 1.3 over their winter median values of 0.11, 0.10, and 0.06 respectively. In contrast, benzene did display strong seasonal variability with a median mixing ratio that was a factor of 2.5 higher in winter (0.20 ppbv) than in summer (0.08 ppbv). Aside from its winter increase, benzene levels remained fairly constant throughout the remainder of the year (0.08–0.09 ppbv median mixing ratios).

Acetonitrile exhibited fairly uniform median mixing ratios over 3 seasons (0.08–0.09 ppbv) with a summer value (0.13 ppbv) a factor of 1.6 higher than that in winter. Finally, DMS showed a weaker seasonal variation with spring and summer median mixing ratios of ~ 0.04 ppbv, a factor of 1.3 higher than in winter (0.03 ppbv). However, it should be noted that unlike the other compounds here, DMS was generally below the 0.025 ppbv limit of detection. Overall, it was above the detection limit only 22% of the time, with values above detection in winter 12% of the time and 29% in summer.

Table 2. Medians (10th–90th percentiles).

	<i>n</i>	Isoprene (69)	MVK+MACR (71)	Monoterpenes (137)	Methanol (33)	Acetone (59)	MEK (73)	Acetaldehyde (45)
Overall	249 036	0.10 (0.03–0.82)	0.07 (0.03–0.78)	0.24 (0.07–1.46)	1.44 (0.53–4.56)	1.02 (0.42–2.87)	0.13 (0.05–0.37)	0.37 (0.16–0.96)
Winter	58 586	0.05 (0.03–0.15)	0.04 (0.02–0.08)	0.10 (0.06–0.36)	0.97 (0.43–2.39)	0.57 (0.35–1.07)	0.11 (0.06–0.23)	0.33 (0.16–0.74)
Winter 2005	20 348	0.06 (0.03–0.17)	0.04 (0.02–0.08)	0.11 (0.06–0.54)	1.03 (0.41–2.40)	0.60 (0.37–1.16)	0.11 (0.06–0.23)	0.33 (0.17–0.72)
Winter 2006	20 706	0.05 (0.02–0.12)	0.04 (0.02–0.08)	0.08 (0.05–0.21)	0.91 (0.42–2.31)	0.53 (0.33–1.14)	0.12 (0.06–0.28)	0.30 (0.15–0.78)
Winter 2007	17 532	0.05 (0.03–0.15)	0.04 (0.02–0.09)	0.09 (0.06–0.27)	0.98 (0.46–2.51)	0.56 (0.36–0.93)	0.11 (0.06–0.19)	0.34 (0.18–0.73)
Spring	52 466 ^a	0.05 (0.02–0.14)	0.04 (0.02–0.12)	0.12 (0.06–0.61)	1.31 (0.50–5.04)	0.93 (0.41–2.10)	0.11 (0.05–0.25)	0.31 (0.14–0.81)
Spring 2006	22 516	0.05 (0.02–0.14)	0.04 (0.02–0.11)	0.12 (0.06–0.70)	1.31 (0.46–4.39)	1.05 (0.44–2.24)	0.11 (0.04–0.27)	0.36 (0.16–0.86)
Spring 2007	13 430	0.06 (0.02–0.17)	0.05 (0.02–0.17)	0.13 (0.06–0.78)	2.23 (0.78–8.31)	1.02 (0.53–2.50)	0.14 (0.07–0.31)	0.34 (0.16–0.92)
Spring 2008	16 381	0.04 (0.02–0.10)	0.04 (0.02–0.08)	0.12 (0.06–0.41)	0.91 (0.45–2.70)	0.71 (0.31–1.45)	0.10 (0.04–0.20)	0.24 (0.10–0.60)
Summer	75 513	0.42 (0.09–1.53)	0.33 (0.06–1.47)	0.50 (0.13–2.51)	2.69 (1.14–6.54)	2.11 (0.98–4.08)	0.22 (0.08–0.60)	0.54 (0.21–1.27)
Summer 2004	4 113	0.37 (0.08–1.11)	0.33 (0.06–1.04)	0.46 (0.12–2.71)	1.97 (0.82–3.86)	1.43 (0.71–2.91)	0.17 (0.05–0.46)	0.39 (0.12–0.92)
Summer 2005	31 077	0.49 (0.11–1.69)	0.36 (0.07–1.52)	0.71 (0.17–3.31)	2.81 (1.18–7.29)	2.19 (0.95–4.07)	0.25 (0.09–0.62)	0.64 (0.23–1.38)
Summer 2006	26 638	0.41 (0.08–1.44)	0.32 (0.05–1.45)	0.35 (0.12–1.57)	2.76 (1.24–6.22)	2.13 (1.06–4.24)	0.20 (0.07–0.63)	0.49 (0.20–1.18)
Summer 2007	13 685	0.34 (0.08–1.34)	0.27 (0.05–1.54)	0.43 (0.11–2.01)	2.61 (1.00–6.26)	2.01 (1.01–4.14)	0.21 (0.08–0.58)	0.47 (0.20–1.15)
Fall	62 471	0.09 (0.03–0.41)	0.06 (0.03–0.37)	0.23 (0.07–0.98)	1.13 (0.51–2.70)	1.00 (0.45–2.20)	0.10 (0.04–0.29)	0.33 (0.15–0.86)
Fall 2005	22 896	0.08 (0.03–0.57)	0.06 (0.03–0.47)	0.30 (0.10–1.46)	1.11 (0.50–2.91)	1.04 (0.43–2.32)	0.10 (0.04–0.32)	0.39 (0.17–0.99)
Fall 2006	25 789	0.08 (0.03–0.31)	0.05 (0.03–0.20)	0.18 (0.06–0.79)	1.06 (0.49–2.40)	0.97 (0.49–2.00)	0.10 (0.05–0.26)	0.30 (0.14–0.73)
Fall 2007	13 786	0.10 (0.03–0.37)	0.06 (0.03–0.52)	0.20 (0.07–0.90)	1.31 (0.58–3.06)	1.01 (0.42–2.43)	0.10 (0.04–0.30)	0.31 (0.14–0.87)
	<i>n</i>	Acetic Acid (61)	Toluene (93)	C ₈ Aromatics (107)	C ₉ Aromatics (121)	Benzene (79)	Acetonitrile (42)	DMS (63)
Overall	249 036	0.40 (0.14–1.52)	0.11 (0.03–0.31)	0.10 (0.04–0.27)	0.06 (0.03–0.15)	0.11 (0.04–0.26)	0.09 (0.05–0.16)	0.038 (0.027–0.079)
Winter	58 586	0.39 (0.16–1.06)	0.11 (0.05–0.32)	0.10 (0.04–0.28)	0.06 (0.03–0.14)	0.20 (0.11–0.40)	0.08 (0.05–0.13)	0.032 (0.026–0.048)
Winter 2005	20 348	0.38 (0.16–0.97)	0.14 (0.06–0.40)	0.12 (0.04–0.33)	0.07 (0.03–0.16)	0.22 (0.13–0.49)	0.08 (0.05–0.14)	0.032 (0.026–0.046)
Winter 2006	20 706	0.40 (0.16–1.18)	0.09 (0.04–0.23)	0.08 (0.03–0.20)	0.05 (0.03–0.10)	0.16 (0.09–0.29)	0.08 (0.06–0.14)	0.031 (0.026–0.044)
Winter 2007	17 532	0.40 (0.16–1.06)	0.11 (0.05–0.30)	0.10 (0.04–0.27)	0.06 (0.03–0.14)	0.21 (0.13–0.41)	0.07 (0.04–0.11)	0.033 (0.026–0.059)
Spring	52 466 ^a	0.39 (0.13–1.22)	0.06 (0.02–0.22)	0.07 (0.03–0.21)	0.05 (0.03–0.10)	0.09 (0.04–0.19)	0.08 (0.05–0.13)	0.039 (0.027–0.092)
Spring 2006	22 516	0.40 (0.13–1.22)	0.06 (0.02–0.23)	0.07 (0.03–0.22)	0.04 (0.03–0.11)	0.08 (0.03–0.16)	0.08 (0.05–0.13)	0.042 (0.027–0.107)
Spring 2007	13 430	0.46 (0.17–1.54)	0.07 (0.03–0.24)	0.08 (0.03–0.24)	0.05 (0.03–0.12)	0.10 (0.04–0.19)	0.09 (0.06–0.14)	0.037 (0.027–0.074)
Spring 2008	16 381	0.33 (0.12–0.95)	0.05 (0.02–0.16)	0.06 (0.03–0.17)	0.04 (0.03–0.09)	0.12 (0.06–0.22)	0.07 (0.04–0.11)	0.037 (0.027–0.071)
Summer	75 513	0.62 (0.16–2.49)	0.14 (0.04–0.34)	0.12 (0.04–0.30)	0.08 (0.04–0.18)	0.08 (0.03–0.16)	0.13 (0.07–0.18)	0.041 (0.027–0.089)
Summer 2004	4 113	0.62 (0.15–2.05)	0.10 (0.04–0.26)	0.10 (0.04–0.27)	0.08 (0.03–0.18)	0.06 (0.03–0.13)	0.11 (0.06–0.16)	0.039 (0.027–0.105)
Summer 2005	31 077	0.70 (0.17–2.74)	0.15 (0.05–0.34)	0.14 (0.05–0.33)	0.10 (0.04–0.20)	0.08 (0.04–0.14)	0.13 (0.07–0.18)	0.045 (0.028–0.094)
Summer 2006	26 638	0.54 (0.14–2.23)	0.13 (0.04–0.34)	0.10 (0.04–0.25)	0.07 (0.04–0.14)	0.08 (0.03–0.16)	0.13 (0.07–0.19)	0.036 (0.026–0.072)
Summer 2007	13 685	0.62 (0.17–2.29)	0.13 (0.04–0.35)	0.12 (0.04–0.29)	0.08 (0.04–0.17)	0.09 (0.04–0.18)	0.13 (0.07–0.20)	0.041 (0.027–0.092)
Fall	62 471	0.28 (0.12–1.06)	0.11 (0.03–0.31)	0.11 (0.04–0.27)	0.07 (0.03–0.15)	0.09 (0.04–0.23)	0.09 (0.05–0.15)	0.037 (0.027–0.067)
Fall 2005	22 896	0.31 (0.12–1.27)	0.10 (0.03–0.28)	0.10 (0.04–0.28)	0.07 (0.04–0.17)	0.07 (0.03–0.18)	0.09 (0.04–0.15)	0.039 (0.027–0.071)
Fall 2006	25 789	0.26 (0.11–0.80)	0.11 (0.03–0.33)	0.11 (0.04–0.27)	0.06 (0.03–0.14)	0.10 (0.04–0.25)	0.10 (0.05–0.15)	0.033 (0.026–0.056)
Fall 2007	13 786	0.30 (0.12–1.35)	0.11 (0.03–0.31)	0.11 (0.04–0.28)	0.06 (0.03–0.14)	0.11 (0.05–0.27)	0.09 (0.05–0.15)	0.035 (0.027–0.067)

^a includes 139 points from Spring 2005

In general the seasonal variability revealed in Fig. 2 and Table 2 reflect the expected influence of the summer growing season along with enhanced photochemistry at this time of year, the persistence of anthropogenic emissions throughout the year, and the prevalence of continental outflow at this site.

3.2 Inter-annual comparisons

In addition to these overall seasonal comparisons, Table 2 shows the yearly seasonal statistics. All seasons were measured for three years (1 June 2005 through 31 May 2008), plus there is an additional summer (2004). Note, Summer 2004 is significantly underrepresented with only ~5 weeks of data, 24 July–31 August. When comparing the summer median mixing ratios an interesting feature is apparent (Table 2): methanol, acetone, MEK, acetaldehyde, toluene, benzene, and acetonitrile median mixing ratios in summer 2004 are only 61% to 85% of medians reported in summer for the other 3 years. However, this is not the case for isoprene,

monoterpenes, MVK+MACR, DMS, acetic acid, and the C₈ and C₉ aromatics. This result suggests that photochemistry (acetic acid), light and temperature (biogenics), and mobile emissions and photochemical removal (C₈ and C₉ aromatics) were fairly consistent over these four summers. Hence these parameters are not likely candidates to explain the low median mixing ratios observed in summer 2004 for the other compounds.

Interannual comparisons for the other three seasons generally show modest variability from year to year. There are two notable exceptions (Fig. 2, Table 2): monoterpenes were higher in fall and winter 2005 than in 2006 or 2007, and methanol was much higher in spring 2007 than spring 2006 or 2008. Work is ongoing to investigate these unusual observations.

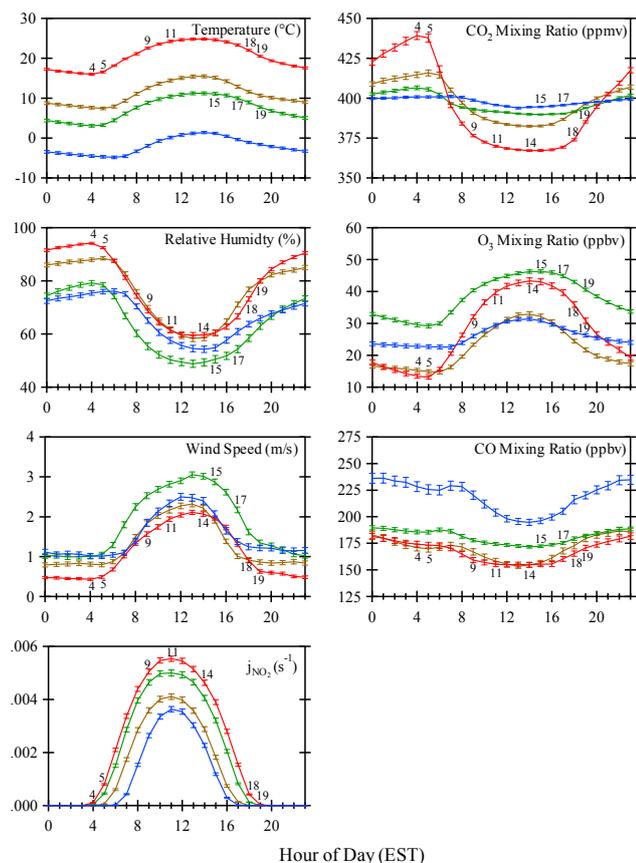


Fig. 3. Mean diurnal temperature, relative humidity, wind speed, j_{NO_2} , CO_2 , O_3 , and CO for summer (red), fall (gold), winter (blue), and spring (green). Time is in Eastern Standard Time (for all seasons, including summer) which is equivalent to Universal Time – 5 h.

4 Discussion

4.1 Diurnal variability

Mean diurnal curves are useful in illustrating typical behavior of various parameters, even though individual events, driven by transport and other specific meteorology may vary from the averages presented here. The physical parameters of temperature, relative humidity, wind speed, and j_{NO_2} all exhibited consistent diurnal patterns throughout the year, with the expected shifts in daylight (j_{NO_2}) and temperature (Fig. 3). Relative humidity was highest in summer and fall, with pre-dawn maxima and mid-day minima. Wind speeds were highest in spring and winter, with mid-day maxima and nighttime minima.

Diel cycles of CO_2 , O_3 , and CO are also shown in Fig. 3. CO_2 and O_3 exhibited their largest diurnal amplitudes in summer as expected from enhanced photosynthesis (CO_2) and photochemical processes (O_3) during this season. CO_2 is observed to build up under the nocturnal inversion and was

drawn down during the day, primarily during summer and fall, and to a lesser degree in spring and winter. O_3 removal was apparent during nighttime hours, most strongly in summer and spring, and built up during the day reaching its diurnal maxima in mid-afternoon. CO emissions are fairly uniform throughout the year, hence the higher values in winter reflect reduced OH photooxidation. In all seasons, CO was highest at night with a daytime minima.

4.1.1 Marine tracer – DMS ($(\text{CH}_3)_2\text{S}$, m/z 63)

Given the proximity of TF to the coast, DMS was monitored for evidence of oceanic air impacting this site. DMS is produced by phytoplankton (Bates et al., 1992) and has been reported to exhibit a diurnal cycle of daytime minima and nighttime maxima (Warneke and de Gouw, 2001; Hayward et al., 2002) attributed to its continuous production by phytoplankton with daytime removal primarily by OH (Cooper and Saltzman, 1991). As noted in Sect. 3.1, DMS measured by PTR-MS is usually below detection at TF. Little diurnal variation was observed (Fig. 4), and what there was may not be representative of the diurnal cycle at the coast. Values at TF were much lower (medians of 0.03–0.04 ppbv year round, Table 2) than those observed at various marine sites, ~ 0.15 –0.35 ppbv (Hayward et al., 2002, and references therein).

Marine sources of trace constituents have been shown to be important at TF (Zhou et al., 2005 and 2008; Chen et al., 2007; Varner et al., 2008). Previously reported measurements of marine tracers at TF (including DMS) have been performed with gas chromatography. Such measurements, primarily of various halocarbons, have been on the order of a few pptv or less (Zhou et al., 2005 and 2008; Varner et al., 2008). The apparent lack of DMS from the PTR-MS observations is principally due to the relatively high detection limit (0.025 ppbv). DMS is observed to exceed the detection limit when meteorological conditions are such that on-shore flow brings marine-influenced air to the site from the Gulf of Maine, but is generally below detection for PTR-MS under other synoptic flow patterns, consistent with previously reported values at TF (Zhou et al., 2008).

4.1.2 Biomass burning tracer – acetonitrile (CH_3CN , m/z 42)

Acetonitrile is a tropospheric tracer of biomass burning (Lobert et al., 1990; Holzinger et al., 1999; Bange and Williams, 2000). Direct industrial emissions, fossil fuel combustion, and indirect production from agricultural fumigants are all minor sources contributing <5% to its total emissions (Wisthaler et al., 2002, and references therein). There are no known sources from plants or soils (Wisthaler et al., 2002). Acetonitrile is removed from the atmosphere via reaction with OH, wet deposition, and possibly loss to the ocean (via dissolving into the water and/or biological processes, de Gouw et al., 2003b). None of these loss processes are

Table 3. Deposition velocity (cm s^{-1}) calculated from observed rate of depletion in summer diurnal average (from 22:00 to 04:00 EST). Also, ratio of the mixing ratios at selected pairs of hours.

<i>Compound(s)</i>	<i>Protonated m/z</i>	<i>Deposition Velocity (cm s^{-1})</i>	<i>05:00/04:00 EST Ratio</i>	<i>06:00/05:00 EST Ratio</i>
Acetic Acid	61	0.68	1.13	1.27
MVK + Methacrolein	71	0.67	1.06	1.53
Isoprene	69	0.35	1.22	1.57
MEK	73	0.34	1.07	1.19
Acetaldehyde	45	0.31	1.06	1.17
Acetone	59	0.20	1.01	1.11
Methanol	33	0.18	1.23	1.19
Acetonitrile	42	0.16	1.01	1.06

particularly efficient, leading to a lifetime in the atmosphere of ~ 0.5 – 1.5 y depending upon whether an ocean sink is considered (former) or removal is restricted to wet deposition and reaction with OH (latter) (Hamm et al., 1984; Hamm and Warneck, 1990; Singh et al., 2003). Recent work (Sanhueza et al., 2004) has indicated that the ocean may act as a reservoir for acetonitrile, being a source in warm regions and a sink in cold regions.

Acetonitrile mixing ratios at TF in summer increased from ~ 0.10 ppbv before dawn (04:00 EST) to ~ 0.14 ppbv in mid-morning (09:00 EST) with the mixing ratio constant throughout the rest of the day (Fig. 3). In early evening (19:00 EST) acetonitrile decreases, presumably as the nocturnal inversion sets up and reduces surface layer exchange from the remnant boundary layer aloft (Talbot et al., 2005). Dry deposition appears to reduce the mixing ratio under the inversion. A decrease was seen from 18:00 to 20:00, with a leveling off or slight increase observed from 20:00 to 21:00 prior to a steady decrease throughout the remainder of the night. The average diurnal cycle in summer suggests that acetonitrile does not have any local sources and that dry deposition is the primary sink. This interpretation of the diurnal cycle of acetonitrile is consistent with that of total gaseous mercury reported to have diel behavior controlled solely by mixing and dry deposition at this site (Mao et al., 2006).

Deposition velocities were calculated based on the observed depletion rate from 22:00 to 04:00 EST in summer. Assuming a boundary layer height of 125 m (Talbot et al., 2005) and a median nighttime mixing ratio of 0.11 ppbv, we obtain a dry deposition velocity of 0.16 cm s^{-1} (Table 3) which is consistent with the 0.14 cm s^{-1} value reported for a tropical savanna ecosystem (Sanhueza et al., 2004).

The mean diurnal mixing ratios observed throughout the year here range from ~ 0.08 – 0.14 ppbv. These values are comparable to background values (0.10 – 0.15 ppbv) reported elsewhere (Hamm and Warneck, 1990; Warneke and de Gouw, 2001; Wisthaler et al., 2002; Williams et al., 2004). The acetonitrile diurnal cycle in fall was similar to that in summer, but the difference in day/night mixing ratios was

much smaller. The higher summertime values likely reflect increased occurrence of North American biomass burning and subsequent transport of plumes from this burning to the Northeastern US (Duncan et al., 2003; Duck et al., 2007; Park et al., 2007). In spring, the diurnal profile of acetonitrile was nearly flat with the difference between maxima (~ 0.09 ppbv at 21:00 EST) and minima (~ 0.08 ppbv at 14:00 EST) mean diurnal mixing ratios only ~ 0.01 ppbv. Similarly, winter exhibited this same diurnal behavior with slightly enhanced amplitude, a difference of ~ 0.02 ppbv between maxima (~ 0.10 ppbv at 21:00 EST) and minima (~ 0.08 ppbv at 11:00 EST). The mean seasonal diurnal behavior of acetonitrile suggests it may be used as a conservative tracer of boundary layer dynamics in interpreting the mean seasonal diurnal curves for the other species reported here.

4.1.3 Biogenics – isoprene (C_5H_8 , m/z 69) and MVK + MACR ($\text{C}_4\text{H}_6\text{O}$, m/z 71)

Isoprene is mainly emitted by chloroplasts as a function of light and temperature (Steeghs et al., 2004). Hence, isoprene emissions occur in the daytime and stop at night with summertime emissions exceeding those in winter. Isoprene readily reacts with OH, its main daytime sink with an estimated lifetime of 0.07 d (Table 4). Two principal oxidation products of isoprene are MVK and MACR.

Although nighttime reaction of isoprene with NO_3 (Table 4) can be an important removal mechanism affecting its diurnal cycle (Stroud et al., 2002), NO_3 is likely suppressed at night both by prevalent monoterpenes (Warneke et al., 2004) and fresh NO emitted into the shallow nocturnal boundary layer by regional traffic (Stroud et al., 2002; Talbot et al., 2005; Ambrose et al., 2007). Hence, the nighttime oxidizing capacity of the nocturnal boundary layer is expected to be low at this site in summer. If the nighttime mixing ratio of isoprene is controlled by NO_3 oxidation, then the ratio of MVK+MACR to isoprene should increase as isoprene is much more reactive with NO_3 (Table 4). However, this ratio decreased from 0.86 to 0.62 over the nighttime interval of 22:00 to 04:00 EST in summer suggesting

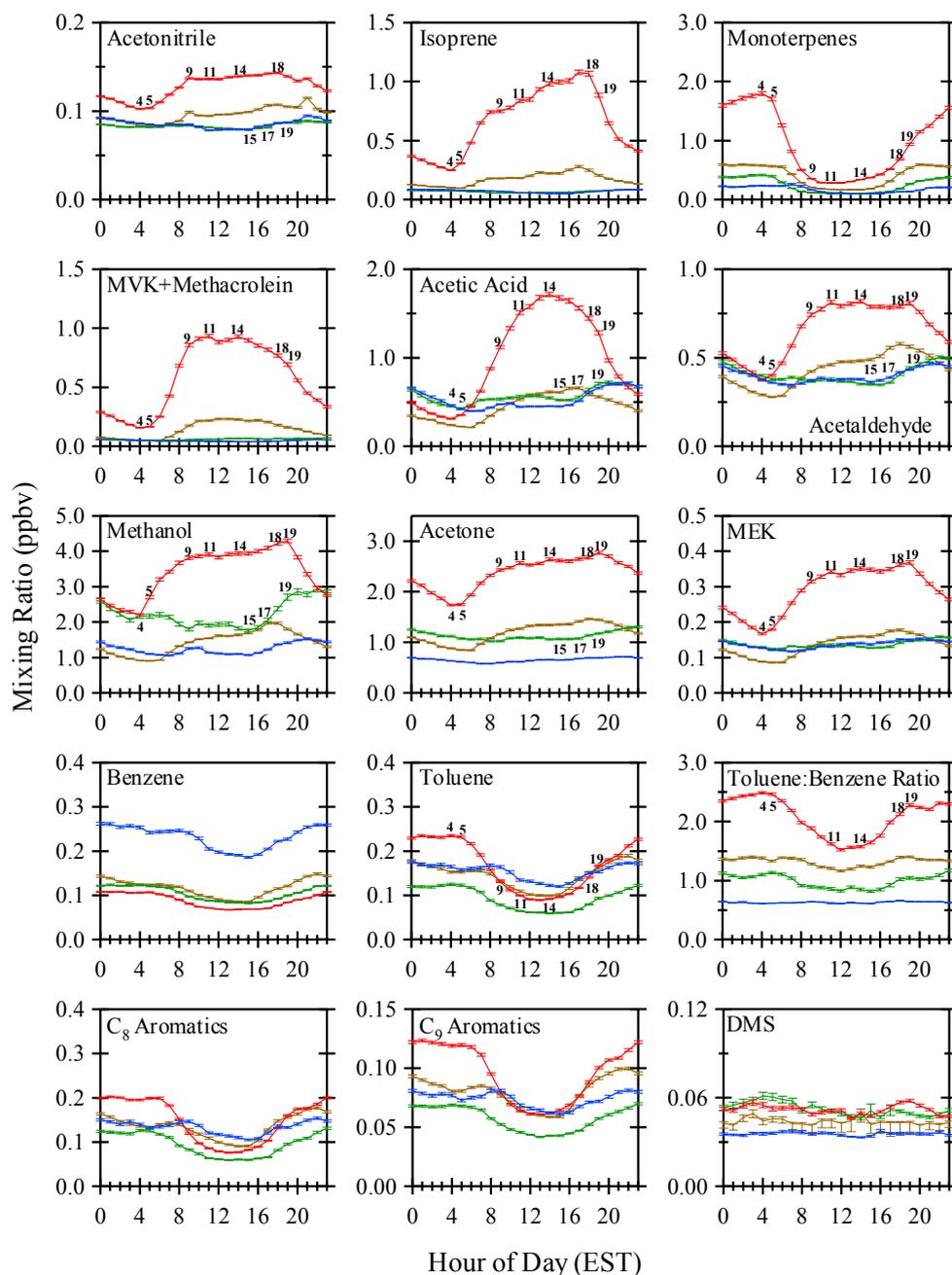


Fig. 4. Mean diurnal mixing ratios for each reported compound with summer in red, fall in gold, winter in blue, and spring in green. Time is in Eastern Standard Time (including summer) which is equivalent to Universal Time – 5 h.

dry deposition was the dominant nighttime removal mechanism. Calculating the deposition velocities (Table 3) as described for acetonitrile, we found values of 0.35 (isoprene) and 0.67 cm s^{-1} (MVK+MACR). These represent two of the three highest deposition velocities estimated for TF (acetic acid is 0.68 cm s^{-1}).

As seen in the acetonitrile diurnal profile, there was a rapid mixing ratio increase after dawn as the inversion dissipated and the surface layer mixed with the remnant boundary

layer air. The air mass mixing appeared to be complete by 08:00 EST rather than 09:00 EST as was seen with acetonitrile, but this difference likely reflects the balance between fresh emissions of isoprene and its removal by OH.

Isoprene is observed to increase throughout the day in summer (Fig. 4) with inflections in the diurnal profile likely the result of shifts in the balance between emissions and loss by reaction with OH. This is best seen by comparing the shape of the diurnal curve between isoprene and its

Table 4. Rate constants at 298 K and estimated day and night lifetimes in summer.

Compound	$k_{\text{OH}} \times 10^{12}$ $\text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$	$k_{\text{NO}_3} \times 10^{12}$ $\text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$	$k_{\text{O}_3} \times 10^{18}$ $\text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$	Daytime Lifetime in Summer (d)	Nighttime Lifetime in Summer (d)
<i>Biogenics</i>					
Isoprene	100 ^a	0.7 ^a	12.7 ^a	0.07	0.06
Methyl vinyl ketone (MVK)	20 ^a	<0.0006 ^a	5.2 ^a	0.32	4.21
Methacrolein (MACR)	29 ^a	0.0034 ^a	1.2 ^a	0.26	7.98
<i>Monoterpenes</i>					
α -pinene	53 ^a	6.2 ^a	90 ^a	0.06	0.01
β -pinene	78.9 ^b	2.51 ^b	15 ^b	0.09	0.02
<i>OVOCs</i>					
Acetone	0.18 ^a	–	–	42.9	–
Acetic Acid	0.74 ^a	–	–	10.4	–
Methanol	0.9 ^a	–	–	8.57	–
Methyl ethyl ketone (MEK)	1.2 ^a	–	–	6.43	–
Acetaldehyde	15 ^a	0.0027 ^a	–	0.51	17.1
<i>Aromatics</i>					
Benzene	1.23 ^b	–	–	6.27	–
Toluene	5.96 ^b	–	–	1.29	–
<i>C₈ Aromatics</i>					
o-xylene	13.7 ^b	–	–	0.56	–
m-xylene	23.6 ^b	–	–	0.33	–
p-xylene	14.3 ^b	–	–	0.54	–
<i>C₉ Aromatics</i>					
1,2,4-trimethylbenzene	32.5 ^b	–	–	0.24	–
<i>Tracers</i>					
Acetonitrile	0.022 ^a	–	–	351	–
DMS	5.00 ^b	1.00 ^b	<1 ^c	1.34	0.05

^a Atkinson et al., 2006.

^b From Tables B.1 and B.7 in Seinfeld, J. H. and Pandis, S. N. (1998)

^c http://jpldataeval.jpl.nasa.gov/pdf/Atmos97_Anotated.pdf

Values used to calculate lifetimes: day: $[\text{OH}] = 1.5 \times 10^6 \text{ cm}^{-3}$; $[\text{NO}_3] = 0$; $[\text{O}_3] = 1.125 \times 10^{12} \text{ cm}^{-3}$ (45 ppbv).
night: $[\text{OH}] = 0$; $[\text{NO}_3] = 2.5 \times 10^8 \text{ cm}^{-3}$ (10 pptv); $[\text{O}_3] = 5.0 \times 10^{11} \text{ cm}^{-3}$ (20 ppbv).

products (following from reaction with OH) MVK+MACR. j_{NO_2} peaks at midday (Fig. 3) resulting in peak mixing ratios of OH. However, at the same time isoprene production should also peak. By 14:00 EST, as $[\text{OH}]$ begins to decline, the diurnal curve of MVK+MACR begins its decline for the remainder of the day as less of these compounds are produced from isoprene and they are lost by OH attack. Isoprene was seen to continue increasing until early evening, as it continued to be emitted by trees in daylight, yet its loss was slowed as $[\text{OH}]$ decreased. After 18:00 EST isoprene rapidly dropped as emissions ceased and removal processes dominated (White et al., 2008a).

As was the case for acetonitrile, the mean diurnal curve in autumn is similar to that of summer, but with lower mixing ratios. While in winter and spring, little variation was observed in the diurnal cycle, suggesting fresh emissions are minimal as was photochemical removal.

4.1.4 OVOCs – acetic acid (CH_3COOH , m/z 61)

Acetic acid is one of the most abundant organic acids in the atmosphere (Khare et al., 1999). The sources and sinks of acetic acid remain uncertain, hence the global budget is not well known (Rosado-Reyes and Francisco, 2006). Sources of acetic acid include vehicle emissions (Kawamura et al., 1985; Talbot et al., 1988), biomass burning (Talbot et al., 1988, 1995), emissions from ants (Graedel and Eisner, 1988), plants (Andreae, et al., 1988; Keene and Galloway, 1988; Talbot et al., 1990), soil (Sanhueza and Andreae, 1991; Enders et al., 1992; Sanhueza et al., 1996), oxidation of isoprene (Keene and Galloway, 1986; Talbot et al., 1988; Andreae et al., 1988; Jacob and Wofsy, 1988), ozonolysis of alkenes (including isoprene and monoterpenes, Calvert and Stockwell, 1983), peroxy acetyl radical reactions (Madronich and Calvert, 1990), and aqueous-phase oxidation of formaldehyde in cloud water (Chameides and

Davis, 1983). Sinks of acetic acid are primarily dry and wet deposition (Rosado-Reyes and Francisco, 2006).

In summer and fall the diurnal cycle of acetic acid was similar to that of MVK+MACR (Fig. 4) and O₃ (Fig. 3). Acetic acid exhibited the highest summertime deposition velocity reported here, 0.68 cm s⁻¹ (Table 3). As with the previously discussed compounds, the mixing ratio of acetic acid rapidly increased after dawn and continued to increase until 14:00 EST. Like O₃ and MVK+MACR, after this time, acetic acid mixing ratios declined. This was likely due to loss mechanisms dominating over production via photochemical processing. The close similarity of this curve to that of MVK+MACR suggests that this OVOC is predominantly produced in situ in the vicinity of this site, rather than directly emitted from biogenic (or other) sources.

Unlike isoprene, MVK+MACR, and acetonitrile, winter and spring mixing ratios of acetic acid exceeded those in summer and fall at night. For these colder seasons, there does appear to be nighttime loss over the 22:00 to 04:00 EST interval followed by a morning increase (delayed from that seen in summer, consistent with j_{NO_2} , Fig. 3). The mixing ratios remained constant throughout the day until an increase was observed in the late afternoon and evening.

4.1.5 Biogenics - monoterpenes (C₁₀H₁₆, m/z 137)

Monoterpenes are emitted by trees, both coniferous and deciduous (Kesselmeier and Staudt, 1999). These emissions are primarily a function of temperature (from stored pools such as resin ducts), although some species may also emit recently synthesized monoterpenes (as a function of light as well as temperature) (Lee et al., 2005 and references therein). Monoterpenes are highly reactive with OH (comparable to isoprene), NO₃ and O₃ (more so than isoprene for both of the latter oxidants, Table 4).

The contrast between the summertime diurnal cycle of isoprene versus that of monoterpenes was dramatic (Fig. 4), particularly given their comparable daytime reactivity with OH (Table 4). The difference between these profiles must result from a strong isoprene source, exceeding the capacity of OH at this site to remove it. However, the source of monoterpenes was insufficient to compete with daytime OH removal. As seen in other diurnal profiles, albeit in reverse, the monoterpenes mixing ratio begins to recover as OH declines and emissions continue, beginning slowly around 14:00 EST and increasing more rapidly after 16:00 EST. Daytime removal occurs in all four seasons (Fig. 4).

In summer, mixing ratios of monoterpenes were observed to increase throughout the night, but this was not observed during the other seasons. This difference is probably attributable to both enhanced nighttime emissions in this warm season and reduced O₃ (Fig. 3) and NO₃ sinks under the nocturnal inversion at this time of year (Talbot et al., 2005). This nighttime build-up of monoterpenes in summer also supports the contention of limited NO₃ in the nighttime bound-

ary layer as discussed above for isoprene and MVK+MACR (White et al., 2008a). Monoterpenes are highly reactive with both NO₃ (lifetime ~0.01–0.02 d using data given in Table 4) and O₃ (lifetime ~0.26–1.54 d), with NO₃ dominating the overall lifetime as shown in Table 4. The fact that monoterpenes are observed to accumulate at night suggests there is limited NO₃ (certainly <10 pptv (Brown et al., 2007) used in the Table 4 calculation).

4.1.6 OVOCs

The remaining OVOCs (acetaldehyde, methanol, acetone, and MEK) all appeared to have diurnal cycles similar to isoprene, suggesting these compounds may be emitted directly from biogenic sources, in addition to being produced photochemically from gas-phase precursors. All of these compounds exhibited profiles with peak mixing ratios in summer and fall just prior to sunset. The peak arrived an hour after that observed for isoprene suggesting either emissions continue later in the day or loss mechanisms were less efficient (all four of these compounds have lower deposition velocities than isoprene, Table 3), or both.

4.1.7 OVOCs – acetaldehyde (CH₃CHO, m/z 45)

Acetaldehyde exhibits a relatively constant temporal profile from 11:00 to 19:00 EST. This could be interpreted in a similar fashion as acetonitrile (i.e., that the diurnal curve reflects boundary layer dynamics coupled with dry deposition). However, its short lifetime with respect to OH (0.51 d, Table 4), comparable to that of MVK and MACR, argues against this interpretation. In addition, following its nighttime removal, its mixing ratio recovered from 04:00 to 09:00 EST (Fig. 4) as seen for acetonitrile. However, acetaldehyde mixing ratios further increased until 11:00 EST, a feature not seen in acetonitrile. This increase suggests either photochemical production or direct emission.

The mid-afternoon inflection observed between 11:00 and 12:00 (observed for all biogenic and OVOC compounds here) suggests removal exceeded production over this interval prior to increasing again until 14:00 EST. This loss was likely attributable to removal via OH at this time of day (see j_{NO_2} in Fig. 3). After 14:00 EST the curve decreased slightly, remained flat from 15:00 to 18:00 EST, with a slight increase at 19:00 EST then decreased throughout the night (with a calculated deposition velocity of 0.31 cm s⁻¹, Table 3).

These results suggest that acetaldehyde sources and sinks are finely balanced throughout the day. The fact that the mixing ratio does not decline throughout the afternoon and evening like MVK+MACR, acetic acid and O₃, suggests there are other sources than production from gas-phase precursors reacting with OH. Acetaldehyde has been reported to have vegetation sources (Kesselmeier and Staudt, 1999). A laboratory study suggested acetaldehyde may be released throughout the day in forest canopies under shifting light

conditions as part of normal leaf metabolism (Karl et al., 2002); perhaps such emissions affected the diurnal curve observed at TF.

Similar to acetic acid, winter and spring diurnal curves for acetaldehyde showed that the highest mixing ratios occurred around midnight, decreased to low early morning values with the mixing ratios remaining flat until 17:00 EST and increasing until midnight. This behavior may be a function of boundary layer height dynamics rather than either photochemical production or loss, since similar behavior is seen for acetonitrile.

4.1.8 OVOCs – methanol (CH_3OH , m/z 33)

Methanol is ubiquitous with mixing ratios in remote regions reported to be ~ 1 ppbv, attributed to large vegetation sources and a relatively long atmospheric lifetime (here estimated to be 8.6 d, Table 4) (de Gouw et al., 2003a). The source apportionment globally has been estimated to be 2% primary anthropogenic sources (from evaporation of solvents), 61% primary biogenic sources, 15% methane oxidation, 5–10% biomass burning, with the remaining 12–17% attributed to plant decay and/or ocean sources (Singh et al., 2000; Holzinger et al., 2005). In addition to the ocean and OH oxidation, wet and dry deposition to terrestrial ecosystems are also sinks for methanol (Galbally and Kirstine, 2002).

Biogenic emissions of methanol have been reported to occur in daylight and to be dependent on temperature (Baker et al., 2001; Schade and Goldstein, 2001; Harley et al., 2007) and stomatal control (MacDonald and Fall, 1993; Hüve et al., 2007; Harley et al., 2007). Such daytime emissions are consistent with isoprene, hence the similarity in their seasonal diurnal curves (Fig. 4). Methanol exhibited a much larger increase from 04:00 to 05:00 (0.50 ppbv) in summer than all other compounds except isoprene, increasing by a factor of 1.23 (Table 3). Isoprene increased by a factor of 1.22, indicating that methanol has a very strong biogenic source. However, the shape of the curve throughout the remainder of the day, along with the relatively long lifetime of methanol, does not support that inference. If the source of methanol was as strong as isoprene, with a smaller sink, then it should steadily increase throughout the day. However, methanol's diurnal profile is quite similar to acetaldehyde, which appears to have relatively balanced sources and sinks. Looking at the rate of increase of all compounds over the next hour, 05:00 to 06:00, only methanol is observed to have a lower rate of increase than observed in the previous hour (1.19, Table 3).

Biogenic emissions of methanol have been reported to be controlled by the opening and closing of stomata (MacDonald and Fall, 1993; Hüve et al., 2007; Harley et al., 2007). Studies have shown that methanol can build up within the stomata during the night, releasing a large burst to the atmosphere when the stomata open, followed by emissions consistent with changes in stomatal conductance (Kirstine et al., 1998; Hüve et al., 2007) and temperature (Harley et

al., 2007). The diurnal curve shown here is consistent with these laboratory studies reporting an early morning burst. Subsequently, methanol was observed here to increase until 11:00 EST, followed by a small downturn over the next hour, then a steady increase throughout the afternoon.

Intriguingly in springtime, a pronounced late afternoon rise was observed commencing at 15:00 EST. At this hour, slight increases in acetonitrile and acetone occurred (10% and 15%, respectively, from 15:00 to 20:00 EST), with larger increases in acetaldehyde and acetic acid (31% and 38%, respectively, over this interval), but no other OVOC increased as dramatically as methanol (62% from 15:00 to 20:00 EST). Because methanol is not very reactive with OH (compared to most other compounds reported here), it is unlikely that this rise results from a reduced loss via reaction with OH (as is the case for monoterpenes and the aromatics); instead, this suggests an important fresh emission occurred.

Methanol has been reported to be associated with plant growth (a by-product of pectin hardening around cellulose) (Galbally and Kirstine, 2002; Keppler et al., 2004; Hüve et al., 2007). Methanol emissions from plant leaves are several-fold higher when the leaves are young and expanding than when they reach maturity (MacDonald and Fall, 1993; Nemecek-Marshall et al., 1995; Hüve et al., 2007; Harley et al., 2007). Indeed, growing tissues have been reported to contribute the most to plant-generated methanol in the atmosphere (Hüve et al., 2007). Hence, it is anticipated that methanol emissions will exhibit a seasonality consistent with plant growth (Galbally and Kirstine, 2002). We collected enclosure samples of methanol emissions in spring collected from loblolly pine and sweetgum trees at Duke Forest. These showed peak methanol emissions occurred in mid-afternoon. The sweetgum emissions remained high throughout the remainder of the day (unpublished data). Perhaps such plant growth emissions accumulate in the near surface boundary layer over the course of the day, resulting in the slowly increasing diurnal curve shown here (note, the ambient Duke Forest diurnal curve is very similar to this one). This is particularly provocative, since the rapid increase from 15:00 to 20:00 LT was second only to the rapid increase observed from 04:00 to 09:00 in summer (73%) as the nocturnal inversion broke down.

4.1.9 OVOCs – MEK ($\text{C}_2\text{H}_5\text{COCH}_3$, m/z 73)

There are few reports of MEK (butanone) in the literature, hence, sources and sinks remain uncertain. MEK has been observed to have biogenic sources (Kirstine et al., 1998; de Gouw et al., 1999), and it is expected to be produced in the atmosphere from the oxidation of butane and higher hydrocarbons (de Gouw et al., 2003a). MEK was observed to constitute 45–50% of the VOC emissions from clover pastures in Australia (followed by methanol (15–33%) and acetone (13–23%), Kirstine et al., 1998). The biological mechanism that produces MEK, and the manner of its release to

the atmosphere is unknown. However, the observations of Kirstine et al. (1998) indicate the emissions from undisturbed pasture were both a function of temperature and light, peaking at mid-day and ceasing at night. Kirstine et al. (1988) attribute this behavior to photosynthesis, stomatal control, or evaporation from leaf surface. By analogy with isoprene, they assert these emissions originate from the action of light-dependent enzymes within leaf tissue, and MEK is not stored in significant amounts within the plant.

At TF MEK was removed at night with a deposition velocity of 0.34 cm s^{-1} (Table 3). Its diurnal cycle follows the same pattern discussed thus far, with mixing following the breakdown of the nocturnal inversion, additional sources contributing to enhanced mixing ratios until 11:00 EST, a small downturn during peak [OH] at mid-day, with a peak observed at 19:00 EST. Again this late day peak likely reflects a biogenic primary source, rather than in situ production via OH reactions with precursors at this late hour.

The diurnal cycle of MEK in fall was similar to that in summer, but having lower mixing ratios. Daytime fall mixing ratios of MEK were only slightly higher than those in winter and spring. The lower nighttime values in fall likely reflect more efficient nighttime deposition under the nocturnal inversion, consistent with the lower nocturnal wind speeds observed at this time of year compared to winter and spring (Fig. 3).

4.1.10 OVOCs – acetone (CH_3COCH_3 , m/z 59)

Acetone is ubiquitous in the atmosphere (Warneke and de Gouw, 2001). The global budget of acetone has been apportioned (Jacob et al., 2002) to 1% primary anthropogenic emissions (from solvents and vehicle emissions), 35% primary biogenic emissions, 22% secondary production from propane oxidation, 5% biomass burning, with most of the rest emitted from oceans. Sinks are photolysis (65%), OH oxidation (25%), and 10% due to wet and dry deposition (Singh et al., 1994, 1995). Deposition velocities of ~ 0.17 – 0.36 cm s^{-1} have been reported for the ocean (Mao et al., 2006; Warneke and de Gouw, 2001). Since acetone is both emitted from oceans and deposited to them, it has been suggested that oceans act as a reservoir for acetone, i.e., a sink for polluted air masses and a source for relatively clean air masses (Wisthaler et al., 2002; de Reus et al., 2003; Williams et al., 2004). In rural areas biogenic emissions of acetone have been reported to be substantial, e.g., 23% of total C emissions from a pasture of grass and clover in Australia (Kirstine et al., 1998).

Acetone exhibited a very similar diurnal profile to that of methanol and MEK, suggesting that in summer its diurnal cycle reflected a composite of daytime primary biogenic emissions, secondary formation, and nighttime removal. As with methanol (and unlike MEK), there was a clear distinction between spring and winter, with the former having mixing ratios almost a factor of 2 higher. In both seasons the diurnal

curves were flat, resembling those of acetonitrile, suggesting that the mixing ratios during these seasons were controlled largely by transport and boundary layer height dynamics rather than in situ production and loss. The absence of a late afternoon spring peak suggests that any biogenic emissions of acetone emanate from a different source than methanol. The fall diurnal cycle was similar to the summer cycle, but at lower mixing ratios, as has been the case for acetonitrile and all biogenics and OVOCs.

4.1.11 Aromatic compounds – benzene (C_6H_6 , m/z 79), toluene (C_7H_8 , m/z 93), C_8 (m/z 107) and C_9 (m/z 121) aromatics

Aromatic compounds are emitted to the atmosphere primarily via anthropogenic combustion given their prevalence in gasoline, with smaller additional contributions from industrial processes (Roberts et al., 1984). The principal loss mechanism for aromatics is reaction with OH (Table 4) resulting in atmospheric summer lifetimes typically on the order of hours (0.24 d, C_9 aromatics) to days (6.27 d, benzene). In general, hydrocarbons have been observed to exhibit the same seasonal behavior as CO, with mixing ratios at a minimum in summer and maximum in winter (Bottenheim and Shepherd, 1995; Goldstein et al., 1995). As with CO, anthropogenic emissions of hydrocarbons are largely seasonally invariant, with their seasonal variability attributed to their removal via OH (Bottenheim and Shepherd, 1995; Goldstein et al., 1995). Further, seasonal variations in rates for long-range transport of hydrocarbons play a relatively minor role in their seasonal cycles (Goldstein et al., 1995).

Here the diurnal cycle of benzene (Fig. 4) exhibits similar seasonality to CO (Fig. 3). Both have their highest mixing ratios in winter throughout the day and night. The remaining three seasons have comparable diurnal cycles and mixing ratios, although for CO spring is a bit higher than fall and summer, with more limited daytime removal.

Surprisingly, this is not the case for toluene and the C_8 and C_9 aromatics. Toluene has been reported to exhibit unusual seasonal behavior at TF (White et al., 2008b). Daily can measurements (usually obtained at mid-day) showed that unlike other anthropogenic hydrocarbons, toluene was elevated in summer and fall as well as winter (85 ± 5 , 88 ± 5 and 95 ± 3 pptv, respectively), with a spring minima (56 ± 4 pptv). White et al. (2008b) examined the summer enhancement of toluene in detail, attributing it to primarily a combination of enhanced fuel evaporation of reformulated gasoline with its higher toluene content (Lough et al., 2005) and to vegetative emissions, with a minor contribution from local industrial emissions. The vegetative emissions of toluene observed by White et al. (2008b) from a loblolly pine at Duke Forest were well correlated with monoterpenes.

Here, the diurnal cycles of toluene and the C_8 and C_9 aromatics are consistent with those findings based on daily data. All three of these exhibit their highest mixing ratios at night

in summer, with a diurnal cycle consistent with monoterpenes (Fig. 4). Unlike monoterpenes, all three have elevated winter mixing ratios (due to reduced removal via OH). The fall mixing ratios are comparable to or slightly higher than the winter values, with enhanced mid-day removal. Spring exhibits the lowest mixing ratios in all three cases.

4.1.12 Aromatic compounds – toluene:benzene ratio

For urban plumes traveling away from sources, the differing reaction rates of toluene and benzene with OH allows their ratio to be used as a photochemical clock. The ratio will change as a function of time as more of one compound is removed from the atmosphere than the other over a given interval (Roberts et al., 1984; McKenna et al., 1995). However, closer to sources where emissions should keep the ratio fairly constant, differing amounts of OH present in the atmosphere ($\sim 1.5 \times 10^6$ molecules cm^{-3} in summer, $\sim 1.5 \times 10^5$ molecules cm^{-3} in winter for northern midlatitudes (Goldstein et al., 1995)), will lead to a distinct seasonal cycle in the ratio (lower in summer, higher in winter). In addition, for a ground station within a nocturnal inversion as is the case for TF, a strong diurnal cycle would be expected (higher nighttime ratio reflecting emissions, lower daytime ratio reflecting a lower value in the well-mixed boundary layer combined with OH preferentially removing toluene).

The summer toluene:benzene ratio exhibits the expected diurnal variability (Fig. 4) with mean nighttime values peaking at ~ 2.5 at 04:00 EST and midday values ~ 1.5 . The observed nighttime peak is consistent with anthropogenic emissions of toluene:benzene reported to range from ~ 2 – 3 (Salisbury et al., 2003). However, seasonally, the ratio does not change as expected. White et al. (2008b) found the toluene:benzene ratio from daily can measurements at TF reached their maximum in summer, 1.9 ± 0.1 , significantly higher than the remainder of the year, 0.9 ± 0.02 . Yet, the ethyne:CO ratio (also dependent on OH reactivity, with ethyne the more reactive) had the expected summer minimum due to higher OH mixing ratios. They attribute the enhanced summertime ratio to enhanced summertime sources of toluene as discussed above. However, the low wintertime ratio reported here also requires scrutiny.

Benzene and CO exhibit similar diurnal variation in all four seasons (Figs. 3 and 4, respectively). CO emissions to the atmosphere are dominated by mobile combustion sources (Parrish, 2006). With fairly uniform emissions year round, the observed seasonal variations in CO reflect the efficiency of its removal via OH photooxidation (Penkett et al., 1993; Jobson et al., 1994). At TF the mean winter diurnal cycle of CO had a 13% drop in the mixing ratio between 06:00 (232 ppbv) and 14:00 h (202 ppbv, Fig. 3). This neglects the brief morning rush hour increase in CO up to 237 ppbv at 07:00. A drop of 13% requires an OH concentration on the order of 10^7 much too high for this region at this time of year. For 10^5 molecules cm^{-3} of OH, <1 ppb of CO is removed

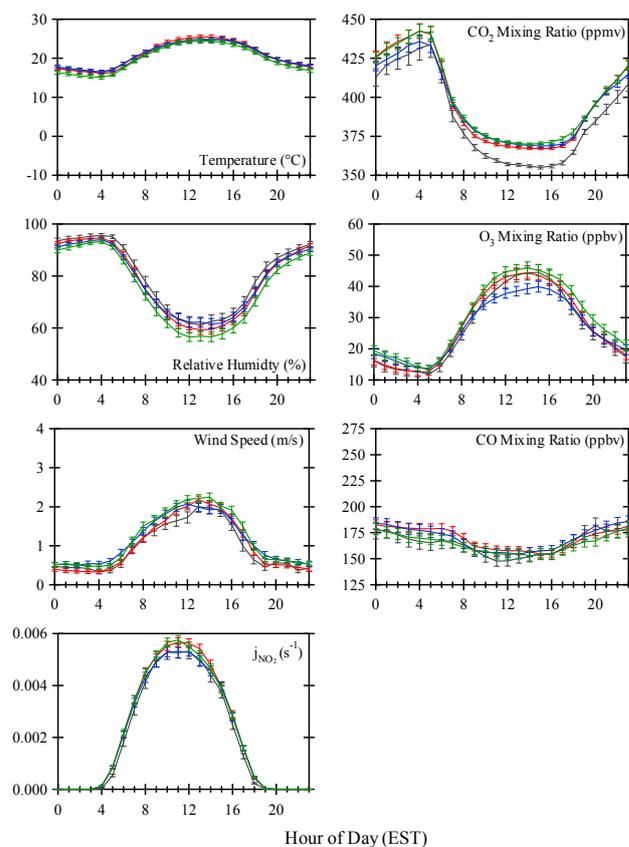


Fig. 5. Meteorological data along with CO₂, CO, and O₃ for Summer (Jun–Aug) 2004 (gray), 2005 (red), 2006 (blue), and 2007 (green).

over this 8 h period. This suggests CO accumulates at night near the surface and mixes during the day with background air with lower mixing ratios of CO.

Similarly, benzene and toluene also exhibit a decrease of $\sim 23\%$ over the interval from 06:00 to 14:00. If CO is accumulating near the surface at night from mobile sources, then the nighttime toluene:benzene ratio should approach that of mobile sources as well. Salisbury et al. (2003) have reported such ratios should be in the range of 2–3. Recently, Schnitzhofer et al. (2008) have suggested that the toluene:benzene ratio in winter should be lower than that in summer due to reduced evaporation of toluene. However, Lough et al. (2005) conducted tunnel studies in Milwaukee, WI (latitude 43.11° N, the same as TF) that show emissions of toluene are nearly constant throughout the year with mean emissions of 357 ± 143 mg L^{-1} fuel in summer (largely due to evaporation) and 363 ± 232 mg L^{-1} fuel in winter (largely due to incomplete combustion). Benzene emissions from mobile sources were observed to be 167 ± 59 mg L^{-1} fuel in summer and 95 ± 26 mg L^{-1} fuel in winter (Lough et al., 2005). Their results from two winter tunnel studies and a study of cold starts in a parking ramp suggest that even in

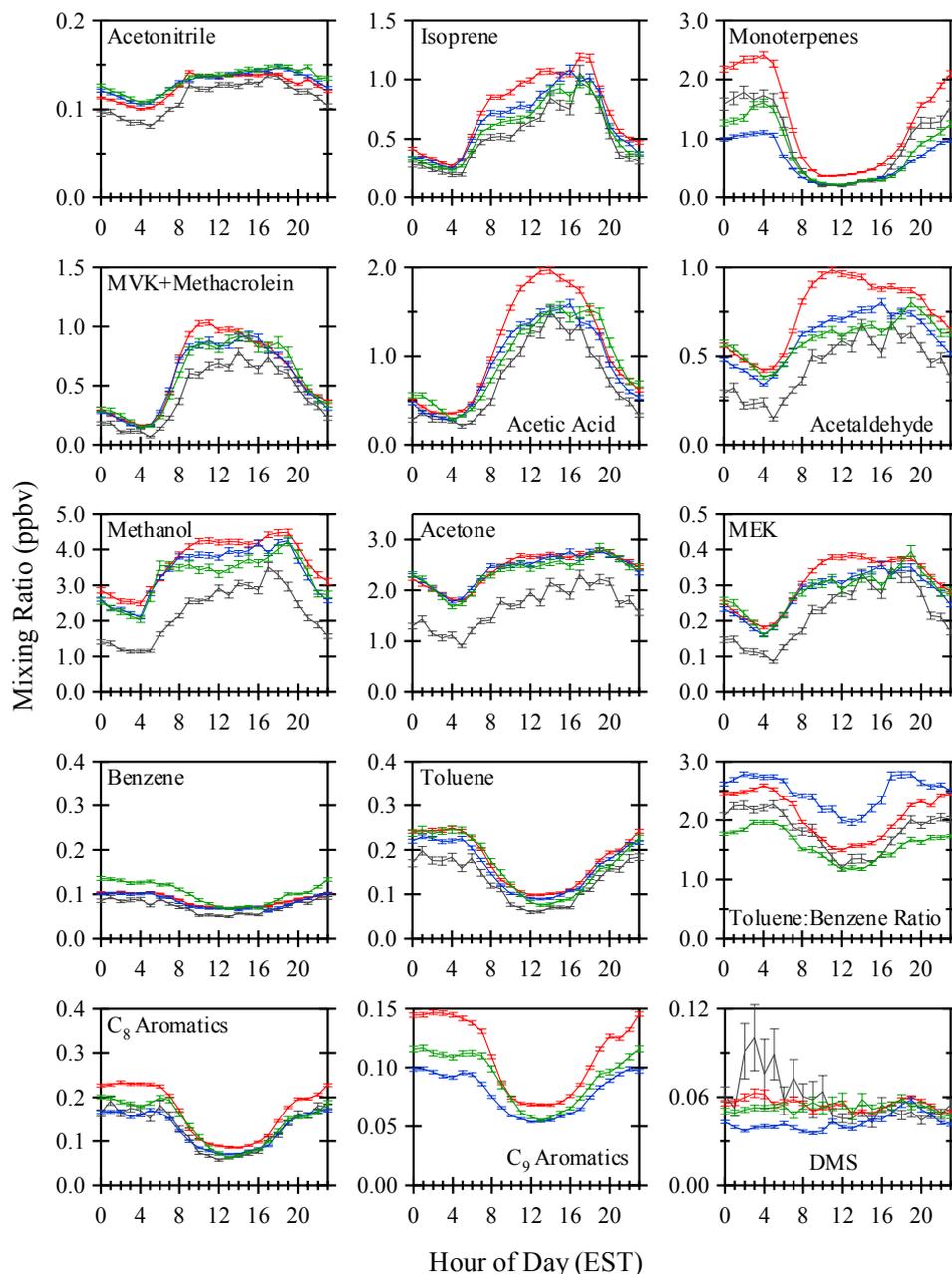


Fig. 6. PTR-MS data for Summer (Jun–Aug) 2004 (gray), 2005 (red), 2006 (blue), and 2007 (green).

winter mobile emissions of toluene and benzene should lead to a ratio in the range from ~ 2 –5 (Lough et al., 2005). So at TF, it would be expected that the toluene:benzene ratio would exhibit a diurnal cycle where the ratio increases at night to reflect recent mobile emissions, but it does not. The ratio is observed to remain constant throughout the day and night at ~ 0.7 (Fig. 4). This unchanging diurnal value is difficult to explain in the presence of accumulating fresh nighttime mobile emissions.

In addition to ratios measured from urban mobile emissions, toluene:benzene emission ratios have also been re-

ported from various forms of biomass burning. While highly uncertain, the data suggest the ratio is consistently < 1 with biofuel burning ~ 0.58 and extratropical forest fires ~ 0.82 (Andreae and Merlet, 2001). Charcoal burning and agricultural residues exhibit very low ratios, < 0.5 , but these numbers are based on very limited data (Andreae and Merlet, 2001). Perhaps then, the low value for this ratio observed here in winter reflects wood burning used for residential heating.

In the United States emissions of CO from wood-burning stoves and furnaces accounts for only 2% of the total CO emissions annually (Parrish, 2006). However, the highest use of residential biofuel in the United States is in the northeast (Park et al., 2007). In the two counties closest to TF CO emissions from heating contribute $\sim 6\%$ to the total winter CO emissions, 97% of which come from residential wood heating as estimated from the NEI99 (US EPA, 1999).

In New Hampshire, only 4.4% of homes use wood heat. The remainder use fuel oil (55.2%), gas (31.3%), electric (7.8%) with other sources or no heat at all accounting for the rest (1.3%) (http://factfinder.census.gov/servlet/DTTable?_bm=y&-geo.id=04000US33&-ds.name=ACS_2006_EST_G00.&-mt.name=ACS_2006_EST_G2000.B25117). Such a small fraction of wood-burning for heating (not including aesthetic fireplaces) may be insufficient to reduce the overall toluene:benzene ratio to 0.7. There is limited information on this ratio from furnaces in general, however one study showed wood-fired boilers exhibited toluene:benzene ratios of $\sim 0.2\text{--}0.4$ (Johansson et al., 2004). For comparison, they also assessed two oil-fired boilers in their study. One, a modern environmental brand (according to Nordic Ecolabeling of oil burners 2000–2004) had a ratio of 2. The other, a multi-fuel boiler that could also burn wood logs and pellets (here run with oil) had a ratio of 0.5. It should be noted that the emissions of toluene and benzene from the boilers in the Johansson et al. (2004) study ranged over four orders of magnitude with the largest emissions from old-style wood burners and lowest from the oil burners. There is insufficient information about toluene and benzene emissions from furnaces generally, or those in use in New Hampshire specifically, to estimate what such emissions might be. However, the diurnal cycle of CO and toluene:benzene when viewed together, suggest this question merits more attention.

It should be noted that the Schnitzhofer et al. (2008) study ruled out domestic wood combustion as a source of enhanced benzene (and hence lowered toluene:benzene ratio) on the basis of its ratio with acetonitrile. Here we see little diurnal variation of acetonitrile in winter, but there is a 17% difference between the nighttime maxima (99 pptv at 21:00 h) and daytime minima (82 pptv at 11:00 h). Nonetheless, it is not clear how much acetonitrile is emitted from domestic wood burning. Andreae and Merlet (2001) note there is very little data on emissions from wood and dung burning for domestic fuel, so they do not include any estimates for emissions from those sources. They note acetonitrile in particular as a compound for which much more data are needed. They also point out that NO, NO₂, N₂O, and molecular N₂ are emitted during flaming combustion, while nitriles (and NH₃ and amines) are emitted under smoldering conditions. This raises the possibility that less acetonitrile is released in the controlled burning of a wood-fired boiler or stove, than is the case in an open fire. Unfortunately in the one study we could find on furnace emissions (Johansson et al., 2004) no

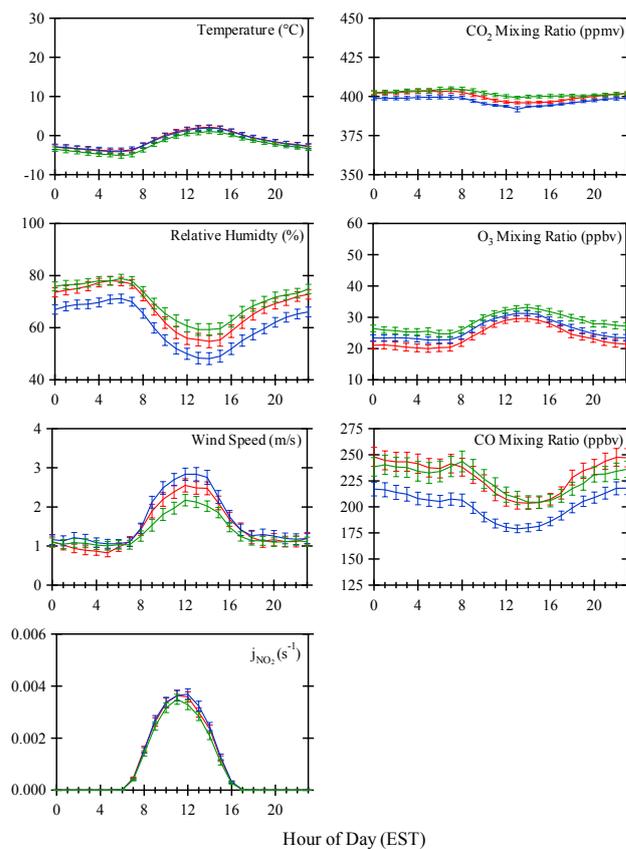


Fig. 7. Meteorological data along with CO₂, CO, and O₃ for Winter (Dec–Feb) 2005/2006 (red), 2006/2007 (blue) and 2007/2008 (green).

data were reported for N containing compounds. It appears the Schnitzhofer et al. (2008) study relied on open biomass burning ratios to calculate their expected emissions of benzene from acetonitrile, but such ratios for domestic heating sources require further data to constrain potential emissions.

4.2 Inter-annual diurnal comparisons

In addition to the comparisons of the diurnal cycles between seasons, the length of time covered by this data set permits an inter-annual comparison of mean diurnal cycles for a given season. Here we briefly highlight some interesting features from comparisons in summer and winter diurnal profiles from different years.

4.2.1 Summer

Comparing the summer meteorological parameters along with CO₂, CO and O₃ (Fig. 5), minor variations in temperature, relative humidity, wind speed and sunlight (as indicated by j_{NO_2}) were observed. Larger inter-annual variations among the diurnal curves of the compounds measured by PTR-MS are revealed in Fig. 6. As noted in the

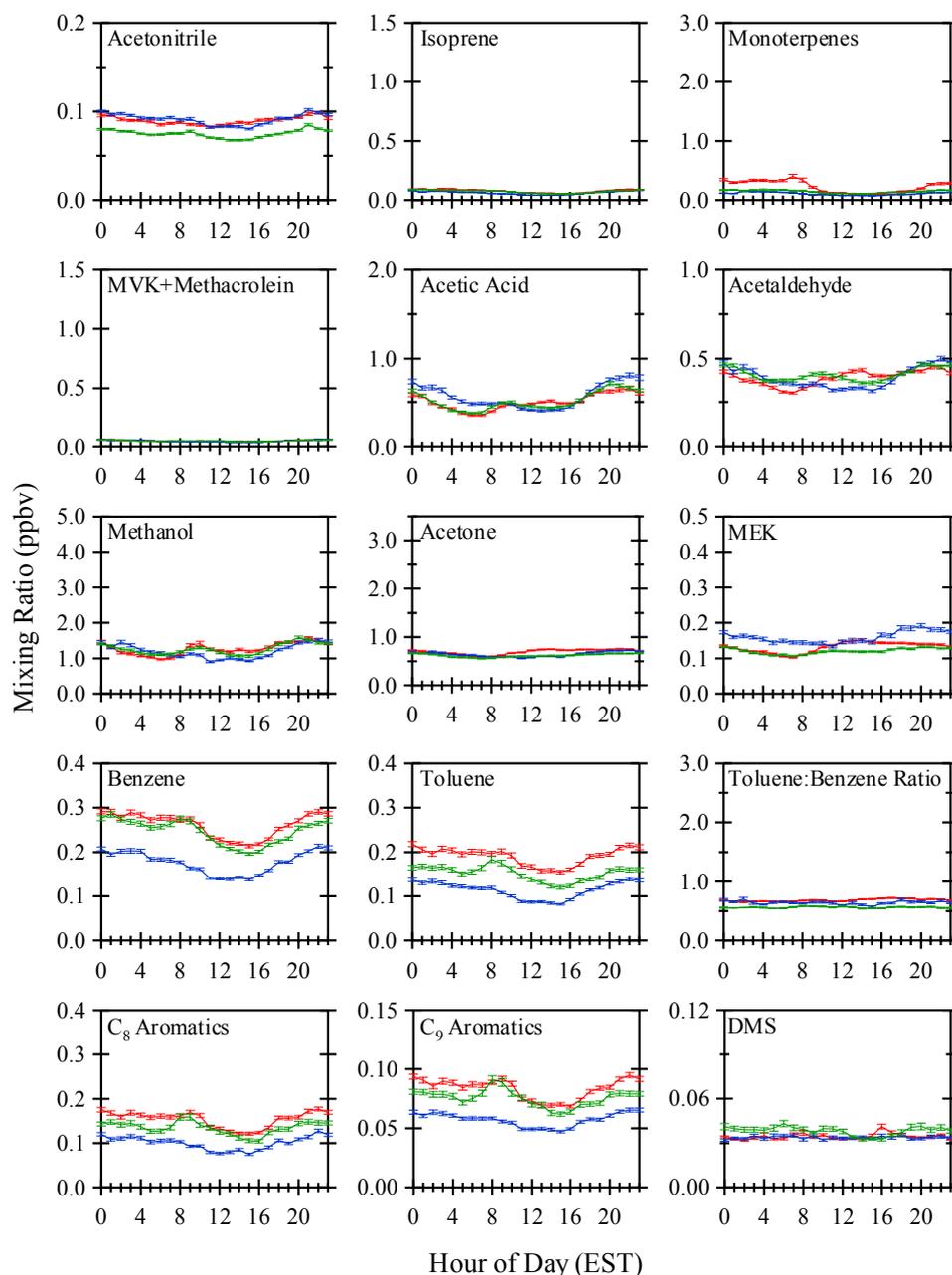


Fig. 8. PTR-MS data for Winter (Dec–Feb) 2005/2006 (red), 2006/2007 (blue), and 2007/2008 (green).

discussion of the statistics, several compounds (particularly acetaldehyde, methanol, acetone, and MEK) showed substantially lower mixing ratios throughout the mean summer day of 2004. There was also quite a bit of variability in the toluene:benzene ratio from year to year, with the highest ratio in 2006 (mean diurnal average ranged from 2.0 at midafternoon up to 2.8 at night) and lowest in 2007 (mean diurnal average 1.2–2.0). This variability likely reflects not just emissions from mobile sources and their subsequent photochemical processing, but also fuel evaporation and biogenic emissions of toluene (White et al., 2008b).

Of particular note was the appearance in 2005 of a mid-day peak in MVK+MACR, acetaldehyde, MEK, and possibly methanol. This suggests that under different meteorological and possibly different transport regimes, the balance between in situ photochemical production and direct biogenic emissions of OVOCs may be shifted at this site, resulting in different shapes to the mean diurnal curve. Although the meteorological data only indicated relatively minor differences between the summers, the differences observed in mean temperature were found to be statistically significant at TF (White et al., 2008b) with 2004 1.4°C cooler than

2005. 2005 had the highest temperature and j_{NO_2} mean diurnal curves (Fig. 5), presumably reflecting less cloud cover on average, which could result in higher photochemical production of secondary compounds.

4.2.2 Winter

The winter meteorological parameters show only minor variations in temperature and daylight between the winters of 2005/2006, 2006/2007 and 2007/2008 (Fig. 7). Similarly, most compounds generally showed minor inter-annual differences in winter, with the notable exception of CO (Fig. 7), monoterpenes, and the aromatics (Fig. 8). The aromatics, like CO, are much higher throughout the day in winter 2005/2006 and 2007/2008 than winter 2006/2007. Interestingly, the toluene:benzene ratio is nearly identical in all three years. This suggests that the sources of the aromatics were consistent in all winters, but that the mixing ratios are lower in winter 2006/2007.

Monoterpenes were also observed to be higher in winter 2005/2006 than the other two winters; however the difference was only observed at night, with daytime values comparable for all winters. This indicates the presence of local winter sources of the monoterpenes. Preliminary results indicate the source of this mean diurnal monoterpene signature for 2005/2006 were nighttime monoterpene emission events that occurred under a nocturnal inversion when the wind speed drops below 0.5 m s^{-1} . However, monoterpene events did not always occur when the wind speed was low. We are continuing to investigate factors that control the occurrence of these events.

5 Summary

We have presented observations from a long-term high time-resolution data set obtained at a rural site in southeastern NH that is subject to urban and marine influences. This extensive (and on-going) data set has been used to establish the mean characteristics of the compounds measured. Comparing multiple compounds sheds light on not just similarities, but differences that may be useful in guiding work to better understand specific sources and production mechanisms of these compounds. Further, these mean characteristics can be used to guide analysis of unusual events of interest that occur at this site. It is hoped that over time continued measurements will be useful in further understanding local controls (such as meteorological conditions, specific vegetation, evolving anthropogenic emissions) on the observed mixing ratios, versus the influence of transport on the air composition and its evolution in this region.

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