

Multi-year (2004–2008) record of nonmethane hydrocarbons and halocarbons in New England: seasonal variations and regional sources

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Abstract. Multi-year time series records of C₂–C₆ alkanes, C₂–C₄ alkenes, ethyne, isoprene, C₆–C₈ aromatics, trichloroethene (C₂HCl₃), and tetrachloroethene (C₂Cl₄) from canister samples collected during January 2004–February 2008 at the University of New Hampshire (UNH) AIRMAP Observatory at Thompson Farm (TF) in Durham, NH are presented. The objectives of this work are to identify the sources of nonmethane hydrocarbons (NMHCs) and halocarbons observed at TF, characterize the seasonal and interannual variability in ambient mixing ratios and sources, and estimate regional emission rates of NMHCs. Analysis of correlations and comparisons with emission ratios indicated that a ubiquitous and persistent mix of emissions from several anthropogenic sources is observed throughout the entire year. The highest C₂–C₈ anthropogenic NMHC mixing ratios were observed in mid to late winter. Following the springtime minimums, the C₃–C₆ alkanes, C₇–C₈ aromatics, and C₂HCl₃ increased in early to mid summer, presumably reflecting enhanced evaporative emissions. Mixing ratios of C₂Cl₄ and C₂HCl₃ decreased by 0.7±0.2 and 0.3±0.05 pptv/year, respectively, which is indicative of reduced usage and emissions of these halogenated solvents. Emission rates of C₃–C₈ NMHCs were estimated to be 10⁹ to 10¹⁰ molecules cm⁻² s⁻¹ in winter 2006. The emission rates extrapolated to the state of New Hampshire and New England were ~2–60 Mg/day and ~12–430 Mg/day, respectively. Emission rates of benzene, toluene, ethylbenzene,

xylenes, and ethyne in the 2002 and 2005 EPA National Emissions Inventories were within ±50% of the TF emission rates.

1 Introduction

Volatile organic compounds (VOCs) (including nonmethane hydrocarbons (NMHCs), alkyl nitrates, oxygenated and halogenated hydrocarbons) are ubiquitous and important chemical constituents in the atmosphere. The reaction of VOCs with various oxidants (e.g., hydroxyl radical (OH), ozone (O₃), nitrate radical, halogens) produces organic (RO₂) and hydro (HO₂) peroxy radicals which react with nitrogen oxides (NO_x) to produce secondary species, such as tropospheric ozone, organic nitrates, and peroxides, and regulates the oxidation capacity of the atmosphere. The relative concentrations and speciation of NO_x and NMHCs in a particular region determine whether ozone production or destruction occurs (e.g., Carter, 1994; Sillman and He, 2002; Kleinman et al., 2005). In addition, the partitioning of low volatility VOC oxidation products into the condensed phase produces secondary organic aerosols (e.g., Odum et al., 1997; Ng et al., 2007; Kroll and Seinfeld, 2008). Ozone and aerosols are components of photochemical smog, are respiratory lung irritants, and are harmful to vegetation and crops. Furthermore, several VOCs, such as benzene, toluene, xylenes, and tetrachloroethene, are classified as toxic air pollutants and are subject to federal regulations (US EPA, 2008). Therefore, it is necessary to identify and characterize the atmospheric distributions and sources of VOCs in order to



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develop and validate emission inventories, reduce the levels of hazardous air pollutants, and to predict and control O₃ and aerosol concentrations.

The regional distributions of VOCs are highly variable because of several confounding factors, including different atmospheric lifetimes and removal mechanisms, varying meteorological conditions, and the wide range of potential sources. In order to minimize these complications and to eliminate site-to-site differences, long-term continuous measurements from the same location are necessary. Multi-year measurements of NMHCs and halocarbons at remote and urban North American sites have been reported (e.g., Jobson et al., 1994; Hagerman et al., 1997; Kang et al., 2001; Mohamed et al., 2002; Gautrois et al., 2003; Swanson et al., 2003; McCarthy et al., 2006; Qin et al., 2007), but not for New England since 1994–2001 (Goldstein et al., 1995; Kleiman and Prinn, 2000; Barnes et al., 2003; Lee et al., 2006). These studies have provided baseline data from which to monitor future changes in sources and ambient mixing ratios.

Air masses containing urban and industrial emissions from southern New England, the US East Coast and mid-Atlantic corridor, and the Midwest are transported to New Hampshire. Previous research has indicated that the trace gas measurements (including O₃, carbon monoxide (CO), nitric oxide (NO), mercury, select VOCs) made at the UNH AIRMAP monitoring site at Thompson Farm (TF) in Durham, New Hampshire are representative of both inland and coastal New England (e.g., Talbot et al., 2005; Chen et al., 2007; Sive et al., 2007; Mao et al., 2008; White et al., 2008; Zhou et al., 2005, 2008). This suggests that the TF results can be applied to regional analyses of the short and long-term temporal variability and sources of VOCs for this region. This is particularly valuable because southern New England, including the seacoast region of New Hampshire, and extending to the southwest through New York and New Jersey is classified as an O₃ nonattainment area (US EPA, 2003, 2008).

We have been conducting VOC measurements at Thompson Farm since 2002. Multi-year VOC data published thus far includes measurements of C₁–C₅ alkyl nitrates (Russo et al., 2010), methyl iodide (Sive et al., 2007), and oxygenated VOCs (OVOCs) and select NMHCs (Jordan et al., 2009). Summertime measurements (2002–2004) of NMHCs, OVOCs, and marine-derived halocarbons at TF were discussed in Talbot et al. (2005), Chen et al. (2007), White et al. (2008), and Zhou et al. (2005, 2008). In this work, four years (2004–2008) of ambient C₂–C₈ NMHC and anthropogenic halocarbon data from daily canister samples collected at the Thompson Farm site in southeastern New Hampshire are presented and discussed. The primary objectives of this study are to characterize the seasonal to inter-annual trends and to identify the possible sources of C₂–C₈ NMHCs and halocarbons. Additionally, emission rates of several NMHCs were estimated and compared with the EPA National Emissions Inventory.

2 Sampling and analytical methods

2.1 Daily canister sample collection and analysis

The University of New Hampshire AIRMAP Observatory at Thompson Farm (TF) is located in Durham, New Hampshire (43.11° N, 70.95° W, elevation 24 m) and is located approximately 20 km inland from the Atlantic Ocean and 100 km north of Boston, MA (www.airmap.unh.edu) (Fig. 1). TF is surrounded by agricultural fields and a mixed deciduous and coniferous forest. An ambient canister sample has been collected at some point between 10:00–15:00 (EST; UTC–5 h) each day at the top of the 15 m tower next to the manifold inlet for all the instruments housed in the TF building. Sample collection began on 12 January 2004 and continues through the present. The sample collection time window is representative of daytime conditions when photochemistry is most active and the boundary layer is likely well mixed. Prior to sampling, the 2-liter electropolished stainless steel canisters (University of California, Irvine, CA) were prepared by flushing with UHP helium that had passed through an activated charcoal/molecular sieve (13X) trap immersed in liquid nitrogen. The canisters were then evacuated to 10^{–2} torr.

The canister samples were analyzed in the laboratory at UNH approximately every 1–3 months for C₂–C₁₀ nonmethane hydrocarbons, C₁–C₅ alkyl nitrates, C₁–C₂ halocarbons, several OVOCs, and select sulfur compounds. A three gas chromatograph system equipped with two flame ionization detectors (FID), two electron capture detectors (ECD), and a mass spectrometer (MS) was used for analysis of each 1500 cc (STP) sample aliquot. The PLOT-FID, OV-1701-ECD, and OV-624-MS column-detector combinations have remained the same throughout 2004–2008 (see Sive et al. (2005) and Zhou et al. (2005, 2006, 2008) for additional information). In 2006, the FID channel used for C₄–C₁₀ NMHC analysis was changed from a DB-1 column (60 m×0.32 mm I.D., 1 μm film thickness) to a VF-1ms column (60 m×0.32 mm I.D., 1 μm film thickness). Also, the OV-624-ECD channel was changed to a CP-PoraBond-Q column (25 m×0.25 mm I.D., 3 μm film thickness) coupled to a Restek XTI-5 column (30 m×0.25 mm I.D., 0.25 μm film thickness). The MS was operated in electron impact mode with single ion monitoring for measuring OVOCs and sulfur compounds, as well as duplicate measurements of several halocarbons and NMHCs. A 1500 cc aliquot from one of two working standards was assayed every ninth analysis. The measurement precision for the whole air standards (i.e., relative standard deviation (RSD) = standard deviation of peak areas/average of peak areas) was <1–4% for the C₂–C₈ NMHCs and 5% for C₂HCl₃ and C₂Cl₄ at 0.50 and 6.0 pptv, respectively.

2.2 Daily canister sample data set

Data for several classes of NMHCs and two halocarbons from the canister samples collected during 12 January 2004 to 8 February 2008 were used for this study. Collection of the daily samples is ongoing. The specific compounds, which represent a wide range of chemical reactivities and sources, are C₂–C₆ alkanes (ethane, propane, i-butane, n-butane, i-pentane, n-pentane, n-hexane), C₂–C₄ alkenes (ethene, propene, 1-butene), C₆–C₈ aromatics (benzene, toluene, ethylbenzene, m+p-xylene, o-xylene), ethyne, isoprene, tetrachloroethene (C₂Cl₄), and trichloroethene (C₂HCl₃). The data for each year and for the combined four year data set was separated into four seasons which are defined as winter: December, January, February; spring: March, April, May; summer: June, July, August; and fall: September, October, November. Note that the data encompasses five winter seasons (2004–2008) and four spring, summer, and fall seasons (2004–2007) with the exceptions of winter 2004 which only includes 12 January to 29 February and winter 2008 which is only through 8 February. Mixing ratios higher than the 95th percentile value for each month were removed in order to ensure that the results were representative of typical conditions and were not skewed by outlying or spurious data points.

2.3 Thompson Farm automated gas chromatograph

Hourly measurements of C₃–C₆ alkanes, ethyne, propene, benzene, toluene, ethylbenzene, m+p-xylene, and o-xylene from an automated GC system during December 2005–January 2006 at TF were also used in this analysis. The sample size of the in situ GC system was also 1500 cc. Details of the four channel (2 FIDs, 1 ECD, 1 MS) GC system, MMR preconcentrator, sample trapping and splitting, calibrations, and instrument control are given in Sive et al. (2005). The system deployed at TF also contained four channels, but VOC detection was made with two FIDs and two ECDs. The channel which replaced the MS was a PoraBond-Q/OV-1 column coupled to an ECD for measuring C₁–C₂ halocarbons. A 1500 cc aliquot from one of two working standards was assayed every tenth analysis. The precision (i.e., RSD) for each of the hydrocarbons discussed in this work ranged from 3–10%.

2.4 Standards and calibration

In order to ensure that the VOC mixing ratios in samples analyzed at different times are comparable, whole air and synthetic standards were routinely analyzed and calibration scales were cross referenced and validated. When conducting the canister sample analysis, one of two whole air standards was analyzed after every eighth sample in order to monitor changes in detector sensitivity and measurement precision and to quickly detect any analytical problems. The

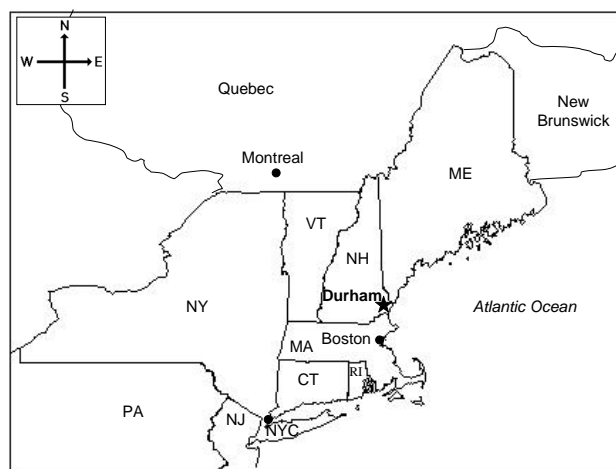


Fig. 1. Location of the UNH AIRMAP Atmospheric Observing Station at Thompson Farm in Durham, New Hampshire.

whole air working standards employed for this work have mixing ratios representative of clean free tropospheric air and suburban air, thus bracketing the low and high ranges for the measurements at TF. Moreover, linearity studies are regularly conducted to evaluate the detector response over the observed mixing ratio ranges for all classes of compounds. The working standards are part of the larger network of whole air standards maintained by B. Sive at UNH as part of the AIRMAP program. In total, there are currently ten high pressure cylinders, six 36-liter electropolished low-pressure pontoons (~350 psi), and three 34-liter electropolished high-pressure pontoons (~900 psi) containing whole air standards that have been filled and calibrated by UCI (D. Blake) and UNH. We estimate the upper limit of the absolute accuracy of the calibrated standards to be on the order of ± 1 –5% for the gases reported here. In addition to the whole air standards, calibrations are conducted using five different high-pressure cylinders containing synthetic blends of selected NMHCs, OVOCs, and halocarbons at the ppbv level (Apel-Reimer Environmental, Inc.). The absolute accuracy for all of the gases in the synthetic standards is less than ± 5 %.

Response factors (RF) for each compound in a particular standard were calculated by dividing the detector response (peak area= A) by the mixing ratio (MR) of that compound in the standard ($RF=A/MR$). Mixing ratios for each gas to be quantified in the ambient samples were subsequently calculated using the average RF determined from the whole air standards during each set of individual analyses. In order to monitor the response of NMHCs with different numbers of carbon atoms, it is useful to evaluate the per-carbon response, particularly when dealing with long-term calibrations. The per-carbon response provides information regarding analytical system performance and standard integrity with time. The per-carbon response factors (PCRF) were determined by dividing the RF for each NMHC by the number of carbon

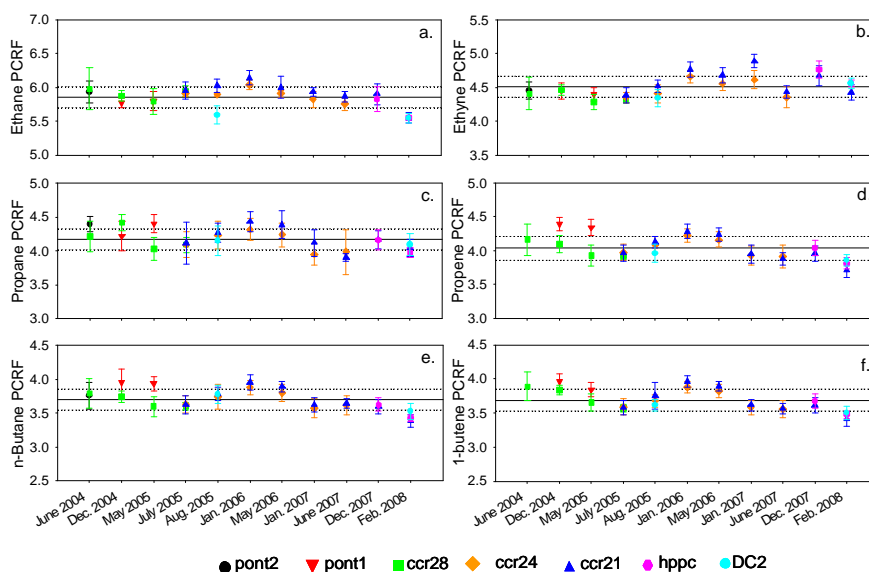


Fig. 2. Per carbon response factors (PCRF) of (a) ethane, (b) ethyne, (c) propane, (d) propene, (e) n-butane, and (f) 1-butene in different standards (pont1, pont2, ccrXY, hppc, DC2) analyzed in the UNH laboratory during 2004–2008. The reference lines are the mean \pm 1 standard deviation of the PCRF included in each plot. The symbols \pm error bars are the mean PCRF \pm 1 relative standard deviation for the individual standard analyzed during the specified time period.

atoms (C) in each particular hydrocarbon ($PCRF=RF/C$). While the response for hydrocarbons containing the same number of carbon atoms should be uniform, this should always be verified by analyzing different classes of compounds (e.g., alkanes, alkenes, alkynes). Examples of the PCRFs for several NMHCs are shown in Fig. 2 as representative examples for the analyses when a new standard began to be used and every \sim 3–6 months when the same two standards were being analyzed throughout 2004–2008. While there is some scatter about the mean PCRF over the four years, the PCRF of the two standards analyzed during each analysis period are self-consistent. Moreover, this illustrates the long-term stability of our analytical system.

The PCRF of the C_2 – C_4 NMHCs measured with the PLOT-FID column-detector pair decreased with increasing carbon number, but remained approximately the same over the four years and did not vary with standard. Additionally, the PCRFs remained constant for the C_3 (mean \pm standard deviation = 4.12 ± 0.19) and C_4 (3.70 ± 0.16) compounds (Fig. 2c–f). The PCRFs of the C_4 – C_{10} NMHCs for the DB-1/VF-1ms-FID column-detector pair have remained essentially constant (1.43 ± 0.03) for compounds with different carbon numbers and for different compound classes since 2005 (Sive, 1998; Zhou, 2006). Periodically, the standards used by the automated GC system at TF were returned to the laboratory and analyzed on the canister analysis system. The PCRFs for the TF standards (e.g., DC2) agreed (within $\pm 5\%$) with the laboratory standards ensuring that the measurements made by the two independent systems are comparable.

3 Seasonal and interannual variability of VOCs at Thompson Farm

3.1 General characteristics of NMHCs and comparison with previous studies

The highest monthly mean and median mixing ratios of NMHCs (excluding isoprene, Sect. 3.2) at TF were observed in the winter (Fig. 3, Table 1). This reflects the slow removal rates from the atmosphere caused by minimum OH radical concentrations at this time of year. Lower boundary layer heights in winter are conducive to the build up of trace gas concentrations and may also contribute to the wintertime peak mixing ratios. In general, the lowest NMHC mixing ratios were observed in spring to summer when the maximum OH concentrations occur and the photochemical removal of NMHCs is the most rapid. It should also be mentioned that there is a variation in dominant air mass transport pathways throughout the year which may contribute to the seasonal variation in NMHC mixing ratios. For example, in the winter, the transport of clean, Canadian air masses to New England, which are representative of background conditions, is more frequent (Munger et al., 1996; Moody et al., 1998; Shipham et al., 1998). In contrast, transport from the south and west is more frequent during the summer (Moody et al., 1998; Fischer et al., 2004; Mao and Talbot, 2004b). Overall, the seasonal variation at TF is consistent with the general tropospheric trend observed at other North American sites (e.g., Jobson et al., 1994; Bottenheim and Shepherd, 1995; Goldstein et al., 1995; Hagerman et al., 1997; Gautrois et al., 2003; Swanson et al., 2003; Lee et al., 2006; Qin et al., 2007).

Table 1. Monthly NMHC statistics (pptv) for January 2004–February 2008. SD is the standard deviation. *N* is the number of samples.

	January	February	March	April	May	June	July	August	September	October	November	December
Ethane												
Mean (SD)	2436 (621)	2395 (443)	2138 (435)	1856 (278)	1423 (205)	1104 (306)	1023 (324)	876 (277)	998 (275)	1238 (367)	1859 (544)	2278 (939)
Median (<i>N</i>)	2248 (125)	2288 (101)	2104 (98)	1835 (86)	1401 (102)	1057 (92)	942 (91)	784 (99)	961 (103)	1099 (86)	1734 (94)	2074 (94)
Range	984–4673	1656–3901	872–3709	947–2604	859–2079	488–2049	453–2655	465–1765	530–1815	720–2567	881–3778	1085–7622
Propane												
Mean (SD)	1498 (612)	1332 (481)	1002 (371)	674 (231)	444 (204)	497 (340)	559 (308)	505 (314)	605 (331)	786 (471)	1217 (527)	1518 (795)
Median (<i>N</i>)	1309 (125)	1161 (101)	933 (98)	622 (86)	387 (102)	380 (92)	522 (91)	399 (99)	532 (103)	666 (86)	1164 (94)	1299 (94)
Range	439–3907	806–3128	358–2419	225–1682	125–1135	103–1488	137–1600	91–1647	134–1766	274–3229	446–2788	608–4549
i-Butane												
Mean (SD)	269 (109)	253 (109)	190 (116)	98 (46)	54 (26)	65 (39)	70 (39)	60 (36)	75 (59)	126 (67)	210 (99)	266 (144)
Median (<i>N</i>)	234 (125)	220 (99)	163 (96)	89 (86)	47 (102)	57 (92)	64 (92)	46 (99)	58 (103)	106 (86)	201 (94)	225 (94)
Range	66–679	140–694	59–655	17–224	13–125	12–172	15–224	6–161	9–276	34–289	64–434	90–866
n-Butane												
Mean (SD)	500 (208)	444 (169)	308 (138)	174 (86)	96 (48)	103 (73)	105 (59)	95 (61)	118 (81)	217 (125)	376 (191)	502 (349)
Median (<i>N</i>)	429 (125)	400 (101)	279 (98)	153 (86)	85 (102)	72 (92)	92 (92)	78 (99)	99 (103)	180 (85)	333 (93)	422 (93)
Range	111–1325	261–1230	108–708	29–423	19–227	16–349	26–350	10–271	21–478	54–577	105–833	171–2160
i-Pentane												
Mean (SD)	202 (112)	163 (74)	125 (93)	74 (47)	67 (46)	105 (77)	115 (60)	110 (75)	109 (80)	127 (90)	177 (104)	211 (140)
Median (<i>N</i>)	170 (125)	151 (100)	95 (98)	63 (86)	59 (102)	79 (92)	106 (92)	88 (99)	92 (103)	100 (86)	150 (94)	176 (93)
Range	55–710	67–427	33–517	13–216	11–265	15–341	30–301	17–377	13–399	23–412	46–467	59–767
n-Pentane												
Mean (SD)	129 (61)	101 (38)	72 (43)	40 (23)	34 (20)	45 (30)	52 (28)	51 (34)	52 (35)	66 (42)	104 (53)	135 (83)
Median (<i>N</i>)	114 (125)	91 (100)	60 (98)	33 (86)	31 (102)	38 (92)	49 (92)	44 (99)	45 (103)	57 (86)	88 (94)	114 (94)
Range	26–374	51–237	21–235	7–124	5–114	7–151	12–140	7–165	10–168	16–179	19–250	49–465
n-Hexane												
Mean (SD)	53 (32)	42 (22)	27 (20)	16 (11)	18 (11)	23 (17)	25 (15)	25 (16)	25 (18)	29 (21)	40 (23)	52 (32)
Median (<i>N</i>)	42 (125)	37 (100)	23 (93)	12 (82)	15 (89)	18 (86)	22 (88)	22 (91)	19 (90)	23 (81)	38 (94)	42 (92)
Range	14–180	17–130	3–116	3–59	2–51	5–90	5–82	4–75	3–83	3–84	6–95	10–144
Ethyne												
Mean (SD)	730 (260)	704 (177)	560 (157)	394 (94)	256 (68)	215 (121)	235 (108)	203 (98)	222 (107)	318 (129)	498 (198)	624 (230)
Median (<i>N</i>)	631 (125)	650 (101)	533 (98)	379 (86)	242 (102)	181 (92)	216 (92)	179 (99)	193 (103)	289 (85)	440 (93)	588 (93)
Range	222–1804	475–1329	251–1146	184–723	118–455	80–643	82–499	56–515	72–614	121–700	247–1331	318–1552
Ethene												
Mean (SD)	579 (387)	437 (259)	346 (291)	337 (335)	216 (185)	216 (169)	192 (104)	184 (136)	192 (118)	240 (154)	437 (284)	679 (412)
Median (<i>N</i>)	455 (125)	364 (101)	257 (98)	162 (86)	158 (102)	165 (92)	177 (91)	155 (99)	158 (103)	209 (86)	380 (93)	534 (93)
Range	168–2552	120–1245	32–1270	41–1181	38–854	31–788	70–717	36–938	41–552	57–758	87–1284	141–2110
Propene												
Mean (SD)	89 (72)	66 (48)	52 (37)	38 (20)	43 (22)	43 (20)	52 (30)	54 (44)	53 (34)	54 (33)	71 (48)	98 (74)
Median (<i>N</i>)	64 (125)	50 (101)	38 (98)	34 (86)	37 (102)	40 (92)	47 (91)	46 (99)	42 (103)	43 (86)	57 (93)	75 (93)
Range	21–427	9–244	11–198	13–95	12–115	10–94	17–214	11–295	13–180	16–164	15–212	21–380
1-Butene												
Mean (SD)	20 (16)	18 (12)	16 (10)	12 (7)	13 (10)	11 (6)	10 (6)	12 (12)	12 (8)	12 (9)	18 (12)	20 (15)
Median (<i>N</i>)	14 (120)	14 (95)	13 (94)	9 (79)	11 (97)	8 (88)	9 (90)	9 (92)	9 (91)	9 (82)	13 (89)	16 (92)
Range	4–26	3–79	4–56	4–38	3–63	3–27	5–47	2–81	3–43	3–43	3–55	4–90
Isoprene												
Mean (SD)	35 (54)	24 (51)	20 (33)	9 (9)	50 (125)	666 (674)	1278 (848)	1078 (657)	464 (420)	86 (116)	16 (15)	93 (150)
Median (<i>N</i>)	17 (40)	10 (34)	9 (23)	5 (31)	15 (84)	376 (92)	1007 (92)	946 (99)	336 (103)	40 (77)	11 (45)	25 (47)
Range	3–303	3–301	3–149	3–49	2–829	13–3131	176–3893	103–3714	26–2486	3–566	2–72	2–551
Benzene												
Mean (SD)	167 (50)	159 (42)	133 (42)	88 (24)	60 (18)	55 (35)	60 (26)	55 (26)	59 (28)	75 (28)	114 (39)	151 (56)
Median (<i>N</i>)	152 (125)	148 (101)	126 (99)	88 (86)	59 (102)	45 (92)	55 (92)	50 (99)	54 (103)	69 (85)	110 (94)	136 (94)
Range	61–364	108–372	72–297	42–182	25–111	18–207	21–123	9–136	15–139	27–147	46–229	57–373
Toluene												
Mean (SD)	136 (91)	126 (102)	125 (215)	67 (53)	73 (48)	109 (74)	106 (68)	91 (63)	102 (80)	99 (80)	122 (87)	131 (85)
Median (<i>N</i>)	104 (125)	96 (101)	61 (99)	49 (86)	56 (100)	92 (92)	87 (91)	74 (98)	78 (103)	77 (85)	101 (94)	111 (93)
Range	48–535	40–621	16–1979	9–235	13–203	16–291	31–379	14–340	6–375	16–352	22–442	33–416
Ethylbenzene												
Mean (SD)	18 (12)	16 (9)	15 (17)	10 (9)	9 (6)	13 (11)	14 (10)	11 (7)	10 (8)	12 (9)	15 (10)	17 (12)
Median (<i>N</i>)	14 (124)	13 (99)	8 (99)	7 (87)	8 (98)	10 (89)	11 (90)	9 (99)	8 (102)	10 (86)	11 (94)	14 (94)
Range	4–68	4–45	3–118	2–62	1–26	0.7–60	3–59	2–40	2–34	2–44	3–44	5–57
m+p-Xylene												
Mean (SD)	23 (19)	18 (13)	17 (20)	11 (10)	11 (8)	18 (24)	19 (22)	12 (12)	12 (10)	15 (13)	20 (15)	24 (18)
Median (<i>N</i>)	15 (124)	15 (99)	8 (99)	8 (87)	8 (98)	10 (89)	12 (90)	8 (99)	8 (102)	12 (86)	16 (94)	19 (93)
Range	4–126	3–64	2–113	1–47	2–47	0.6–150	3–125	2–85	2–47	2–73	2–62	5–107
o-Xylene												
Mean (SD)	13 (11)	10 (7)	9 (10)	7 (5)	6 (4)	11 (13)	12 (11)	9 (9)	8 (6)	9 (7)	11 (8)	13 (10)
Median (<i>N</i>)	9 (123)	9 (97)	5 (98)	5 (86)	5 (98)	7 (88)	9 (90)	6 (99)	6 (102)	7 (86)	9 (94)	11 (93)
Range	2–73	2–33	1–61	2–30	1–22	2–75	2–62	1–61	1–31	2–39	1–36	3–56

The mixing ratios of NMHCs observed at TF are lower than those reported for major US cities (Baker et al., 2008), including Pittsburgh, PA (Millet et al., 2005), Dallas, TX (Qin et al., 2007), and Houston, TX (Gilman et al., 2009). The winter mean and median mixing ratios of ethyne, C₂–C₄ alkanes, n-pentane, and n-hexane at TF were comparable to background (monthly 10th percentile) mixing ratios observed at Harvard Forest (HF) in Massachusetts during 1992–2001 (Goldstein et al., 1995; Lee et al., 2006). Similar behavior was observed during summer with the exception of propane whose mean and median mixing ratios were comparable at TF and HF. It must be kept in mind that the HF results include nighttime data. Winter and summer daytime mixing ratios of ethane, ethene, and ethyne at TF were similar to or higher than levels in the SE US (Hagerman et al., 1997) and at Whiteface Mountain, NY (WFM) (Gong and Demerjian, 1997) while aromatic hydrocarbon mixing ratios were generally lower at TF. This may reflect reduced emissions of aromatic compounds since the 1990's. Additionally, the mixing ratios of C₄–C₆ alkanes at TF in winter were generally lower than observed at various Canadian sites in the mid-1990's which likely reflects the influence of the Arctic air mass and/or the weaker photochemical removal of NMHCs at higher latitudes (Jobson et al., 1994; Bottenheim and Shephard, 1995; Young et al., 1997; Gautrois et al., 2003). In summer, the C₂–C₆ alkanes, ethene, and ethyne were similar to or higher than values reported in Canada the previous decade, including the downwind site at Chebogue Point, Nova Scotia (Jobson et al., 1998). With the exception of HF, summertime mixing ratios of propane, ethene, and ethyne at TF were consistently higher than or similar to values reported for rural sites throughout the continental US and Canada. In contrast to the 1993 NARE campaign, the median mixing ratios of C₃–C₈ NMHCs were factors of 2–3 (factor of 6 for toluene) lower at Chebogue Point, Nova Scotia during summer 2004 (Millet et al., 2006) illustrating the closer proximity to anthropogenic sources at TF.

3.2 Seasonal variation of anthropogenic C₂–C₈ NMHCs

The C₂–C₆ alkanes, ethyne, toluene, and benzene exhibited reproducible seasonal trends where the longer lived compounds had higher mixing ratios and reached minimum annual mixing ratios later in the year. Ethane mixing ratios peaked in winter-early spring and then decreased until mid to late summer when minimum mixing ratios were observed (Fig. 3a). Mixing ratios of the C₃–C₆ alkanes, alkenes, ethyne, and aromatics began to decrease in mid to late winter and reached minimum levels 2–4 months later (Fig. 3; Table 1). Ethene, ethyne, and benzene remained at their annual minimum mixing ratios from late spring to late summer (Fig. 3d). Despite its order of magnitude shorter lifetime, ethene mixing ratios were often similar to or higher than ethyne in summer, fall, and winter indicating the importance of ethene emissions in NH. The monthly mean and

median propane, i-butane, and n-butane mixing ratios were lowest in late spring (May–June) followed by an increase in early summer before reaching a second minimum in late summer (Table 1). In comparison, minimum mixing ratios of the shorter-lived C₅–C₆ alkanes, propene, and toluene occurred earliest (April–May), increased in early summer, and then remained within a similar range through October–November (Fig. 3c, f; Table 1). The mean summer mixing ratios of propene, toluene, and the C₅–C₆ alkanes were ~15–90% higher than the April–May mean mixing ratios. These NMHCs react rapidly with OH (summer lifetime <1.5 days assuming [OH]=2×10⁶ molecules cm⁻³), and thus would be expected to remain at minimum mixing ratios throughout the entire summer. The summer increase in mixing ratios is indicative of a strong influence from evaporative emissions on the NMHC distribution (discussed in more detail in Sect. 4).

On average, 1-butene, ethylbenzene, and xylenes (m+p and o) were also highest in winter, lowest in early to mid spring, and increased in early summer (Fig. 3e–g, Table 1). Superimposed on the general alkene and C₈ aromatic seasonal patterns were unique interannual trends reflecting varying sources or emission rates. For example, a higher and narrower range of propene (~50–80 pptv) and 1-butene (~8–17 pptv) monthly mean and median mixing ratios were observed in spring 2006 through winter 2008 compared to the previous two years when distinct winter peaks and spring-summer minimum mixing ratios occurred. Additionally, the highest monthly mean and median m+p-xylene and o-xylene mixing ratios of the entire four year study period (~25–40 and 25–35 pptv, respectively), as well as the highest summer toluene (90–140 pptv) and ethylbenzene (14–22 pptv) mixing ratios, were observed in summer 2007 and elevated mixing ratios persisted through winter 2008.

3.3 Influence of enhanced NMHC emissions on summer photochemistry

The enhanced summer mixing ratios of reactive NMHCs will likely influence the ambient mixing ratios and regional budgets of secondary photochemical species, such as organic aerosols, OVOCs, and O₃. NMHCs make variable contributions to the production of secondary species because of their different rates of reaction with OH. The incremental reactivity (IR) is a method for determining the various ozone formation potentials (OFP) of VOCs and takes into consideration the different chemical reaction pathways following the initial reaction of the NMHC with OH. The incremental reactivity is defined as the change in O₃ resulting from the addition or subtraction of an increment of VOC to/from an airmass divided by the amount of VOC added or removed (Carter, 1994; Bowman and Seinfeld, 1995). An estimate of the maximum possible amount of O₃ that could be formed resulting from the higher propene, C₅–C₆ alkane, and toluene in summer was made using the following equation: $\Delta O_3 = \Delta NMHC \times MIR$ where $\Delta NMHC$ = maximum

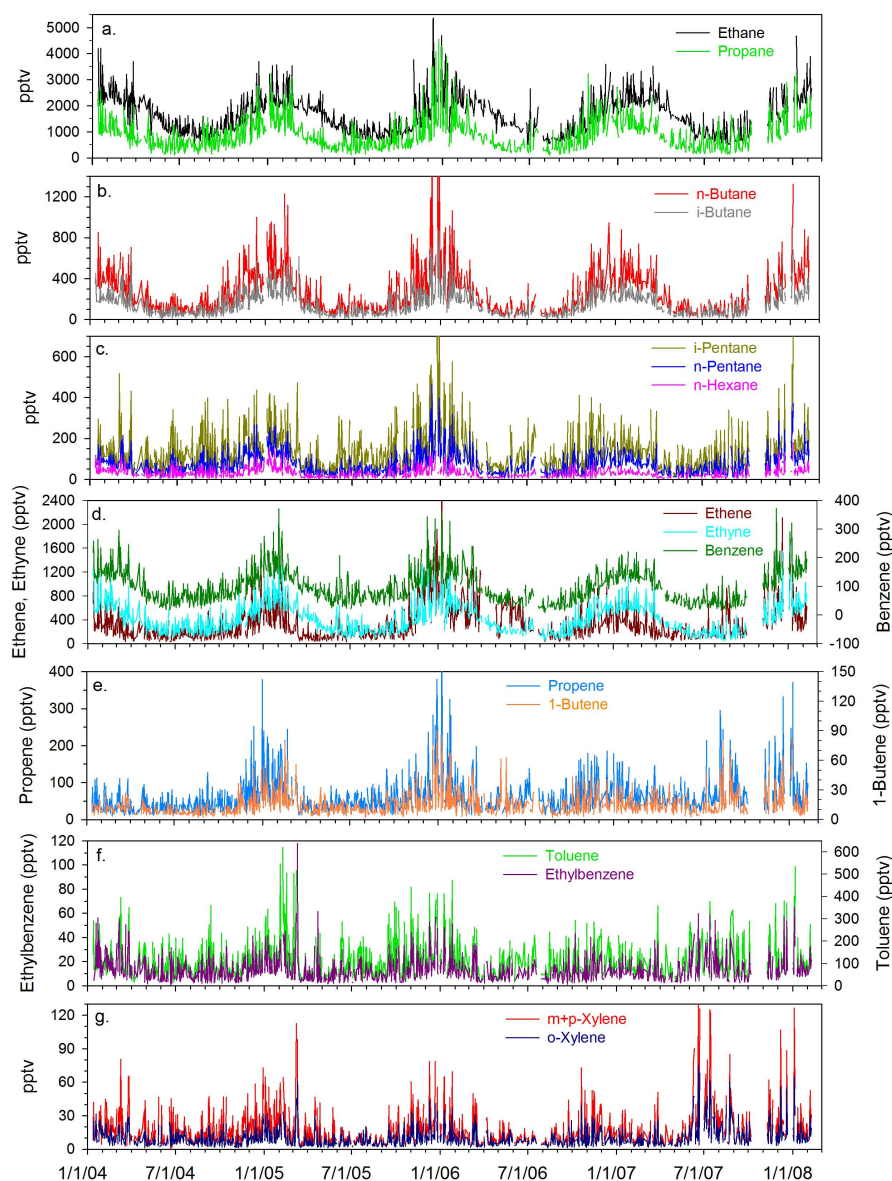


Fig. 3. Time series of NMHCs (pptv) at TF during January 2004–February 2008: (a) ethane, propane, (b) n-butane, i-butane, (c) i-pentane, n-pentane, n-hexane, (d) ethene, ethyne, benzene (note that the benzene axis is offset), (e) propene, 1-butene, (f) toluene, ethylbenzene, and (g) m+p-xylene, o-xylene.

summer mixing ratio – average spring mixing ratio and MIR is the maximum incremental reactivity factor (gram of O_3 produced/additional gram of NMHC) (Carter, 1994, 2008). For these calculations, we are assuming that conditions are favorable for O_3 production. The atmosphere over New England in summer is generally NO_x -limited because of the abundance of biogenic VOCs. Nonetheless, summer NO_x mixing ratios at TF have been observed to range from 0.21–17.5 ppbv (average 2.3 ppbv) (Griffin et al., 2007). These NO_x mixing ratios are sufficient for the NO +peroxy radical reaction to be preferred over peroxy radical self reactions (e.g., Flocke et al., 1991; Roberts et al., 1998). These calculations indicate that 0.5–2.4 ppbv, 0.46–0.65 ppbv, 0.15–

0.24 ppbv, 0.08–0.1 ppbv, and 1.2–2.3 ppbv (total range 2.4–5.7 ppbv) of additional O_3 could be formed as a result of the enhanced propene, i-pentane, n-pentane, n-hexane, and toluene mixing ratios, respectively, in summer at TF. In comparison, the 24 h mean O_3 mixing ratios at TF are ~ 30 ppbv in summer (Mao and Talbot, 2004a; Talbot et al., 2005). These results are not absolute levels of O_3 that will be produced because the MIR factors were derived for conditions that do not necessarily reflect New England (Carter, 1994). Nonetheless, these results are intended to illustrate the potentially significant impact of the enhanced summer mixing ratios of reactive NMHCs on the ozone formation potential in this region.

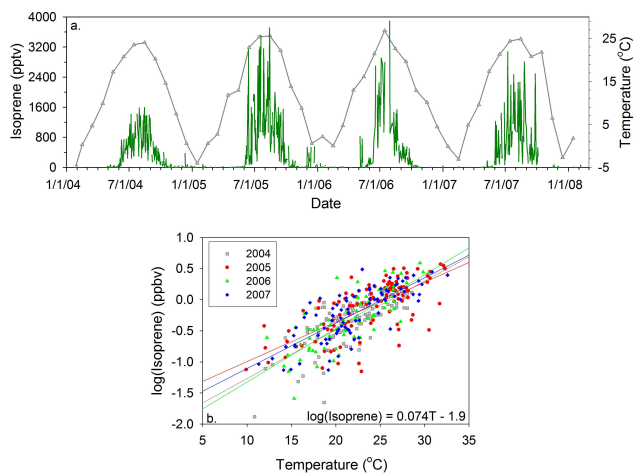


Fig. 4. (a) Time series of isoprene (pptv) (green line) and the monthly mean temperature (°C) (gray line) at TF during January 2004–February 2008. (b) Correlation between log(isoprene) (in ppbv) and the hourly average temperature (corresponding to the hour the canister sample was collected) during June–September of 2004, 2005, 2006, and 2007.

3.4 Isoprene

Isoprene is the only NMHC discussed in this work with a predominantly biogenic origin (deciduous plants and trees) (e.g., Guenther et al., 1995). Isoprene mixing ratios rapidly increased in the beginning of June, remained high through August, and gradually decreased in September–October of each year (Fig. 4a, Table 1). In July–August 2005, 2006, and 2007, isoprene was the most abundant NMHC (monthly mean mixing ratios=1000–2100 pptv) illustrating the importance of biogenic emissions in this region. In comparison, mean ethane (the longest lived NMHC) mixing ratios were ~800–1250 pptv. Isoprene was positively correlated with the ambient temperature during each summer. The relationship can be expressed as $\log(\text{isoprene})=0.074T-1.9$ ($r^2=0.57$) for all of the available June–September data (Fig. 4b) (T in °C corresponding to the hour the sample was collected). The highest isoprene mixing ratios (>3 ppbv) were observed in the warmest summers (2005 and 2006) while the lowest (<1600 pptv) mixing ratios occurred during the coolest summer (2004). The temperature dependence of isoprene was nearly the same each summer, on sunny/clear days, and on cloudy/rainy days. Furthermore, this relationship is consistent with previous studies (e.g., Fehsenfeld et al., 1992; Jobson et al., 1994; Goldan et al., 1995; Gong and Demerjian, 1997; Hagerman et al., 1997; Kang et al., 2001) indicating a similar temperature dependence of ambient isoprene mixing ratios at various North American sites.

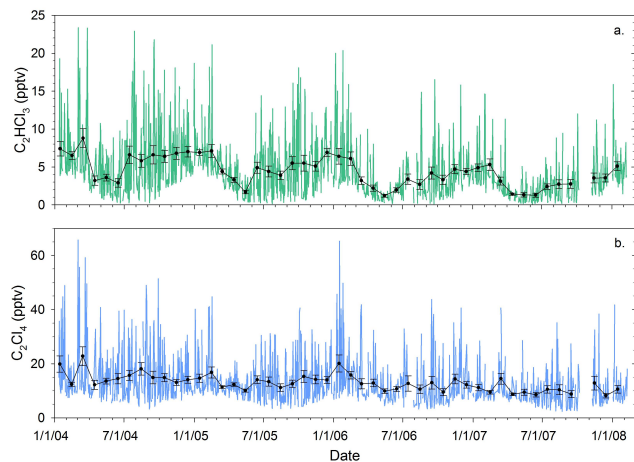


Fig. 5. Time series of (a) C₂HCl₃ and (b) C₂Cl₄ (pptv) at TF during January 2004–February 2008. Black line and circles are the monthly mean ± standard error mixing ratios.

3.5 Halocarbons

Trichloroethene and tetrachloroethene are primarily used as dry cleaning and degreasing solvents and are thus tracers of industrial sources (e.g., Wang et al., 1995; McCulloch and Midgley, 1996). It is necessary to monitor the atmospheric trends of C₂HCl₃ and C₂Cl₄ because they are used as replacements for CFCs and in the production of HFCs and HCFCs and because they are classified as toxic air pollutants and are regulated by the EPA (US EPA, 2007). A wide range of C₂Cl₄ (3–65 pptv) and C₂HCl₃ (<1–23 pptv) mixing ratios were observed at TF (Fig. 5). The shorter-lived (days-weeks) C₂HCl₃ had a similar seasonal variation as the NMHCs with a winter maximum (monthly mean mixing ratios=5–8 pptv), late spring minimum (1–2 pptv), and an early summer increase (2–5 pptv). Similar to propene, the C₅–C₆ alkanes, and toluene, the mean mixing ratios in summer were 50–75% higher than in spring illustrating that evaporative emissions of C₂HCl₃ are important to its atmospheric distribution in this region. In contrast, the monthly mean mixing ratios of the longer-lived (months) C₂Cl₄ were fairly uniform. A seasonal variation was apparent in the C₂Cl₄ background (monthly 10th percentile) mixing ratios which were highest in winter (8–9 pptv) and lowest in late summer (3–5 pptv).

The monthly mean halocarbon mixing ratios at TF are higher than observed at remote sites, such as Mace Head, Ireland (Simmonds et al., 2006), along the US west coast (Simpson et al., 2004), NOAA CMDL sites (Thompson et al., 2004), Chebogue Point, Nova Scotia (Millet et al., 2006), and over the North Atlantic Ocean (Dimmer et al., 2001), reflecting the closer proximity to industrial sources and their continued use in North America, but are lower than observed in heavily urbanized areas, such as Pittsburgh, PA (Millet et

al., 2005), Houston, TX (Gilman et al., 2009), and Mexico City, Mexico (Velasco et al., 2007). The C₂Cl₄ mixing ratios at TF are similar to background levels in Massachusetts during 1996–1999 (Kleiman and Prinn, 2000; Barnes et al., 2003) which suggests that C₂Cl₄ emission rates in more populated areas in the US did not change considerably between the late 1990's and 2004. However, we have observed a decrease in the magnitude of peak mixing ratios, and in the annual mean, median, and background mixing ratios throughout 2004–2008 at TF (Fig. 5, Table 2). More specifically, the background mixing ratios of C₂Cl₄ and C₂HCl₃ were 30% and 65% lower, respectively, in 2007 than in 2004. According to the EPA 2008 Toxics Release Inventory (www.epa.gov/tri), C₂HCl₃ emission reductions were about a factor of two larger than C₂Cl₄ over the same time period.

An estimate of the rate of decrease in atmospheric mixing ratios of both halocarbons was made using the annual statistics in order to minimize the influence of the seasonal variation in C₂HCl₃ and in background C₂Cl₄. The linear regression through the annual background mixing ratios gave decrease rates (\pm standard deviation) of 0.73 ± 0.24 and 0.27 ± 0.05 pptv/year for C₂Cl₄ and C₂HCl₃, respectively (Table 2). In comparison, C₂Cl₄ decrease rates (pptv/year) were estimated to be 1.0 (C₂HCl₃=0.1) in 1991–1996 at Alert, Canada (Gautrois et al., 2003), 0.6–1.2 during 1994–1997 in the continental US (Hurst et al., 1998), 0.1–0.4 throughout 1989–2002 along the North American west coast (Simpson et al., 2004), 0.18 (C₂HCl₃=0.01) during July 2000–December 2004 at Mace Head, Ireland (Simmonds et al., 2006), and 5% per year in 1995–2003 based on analysis of EPA and NOAA CMDL data at remote North American sites (McCarthy et al., 2006). It must be kept in mind that the trends observed at TF and other locations represent different time periods, emission rates, and industrial regulations. Nonetheless, our results indicate that the amounts of C₂Cl₄ and C₂HCl₃ being transported from the northeastern US to the North Atlantic are decreasing.

4 NMHC source identification

4.1 Comparison with tracers and source signatures

The major sources of ethyne, benzene, carbon monoxide (CO), and alkenes are incomplete combustion of fossil fuels, biomass burning, and vehicle exhaust emissions (e.g., Harley et al., 1992, 2001; McLaren et al., 1996; Choi and Ehrman, 2004). The oxidation of VOCs is also a potential secondary source of CO, particularly in summer when biogenic NMHC mixing ratios are high (Sect. 3.4) (Hudman et al., 2008). Studies focused on the northeast US during summer 2004 found that observed CO mixing ratios could largely be explained by primary urban/industrial and biomass burning sources (Warneke et al., 2006; Griffin et al., 2007). Thus, in our analysis, we neglect the possible secondary

Table 2. Annual C₂HCl₃ and C₂Cl₄ statistics (pptv) for 2004–2008, and the rate of decrease (pptv/year) in the annual background mixing ratios \pm standard deviation (SD). *N* is the number of samples. Background is the 10th percentile for the entire year.

	C ₂ HCl ₃	C ₂ Cl ₄
2004		
Mean (SD)	6.0 (4.7)	15.8 (10.5)
Median (<i>N</i>)	4.6 (277)	12.3 (277)
Background	1.3	6.7
Range	0.25–23.4	3.3–65.7
2005		
Mean (SD)	5.0 (3.7)	13.3 (7.6)
Median (<i>N</i>)	4.5 (323)	11.0 (324)
Background	0.9	6.2
Range	0.16–21.1	3.4–44.7
2006		
Mean (SD)	4.0 (3.6)	13.1 (9.2)
Median (<i>N</i>)	2.9 (264)	9.6 (270)
Background	0.7	5.7
Range	0.14–20.3	3.3–65.3
2007		
Mean (SD)	3.0 (2.6)	10.5 (6.5)
Median (<i>N</i>)	2.5 (240)	8.6 (244)
Background	0.5	4.5
Range	0.12–14.6	2.4–40.6
pptv/year (SD)	-0.27 ± 0.05	-0.73 ± 0.24
<i>r</i> ²	0.99	0.95

contribution to CO. Ethyne and CO were fairly well correlated at TF ($r^2=0.5-0.9$) demonstrating a year-round impact from combustion emissions (Fig. 6a). The correlations between alkenes and tracers for combustion (ethyne), liquefied petroleum gas (LPG) (propane), and fuel evaporation (*i*-pentane) were strongest in winter and showed considerable scatter in the other seasons. The short-lived alkenes had presumably undergone mixing and oxidative removal during transport resulting in weaker correlations in spring, summer, and fall. Based on the winter measurements, the ethene and propene correlation slopes with ethyne (1.2 and 0.21, respectively) were similar to light duty gasoline and vehicle exhaust emission ratios (0.9–1.7 and 0.1–0.5, respectively) (Conner et al., 1995; Watson et al., 2001; Choi and Ehrman, 2004; McGaughey et al., 2004) suggesting that vehicular emissions were the dominant source of these alkenes. Propene and 1-butene were well correlated throughout the majority of the study period reflecting a common source (Fig. 6b). The correlation coefficients between ethyne and the alkanes, benzene, and toluene were fairly variable within each season and year ($r^2=0.4-0.9$), but overall suggest that combustion sources were collocated with or were the same as the alkane and aromatic sources.

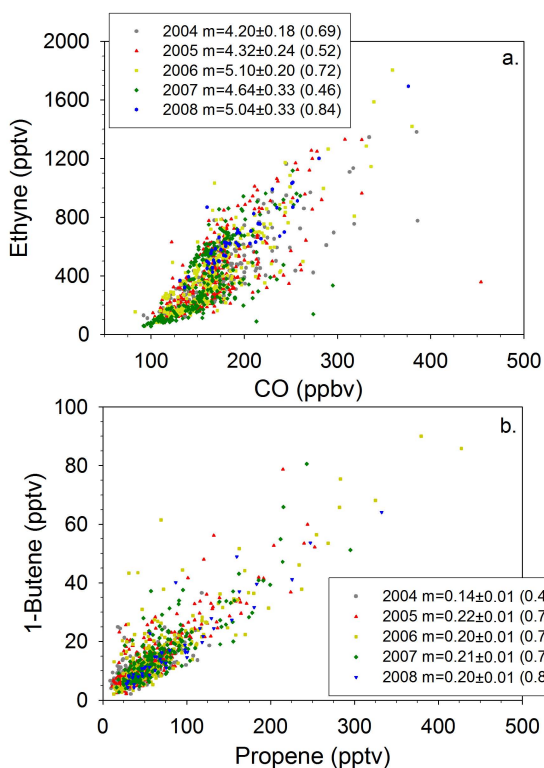


Fig. 6. Correlations (m =slope \pm standard error (r^2)) between (a) CO (ppbv) and ethyne and (b) propene and 1-butene for each year (2004, 2005, 2006, 2007, 2008).

The C₃–C₆ alkanes were well correlated with each other (r^2 =0.6–0.9). The slopes of the correlation between propane and n-butane (2.2–2.7, Fig. 7a) and i-butane (3.8–5.5, not shown) agree with LPG emission ratios (2–4 and 3–7, respectively) (e.g., Scheff and Wadden, 1993; Blake and Rowland, 1995; Goldan et al., 1995; Chen et al., 2001; Fujita, 2001; Watson et al., 2001; Mukerjee et al., 2004; Barletta et al., 2008) indicating that LPG emissions are widespread and prevalent in New England. Moreover, the i-butane/n-butane slope (0.49–0.56, Fig. 7b) was within the range of reported emission ratios from several sources, including urban/vehicular exhaust (\sim 0.2–0.3), LPG (0.46), and natural gas (\sim 0.6 to >1) (B. Sive, unpublished data; Jobson et al., 1998, 2004; Goldan et al., 2000; Fujita, 2001; Watson et al., 2001; Barletta et al., 2002; Choi and Ehrman, 2004; Velasco et al., 2007). Additionally, the slope of the correlation between i-pentane and n-pentane (range for each season each year=1.5–2.6) (Fig. 7c) was within the range of reported emission ratios for vehicle exhaust and tunnel studies (\sim 2.2–3.8), liquid gasoline (1.5–3), and fuel evaporation (1.8–4.6) (Conner et al., 1995; Harley et al., 2001; Watson et al., 2001; Jobson et al., 2004; McCaughey et al., 2004; Lough et al., 2005; Velasco et al., 2007). Overall, these results suggest that a uniform mix of emissions from numerous alkane sources is observed at TF.

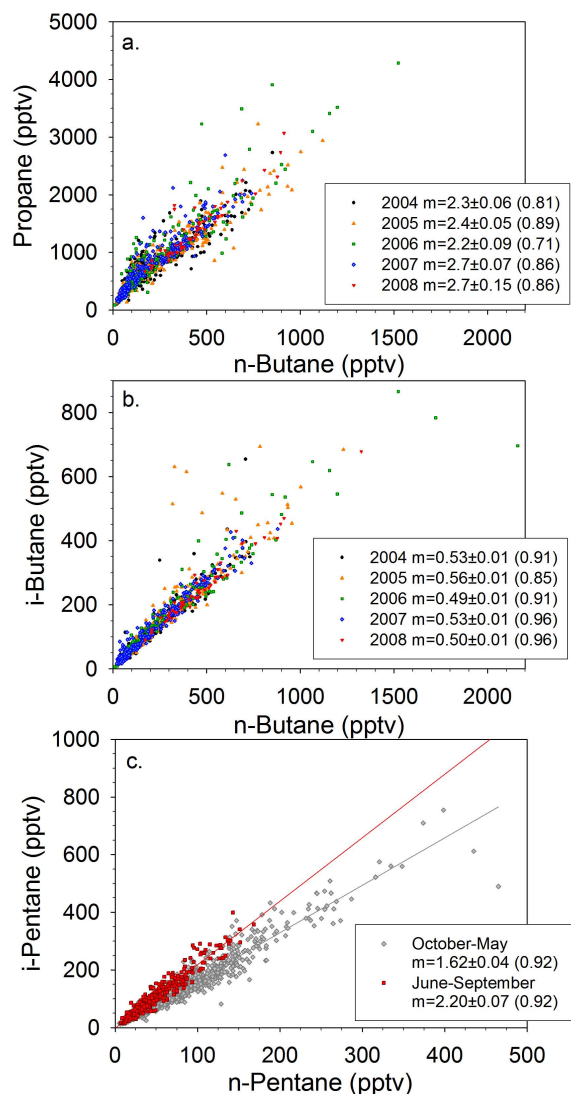


Fig. 7. Correlation (m =slope \pm standard error (r^2)) of n-butane with (a) propane and (b) i-butane for each year. (c) Correlation between n-pentane and i-pentane. Gray diamonds are all of the samples collected in October–May of 2004–2008. Red squares are all of the samples collected in June–September of 2004–2007.

The i-pentane/n-pentane correlation slope was noticeably higher in the warmer months each year (June–September slope=2.2; October–May slope=1.6, Fig. 7c) which likely reflects enhanced evaporative emissions of i-pentane (e.g., Rubin et al., 2006). Additionally, the correlation slopes between the C₅–C₆ alkanes and butanes were factors of \sim 0.5–2 higher in summer. Gasoline retailers in New England are required to sell reformulated gasoline with a lower Reid vapor pressure (RVP) in order to reduce emissions of highly volatile NMHCs in the summer (US EPA, 2003, 2008). Our measurements demonstrate that fuel evaporation and headspace vapor emissions of the C₅–C₆ alkanes were still strong enough to partially counteract OH chemistry throughout the entire

summer each year. These relationships will continue to be monitored in order to identify and evaluate any potential impacts of the switch to using gasoline containing 10% ethanol (E10) in 2007 (www.des.nh.gov) on the ambient distributions of NMHCs in New England.

The C₇–C₈ aromatics were well correlated illustrating their common sources. The toluene/ethylbenzene correlation slope was in good agreement with vehicular and urban emission ratios (Fig. 8a) (e.g., Parrish et al., 1998; Monod et al., 2001). The o-xylene/m+p-xylene correlation slope (0.44–0.55, Fig. 8b) was slightly higher, and the m+p-xylene/ethylbenzene (1.1–1.9, Fig. 8c) and o-xylene/ethylbenzene (0.53–1.1, not shown) slopes were lower than industrial/urban, gasoline, fuel evaporation, and vehicle exhaust emission ratios (~0.36–0.4, 2.2–4.6, and 1.2–1.8, respectively) (Conner et al., 1995; Kirchstetter et al., 1996; Sagebiel et al., 1996; Rogak et al., 1998; Monod et al., 2001; Watson et al., 2001; Choi and Ehrman, 2004; Jobson et al., 2004; Velasco et al., 2007). The differences between the emission and ambient C₈ aromatic ratios likely reflect the preferential loss of the xylenes during air mass transport because of their greater reactivity.

4.2 Ambient ratios: compounds with similar lifetimes

Information on the relative impact of various sources in a region can be obtained by comparing the ambient ratio of two compounds that have similar rates of reaction with OH but different sources (e.g., Klemp et al., 1997; Jobson et al., 1999; Goldan et al., 2000). The ratio should reflect the integration of several factors, such as air mass mixing and dilution, new emission inputs, and oxidative removal, because neither compound will be removed preferentially during transport. Thus, on average, the ratio can be assumed to remain fairly constant and approximately equal to the emission ratio (Parrish et al., 1998). For example, propane, ethyne, and benzene have similar lifetimes (<30% difference in k_{OH}) (Atkinson et al., 2006), but these NMHCs are tracers of different sources. The propane/ethyne, propane/benzene, and benzene/ethyne vehicular exhaust and whole gasoline emission ratios are typically <1 while ratios from natural gas, LPG, or gasoline vapor are ≥ 1 (e.g., Conner et al., 1995; Fujita et al., 1995; Fujita, 2001; Mukund et al., 1996; Lawrimore et al., 1997; Watson et al., 2001; Choi and Ehrman, 2004; Mukerjee et al., 2004; White et al., 2008). Throughout 2004–2008, the propane/ethyne (Fig. 9a) and propane/benzene ratios ranged from 1–5 and 3–25, respectively, demonstrating the stronger influence of natural gas or LPG relative to incomplete combustion as a source of propane throughout the entire year. This corroborates previous work at TF and Appledore Island, Maine (10 km off the NH coast) during summer 2004 which concluded that LPG was the dominant source of propane throughout the entire day in southern NH (White et al., 2008). Furthermore, Goldan et al. (2004) illustrated that the relationship between

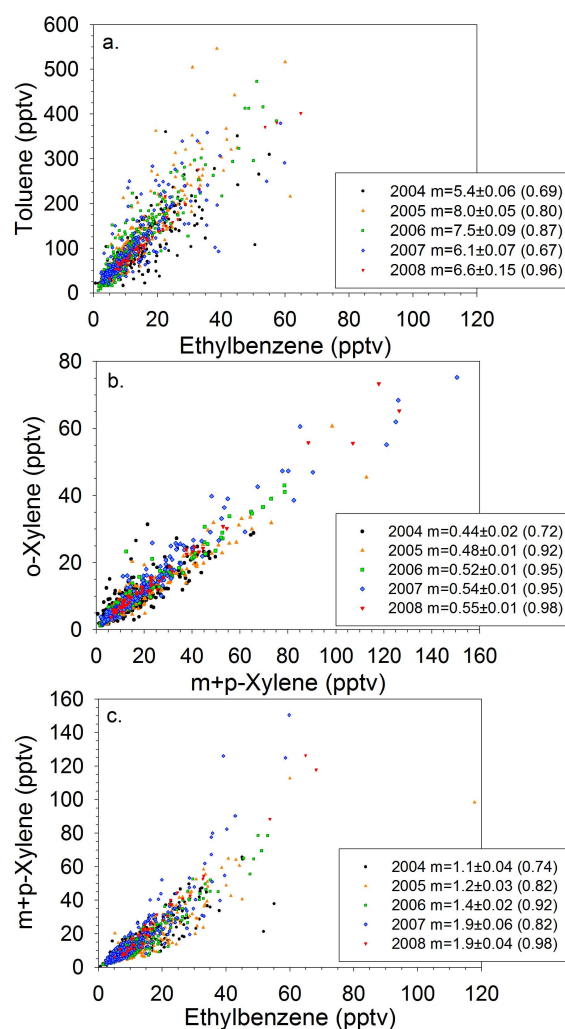


Fig. 8. Correlations (m =slope \pm standard error (r^2)) between (a) toluene and ethylbenzene, (b) o-xylene and m+p-xylene, and (c) m+p-xylene and ethylbenzene for each year.

propane and benzene was unique to the northeast US based on measurements made off the New England coast during the NEAQS 2002 campaign and suggested that this is indicative of a non-vehicular source of propane. This supports our observations of a significant influence from LPG use and/or leakage at TF.

The slope of the benzene vs. ethyne correlation was the same in each season of every year (slope of all data=0.21, r^2 =0.91) (Fig. 9b). This ratio value is indicative of a vehicular source and is consistent with observations of ambient benzene/ethyne ratios measured during several spring-summer field campaigns conducted throughout the US (Fortin et al., 2005; Harley et al., 2006; Parrish, 2006; Sistla and Aleksic, 2007; Warneke et al., 2007) and in major cities (Parrish et al., 2009). The strong correlations between propane and ethyne (Fig. 9a), propane and benzene (r^2 =0.71–0.76, not shown), and benzene and ethyne (Fig. 9b) suggest that emissions from

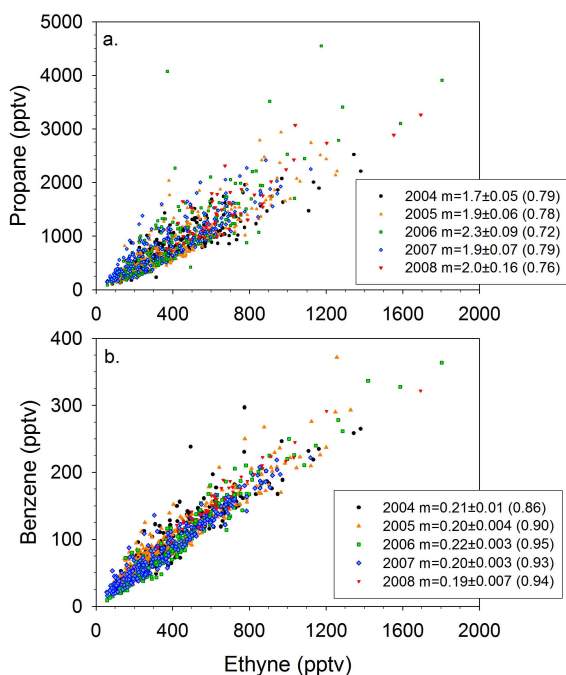


Fig. 9. Correlation (m =slope \pm standard error (r^2)) of ethyne with (a) propane and (b) benzene for each year.

natural gas, petroleum, and fossil fuel/incomplete combustion (e.g., vehicles) sources were concurrent and/or collocated. Moreover, this illustrates a pervasive and continuous influence of emissions from several anthropogenic sources on the chemical composition of air masses observed at TF.

4.3 Ambient ratios: compounds with different lifetimes

Ambient ratios between compounds with different rates of reaction with OH and with well characterized sources and sinks are frequently used to estimate the relative photochemical age of air masses, transport times and distances, or OH concentrations (e.g., Jobson et al., 1994; McKeen et al., 1996; Parrish et al., 1998; Smyth et al., 1999; Dimmer et al., 2001; Kleinman et al., 2003; Russo et al., 2003). A fundamental drawback to estimating air mass processing times using ambient ratios is a lack of information on seasonal variations in sources, especially when analyzing data from short-term field campaigns. Analysis of the long-term measurements from TF provided a unique perspective on the interrelationships between seasonal variations in sources and chemical processing in this region.

Four common ratios with the shorter-lived compound in the numerator are ethyne/CO, propane/ethane, toluene/benzene, and C_2HCl_3/C_2Cl_4 (Fig. 10). The general behavior of these ratios can be predicted based on the differential removal of the compounds in each ratio. For example, if reaction with OH was the only factor influencing the seasonality in mixing ratios, a decrease in ratio values from

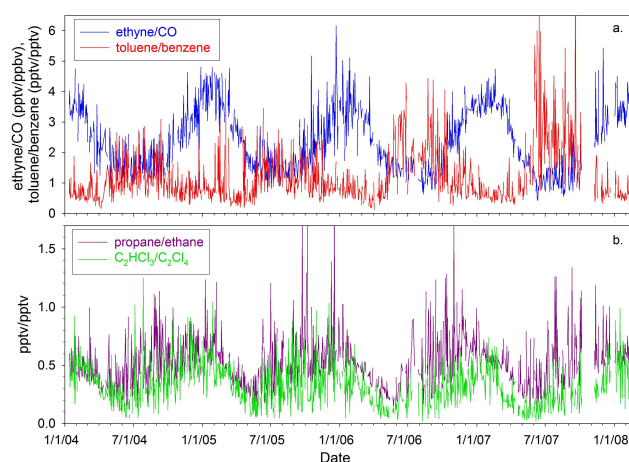


Fig. 10. Time series of the (a) ethyne/CO (pptv/ppbv) and toluene/benzene ratios and (b) propane/ethane and C_2HCl_3/C_2Cl_4 ratios during January 2004–February 2008.

winter to summer would be expected to occur concurrently with the increase in atmospheric OH concentrations because the shorter-lived compound is removed preferentially. The ethyne/CO ratio trend reflects the seasonal variation in OH concentrations with higher winter ratios (4–5 pptv/ppbv) indicating less processed emissions and low summer ratios (1–2 pptv/ppbv) reflecting more processed air masses (Fig. 10a). The propane/ethane and C_2HCl_3/C_2Cl_4 ratios tracked each other very well, and the temporal variation of both ratios resembled the ethyne/CO ratio with maximum values in winter and minimum values in late spring-summer (Fig. 10b). However, the propane/ethane and C_2HCl_3/C_2Cl_4 ratios increased throughout summer and fall which likely reflects the similar lifetimes and seasonal variation of propane and C_2HCl_3 combined with the mid to late summer minimum ethane and C_2Cl_4 mixing ratios.

The seasonal variation of the toluene/benzene ratio was opposite of the ethyne/CO, propane/ethane, and C_2HCl_3/C_2Cl_4 ratio behavior, and thus contrary to the expected photochemical trend (Fig. 10a). The toluene/benzene ratio was lowest in winter-spring (~ 0.5 – 1.5) and highest in summer-fall (0.5–7). These ratio values are comparable to ambient ratios (1–5) observed in numerous continental/urban areas (e.g., Parrish et al., 1998; Monod et al., 2001). However, the fact that the ratio increases in the summer is indicative of an additional source or enhanced emissions of toluene in this region. White et al. (2009) illustrated that the anomalous toluene behavior at TF could not be fully explained by fuel evaporation and industrial emissions and provided evidence for a biogenic contribution to the summer toluene enhancements. It was also noted that the toluene enhancements were larger with each successive year (White et al., 2009). This trend continued into 2007 when the highest toluene/benzene ratios (mean=2.1) were observed (Fig. 10a).

This analysis provides a clear illustration for the necessity of characterizing VOC sources in individual regions. As recently discussed by Schnitzhofer et al. (2008), these results have important implications because numerous studies have used the toluene/benzene ratio to estimate photochemical air mass ages (e.g., Roberts et al., 1984; Gong and Demerjian, 1997; Kang et al., 2001; de Gouw et al., 2005; Warneke et al., 2007) or to distinguish between industrial, evaporative, and exhaust emission sources (e.g., Barletta et al., 2008). The TF measurements demonstrate that the toluene/benzene ratio may not be appropriate for estimating relative air mass ages in this region because variations in the ratio values reflect both chemical processing and additional toluene emissions. An additional source of toluene in this region causes the initial toluene/benzene emission ratio used in the processing time calculations to be erroneously high leading to overestimated photochemical air mass ages and transport distances.

5 Emission rates of NMHCs

5.1 Emission rates estimated from observations at TF

Emission rates of speciated VOCs based on ambient measurements are needed for developing regional budgets, implementing effective control strategies for reducing emissions of photochemical smog precursors and toxic compounds, and evaluating emission inventories and air quality models. Estimates of emission rates are limited and are primarily reported on global scales (e.g., Boissard et al., 1996; Gupta et al., 1998) or in urban areas during specific campaigns (e.g., Blake and Rowland, 1995; Chen et al., 2001; Velasco et al., 2005). Additionally, emissions for individual VOCs are usually lumped into specific classes (i.e., alkane, alkene, aromatic, biogenic). Major reasons for the lack of information on regional VOC emission rates include the complications involved with differentiating between local, regional, and distant sources and the scarcity of long-term continuous measurements. In order to minimize the complications associated with air mass transport, we focus on (1) winter measurements because the C₂–C₈ NMHC lifetimes are longer than regional transport and mixing timescales at this time of year and (2) nighttime data when it has been determined that mixing is minimal. Under these conditions, we can assume that a change in NMHC mixing ratios reflects local sources or sinks. In contrast, the daily canister samples are representative of daytime conditions when mixing and transport may be occurring and can be assumed to reflect sources from a larger area. Thus, emission rates of NMHCs were calculated in two steps.

First, we estimated emission rates of NMHCs using hourly measurements from the automated in situ GC system at TF during December 2005–January 2006. We followed a simple box model approach which has been effectively used in previous studies to calculate emission and removal rates of trace

gases in this region (i.e., Talbot et al., 2005; Zhou et al., 2005; Sive et al., 2007; White et al., 2008; Russo et al., 2010). This method uses measurements made on nights with low wind speeds and when a stable inversion layer has developed because under these conditions, the exchange of air between the nocturnal boundary layer (NBL) and the residual layer above is limited (e.g., Hastie et al., 1993; Gusten et al., 1998; Talbot et al., 2005). Therefore, advection and vertical mixing of air masses can be neglected. Two criteria were used for identifying nights when a stable inversion layer developed: (1) wind speeds <1 m/s and (2) O₃ ≤ 5 ppbv. The two criteria conditions were met on several nights between approximately midnight and 05:00 with concurrent increases in NMHC mixing ratios. Emission rates (ER_{GC}) were calculated by multiplying the slope of the linear regression between the change in hourly average concentrations (dC in molecules cm⁻³) per unit time ($dt=5$ h) by the boundary layer height:

$$ER_{GC} = \left[\frac{dC}{dt} \right] \cdot H \quad (1)$$

Stable nocturnal boundary layer heights typically range from ~50–200 m at midlatitude continental locations (e.g., Hastie et al., 1993; Gusten et al., 1998; McKendry and Lundgren, 2000; White et al., 2003); thus we chose 125 m as a representative value for the TF site (e.g., Talbot et al., 2005; Sive et al., 2007; Mao et al., 2008; White et al., 2008; Zhou et al., 2005). If we use $H=50$ m or 200 m, our emission rate estimates discussed below vary by ±60%. It must be kept in mind that the resulting emission rate estimates are directly proportional to the boundary layer height which varies with meteorological conditions, time of day, and season (Talbot et al., 2005).

In the second step, emission rates (ER_{DC}) were calculated by multiplying the emission ratio for each compound from the daily canister samples by the emission rate of a reference compound (Eq. 2):

$$ER_{DC} = \left(\frac{NMHC}{Ethyne} \right) \cdot ER_{GC_Ethyne} \quad (2)$$

Ethyne was used as the reference compound because of its relatively long lifetime and because its major source (combustion) is well known (e.g., Conner et al., 1995; Goldstein et al., 1995; de Gouw et al., 2005; Lee et al., 2006). Emission ratios using the winter 2006 daily canister data were determined from the slope of the correlation between a specific NMHC and ethyne (NMHC/ethyne). A comparison between the winter 2006 data from the automated in situ GC and the canister samples demonstrated that the mixing ratios agreed well (±10%, $r^2=0.82$ – 0.94 ; orthogonal distance regression) and that the results from the two instruments can be meaningfully compared (Fig. 11). The correlations are based on comparing the TF GC sample corresponding most closely to the time the canister was collected. These times agreed within less than one hour. The canister and GC data tracked each other illustrating that the daily canister samples

captured a wide range of air mass types and compositions including background air masses and significant winter pollution events with enhanced NMHC mixing ratios.

The percent difference between the emission rates calculated from the TF GC nighttime data (Eq. 1) and the daily canister emission ratios (Eq. 2) ranged between ± 5 –80% (Table 3). The emission rate of propane (~ 2 to 4×10^{10} molecules $\text{cm}^{-2} \text{s}^{-1}$) was 1–2 orders of magnitude larger than the other NMHCs (range 0.2 – 7×10^9 molecules $\text{cm}^{-2} \text{s}^{-1}$) (Table 3). The high propane emission rate is another indication of the persistent impact of leakage from LPG tanks or refilling stations throughout the region (Sect. 4.2). Additionally, assuming the TF results are representative of the state and region, the NMHC emission rates extrapolated to the state of New Hampshire and New England are ~ 2 –61 Mg/day and ~ 12 –430 Mg/day, respectively (Table 3). The emission rates of propane, i-butane, and n-butane from New Hampshire were 20–90% lower than observed from LPG leakage in Mexico City, Mexico (Elliott et al., 1997) and in Santiago, Chile (Chen et al., 2001). However, taking into consideration the larger land area for New Hampshire and New England, our results suggest that potential emissions of C_3 – C_4 alkanes from the northeast US are comparable to emission rates that have been observed in densely populated urban areas (see also White et al., 2008). Furthermore, these high levels of precursor compounds in air masses transported to and across the North Atlantic may contribute to O_3 and aerosol production, thus influencing the air quality of downwind regions.

Emission rates determined using the daily canister emission ratios from winters 2004, 2005, 2007, or 2008 were within ~ 10 –50% of the winter 2006 values. In addition, the winter 2006 emission rates of propane, i-butane, n-butane, i-pentane, and propene agreed (within factors of ~ 0.7 –6) with estimates made using nighttime measurements from the automated TF GC during summers 2003 and 2004 (White et al., 2008). The consistency between the estimates for different winters and for winter and summer suggests that emission rates do not appear to be varying detectably with season or year. We consider the fact that the winter 2006 TF GC and daily canister emission rates and the summer 2003 and 2004 emission rates from White et al. (2008) agree within an order of magnitude (with the exception of m+p-xylene) to be good agreement. Furthermore, despite the different areas (i.e., source footprints) potentially represented by the TF GC and daily canister emission rates, both approaches yield similar results. Possible explanations for this similarity include: (1) the two estimates are not completely independent because the daily canister emissions are calculated using the TF GC ethyne emission rate; (2) local NMHC emission rates are similar to rates throughout New England; (3) the mid-day daily canister emission rates retain a signature from local nighttime emissions following the breakup of the NBL and subsequent mixing with remnant air from the previous day's mixed layer in the morning. Overall, this analysis provides

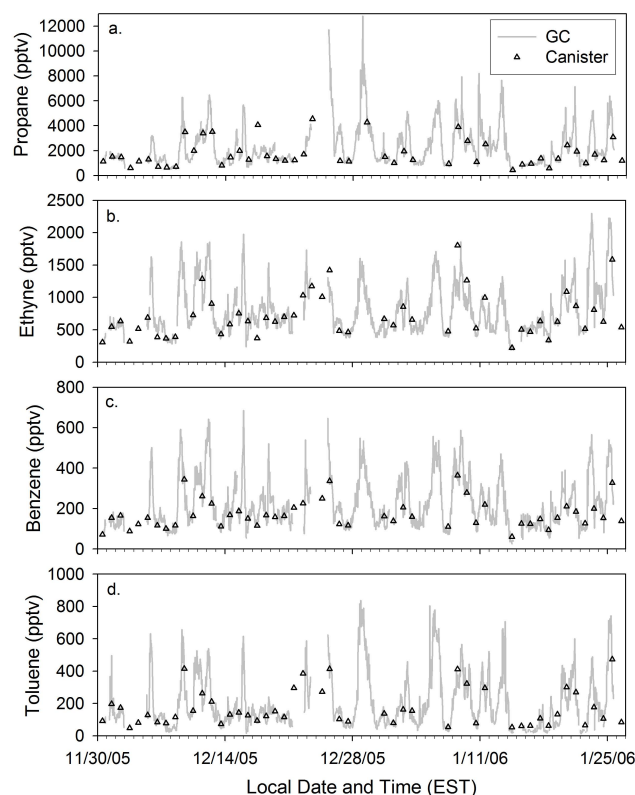


Fig. 11. Comparison between (a) propane, (b) ethyne, (c) benzene, and (d) toluene data from the automated TF GC system during December 2005–January 2006 and the daily canister samples collected during the same time period. Note: the canister samples with mixing ratios >95 th percentile for each month have been removed.

promising results that the daytime canister samples provide representative information on regional emission rates.

5.2 Comparison with the 2002 and 2005 EPA National Emissions Inventory

The emission rates of benzene, toluene, ethylbenzene, xylenes, and ethyne in the two most recent versions (2002 and 2005) of the EPA National Emissions Inventory (NEI) (www.epa.gov/ttn/chief/net) were compared with each other and with the emission rates estimated at TF (Sect. 5.1). These five NMHCs were chosen because the NEI provides speciated emission rates for some toxic compounds (including aromatics) and because ethyne or VOC/ethyne ratios are commonly used as tracers of specific sources. The emission rates of benzene, toluene, ethylbenzene, and xylenes for NH from the major source categories (onroad, nonroad, non-point) were obtained directly from the NEI. Emission rates of ethyne were estimated using the total VOC emissions from its major sources (gasoline and diesel exhaust, recreational equipment, lawn and garden equipment, and stationary source fuel combustion) and the EPA recommended

Table 3. Emission rates ($\text{molecules cm}^{-2} \text{s}^{-1}$) of $\text{C}_3\text{--C}_8$ NMHCs calculated using nighttime measurements made by the automated TF GC when a stable inversion layer developed during winter 2006. The error bars were calculated by propagating the standard error of the linear regression between the change in NMHC concentration per unit time (00:00–05:00 EST) and the assumed variation in nocturnal boundary layer height ($125 \text{ m} \pm 75 \text{ m}$). The winter 2006 daily canister emission ratio (\pm standard error (SE)) was calculated from the slope of the correlation between a NMHC and ethyne. The winter 2006 daily canister emission rate ($\text{molecules cm}^{-2} \text{s}^{-1}$) was calculated by multiplying the daily canister emission ratios by the TF GC ethyne emission rate. The error bars were calculated by propagating the error associated with the winter 2006 TF GC ethyne emission rate and the standard error of the NMHC/ethyne emission ratio. New Hampshire (land area= $2.3 \times 10^{10} \text{ m}^2$) and New England (land area= $1.6 \times 10^{11} \text{ m}^2$) emissions (Mg/day) were extrapolated from the winter 2006 TF GC emission rates.

	Winter 2006 TF GC Emission Rate		Winter 2006 Daily Canister Emission Ratio		Winter 2006 Daily Canister Emission Rate	New Hampshire	New England
	$\times 10^9$ (molec. $\text{cm}^{-2} \text{s}^{-1}$)	r^2	$\left(\frac{\text{NMHC}}{\text{Ethyne}}\right) \pm \text{SE}$	r^2	$\times 10^9$ (molec. $\text{cm}^{-2} \text{s}^{-1}$)	Mg/day	Mg/day
Ethyne	7.4 \pm 4.9	0.78				6.4 \pm 4.2	45 \pm 30
Propane	42 \pm 25	0.96	2.33 \pm 0.25	0.57	17 \pm 12	61 \pm 37	427 \pm 260
Propene	3.2 \pm 2.0	0.86	0.25 \pm 0.02	0.75	1.8 \pm 1.2	4.5 \pm 2.9	32 \pm 20
i-Butane	3.2 \pm 2.0	0.89	0.44 \pm 0.04	0.60	3.3 \pm 2.0	6.1 \pm 3.8	43 \pm 27
n-Butane	3.6 \pm 2.3	0.83	0.85 \pm 0.13	0.40	6.3 \pm 4.1	6.9 \pm 4.4	49 \pm 31
i-Pentane	2.4 \pm 1.5	0.94	0.43 \pm 0.04	0.68	3.2 \pm 2.1	5.8 \pm 3.6	41 \pm 25
n-Pentane	1.4 \pm 0.8	0.96	0.22 \pm 0.03	0.46	1.6 \pm 1.0	3.3 \pm 2.0	23 \pm 14
n-Hexane	0.6 \pm 0.4	0.87	0.09 \pm 0.01	0.61	0.7 \pm 0.4	1.7 \pm 1.1	12 \pm 8
Benzene	1.6 \pm 1.1	0.81	0.19 \pm 0.01	0.94	1.4 \pm 0.9	4.3 \pm 2.8	30 \pm 19
Toluene	2.7 \pm 1.7	0.82	0.30 \pm 0.02	0.79	2.3 \pm 1.5	8.2 \pm 5.3	58 \pm 37
Ethylbenzene	0.5 \pm 0.3	0.86	0.04 \pm 0.003	0.69	0.3 \pm 0.2	1.8 \pm 1.1	13 \pm 8
m+p-Xylene	1.3 \pm 0.8	0.80	0.04 \pm 0.004	0.61	0.3 \pm 0.2	4.4 \pm 2.9	31 \pm 20
o-Xylene	0.5 \pm 0.3	0.88	0.03 \pm 0.002	0.65	0.2 \pm 0.1	1.8 \pm 1.1	13 \pm 8

composite profiles for those sources. The speciation profiles were obtained from the SPECIATE 4.2 database (<http://projects.pechan.com/ttn/speciate4.2.1>).

The emission rates of benzene, toluene, ethylbenzene, xylenes, and ethyne in both the 2002 and 2005 NEI agreed within the error limits and were the same order of magnitude as the TF emission rates (Table 4). The emission rates of benzene, ethylbenzene, and xylenes were fairly similar (within $\pm 15\%$) in the two versions of the NEI. The relative distribution of emissions in the NEI and at TF was the same in 2002 with toluene > xylenes \sim ethyne > benzene > ethylbenzene. Toluene and ethylbenzene had the highest and lowest emission rates, respectively, in the 2005 NEI as well. Overall, it appears that the 2002 NEI emission estimates were in better agreement with the TF emission rates than the 2005 NEI.

A notable difference between the two versions of the NEI is the higher toluene emissions from nonroad sources (specifically recreational, lawn, and garden equipment) in 2005 than in 2002 (Table 4). While still within the error limits, the largest difference between the central TF emission rate and the NEI was for toluene (out of the five compounds shown in Table 4). The 2002 and 2005 total NEI toluene emissions were 30% and 50%, respectively, higher than the TF estimates. Toluene has many potential sources in this region (e.g., vehicular exhaust, fuel evaporation, solvent utilization, biogenic, White et al., 2009) which is a likely fac-

tor contributing to the disagreement between the inventory and our estimates. Previous studies focused on the eastern US have reported that toluene emissions were overestimated in earlier versions of the NEI. For example, Choi et al. (2006) found that toluene emissions were overestimated in a modified version of the 1996 NEI compared to PAMS measurements made in Mid-Atlantic states. In contrast to this work in which the higher toluene in 2005 was associated with larger nonroad emissions, the overestimate reported by Choi et al. (2006) was related to solvent utilization. Furthermore, WRF-CHEM model predictions based on the 1999 NEI of the vertical profile of toluene over the northeast US during the NEAQS-ITCT 2004 campaign were approximately a factor of 3 larger than observations (Warneke et al., 2007). Toluene is an important precursor of O_3 and SOA which highlights the critical need for updated source profiles, improved inventory emission estimates, and additional observational constraints on toluene emissions.

The total 2002 NEI and TF ethyne emission rates agreed remarkably well ($\sim 2300 \text{ Mg/year}$) (Table 4). However, the total 2005 NEI ethyne emission rate was $\sim 40\%$ lower than the central TF value, but was still within the error limits of the TF emission rate. Ethyne emissions in the non-point source category reflect residential stationary source fuel combustion with a minor contribution from open burning (yard and household waste). Residential wood and fireplace

Table 4. Emission rates (Mg/year) of benzene, toluene, ethylbenzene, xylenes (m+p+o), and ethyne and the toluene/benzene and benzene/ethyne ratios from the 2002 and 2005 EPA National Emissions Inventory (NEI) for New Hampshire. The TF column is the emission rate (Mg/year) estimated using the winter 2006 TF GC nighttime measurements from Table 3. The toluene/benzene and benzene/ethyne ratios were calculated by converting the emission rates for TF and for the respective source category listed in this table to molar concentrations. The TF toluene/benzene and benzene/ethyne ratio errors were propagated from the error in the TF emission rates.

		Onroad Exhaust	Onroad Evaporation	Nonroad	Nonpoint	Point	Total
	TF	2002 NEI					
Benzene	1555±1000	540	25	730	520	10	1830
Toluene	3000±1900	1400	160	1660	480	100	3800
Ethylbenzene	660±400	200	30	365	25	30	650
Xylenes	2260±830	790	100	1120	260	120	2390
Ethyne	2350±1540	390		540	1370	2	2300
Toluene/Benzene	1.6±1.4	2.2	5.4	1.9	0.78	8.4	1.8
Benzene/Ethyne	0.22±0.2	0.46		0.45	0.13	1.7	0.26
	TF	2005 NEI					
Benzene	1555±1000	650	30	400	480	10	1570
Toluene	3000±1900	1450	160	2340	520	90	4560
Ethylbenzene	660±400	210	30	275	30	5	550
Xylenes	2260±830	820	100	1280	290	40	2530
Ethyne	2350±1540	405		640	430	5	1480
Toluene/Benzene	1.6±1.4	1.9	4.5	5.0	0.92	7.6	2.5
Benzene/Ethyne	0.22±0.2	0.53		0.21	0.37	0.67	0.35

combustion was the largest nonpoint source of VOC emissions in northern New England in both versions of the NEI. According to the EPA, the emission factor used to calculate emissions for the woodstove and fireplace source category was reduced for the 2005 NEI (www.epa.gov/ttn/chief/net/2005inventory). Consequently, the VOC emission rate from the woodstove and fireplace source category was ~70% lower in the 2005 NEI than in the 2002 NEI. This resulted in the lower ethyne emissions in 2005 and the larger discrepancy with the TF emission rates. This illustrates the necessity of additional studies to accurately quantify the VOC emissions from residential combustion in the northeast US (e.g., Jordan et al., 2009).

The toluene/benzene and benzene/ethyne ratios based on the NEI emissions for New Hampshire were also examined and compared to the ambient ratios (Sects. 4.2 and 4.3) (Table 4). Both the 2002 and 2005 NEI toluene/benzene and benzene/ethyne ratios agreed within the error limits of the TF ratio values. The total benzene/ethyne ratios in the 2002 (0.26) and 2005 (0.35) NEIs were lower than the ratios given in Parrish (2006) for the 1996 and 1999 NEIs (0.9 and 0.7, respectively). The benzene/ethyne ratio in the on-road exhaust source category (~0.5) was higher than ambient ratios (~0.2). Our results are consistent with Parrish (2006) who reported that there was a downward trend in NEI benzene/ethyne ratio values but that there are still problems with the apportioning of benzene and ethyne emissions

in the onroad source category. Overall, the range of NEI toluene/benzene and benzene/ethyne ratio values in the different source categories are within the range of the ambient values observed at TF (Table 4, Figs. 9, 10). The general agreement between our results and the inventory may be fortuitous or it may indicate that VOC emissions are more accurately represented in the 2002 and 2005 NEIs than in earlier versions. Furthermore, these results suggest that the ethyne emission rate from the NEI may be useful for estimating emission rates of other VOCs by using their emission ratios relative to ethyne from the daily canister samples. This may be a valuable tool for modeling or predicting ambient VOC concentrations.

6 Summary

This work characterized the mixing ratios, seasonal to interannual variability, and sources of C₂–C₈ NMHCs, C₂HCl₃, and C₂Cl₄ from samples collected during January 2004–February 2008 at Thompson Farm in Durham, NH. The midday canister samples provided a comprehensive and representative picture of the day-to-day and interannual VOC trends and captured a wide range of mixing ratios and various sources (fossil fuel combustion, gasoline, LPG, fuel or solvent evaporation, industry, biogenic). Estimates of NMHC emission rates using the daily canister sample and

automated in situ TF GC measurements ranged from 10^9 – 10^{10} molecules $\text{cm}^{-2} \text{s}^{-1}$. Additionally, benzene, toluene, ethylbenzene, xylene, and ethyne emission rates from the 2002 and 2005 EPA National Emissions Inventory were within $\pm 50\%$ of the TF emission rates. The alkanes, ethyne, benzene, toluene, and halocarbons exhibited consistent and reproducible seasonal trends each year, whereas the alkenes and C_8 aromatics illustrated greater interannual variability reflecting their shorter lifetimes and/or varying sources or emission rates. Furthermore, this multi-year data set illustrated that the mixing ratios of reactive NMHCs (specifically C_5 – C_6 alkanes, propene, toluene), and C_2HCl_3 were enhanced in the summer relative to their springtime minimums indicating a persistent influence from evaporative emissions each year. Previous fuel emission studies have observed increased evaporative emissions from gasoline containing ethanol (e.g., Durbin et al., 2007; Graham et al., 2008). The results from this study will be valuable for evaluating and documenting the impact of new federal regulations enacted in 2005–2007 for motor vehicle emissions (<http://www.epa.gov/otaq/gasoline>) (i.e., MTBE ban and switch to E10) and dry cleaning solvents on the ambient levels of VOCs in this region.

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