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Spatial Variation, Sources and Emission Rates of Volatile Organic Compounds Over the Northeastern U.S.

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1. Introduction

New England is an ideal region for studying air quality because of its unique geographic location, diverse landscapes and ecosystems, and varying climatic conditions. New England is often referred to as the "tailpipe" of the United States because it is directly downwind of major urban and industrial pollution sources located throughout the Midwest, Ohio Valley, and Washington D.C.-New York City metropolitan corridor (Fig. 1a). Sources in these urban areas emit pollutants into air masses which are then transported to the northeastern U.S. by the prevailing circulation patterns over the U.S. (i.e., the jet stream). Consequently, the air quality of New England reflects a combination of local, regional, and distant anthropogenic and natural trace gas and aerosol sources.

In order to study the chemical and physical mechanisms influencing the atmospheric composition over New England, the University of New Hampshire's (UNH) AIRMAP program has been conducting continuous measurements of important trace gas (e.g., ozone (O_3), carbon monoxide (CO), nitric oxide (NO), total reactive nitrogen (NO_y), sulfur dioxide (SO_2), carbon dioxide (CO_2), mercury) and meteorological parameters throughout the region for the past decade. Continuous measurements of volatile organic compounds (VOCs) have also been made at the UNH Atmospheric Observing Station at Thompson Farm (TF) (43.11 °N, 70.95 °W, elevation 24 m) in Durham, New Hampshire (NH) since 2002 (Fig. 1b). VOCs are ubiquitous components of the atmosphere, and this broad category consists of nonmethane hydrocarbons (NMHCs), halocarbons, oxygenated VOCs (OVOCs), organic nitrates, and reduced sulfur compounds. VOCs enter the atmosphere from numerous primary anthropogenic (i.e., vehicles, natural gas, industrial solvents, fossil fuel combustion) and natural (i.e., vegetation, ocean) sources, and may also serve as precursors to secondary pollutant (i.e., O_3, OVOCs, secondary organic aerosol (SOA)) production (e.g., Fehsenfeld et al., 1992; Singh and Zimmerman, 1992). The oxidation of NMHCs (RH) in the presence of

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sufficient levels of nitrogen oxides (NO_x = NO + NO_2; NO_2 = nitrogen dioxide) is the major production mechanism for O_3 in the lower troposphere (Equations 1-5) (e.g., Carter, 1994). Ozone and particulate matter are the major components of photochemical smog and thus impact visibility, potentially damage vegetation and crops, and serve as respiratory lung irritants (U.S. EPA, 2010). A minor branch in the NMHC-NO_x-O_3 reaction mechanism produces alkyl nitrates ($RONO_2$) (Equations 1-6) (e.g., Roberts, 1990; Flocke et al., 1998).

$$RH + OH \rightarrow R + H_2O \quad (1)$$

$$R + O_2 \rightarrow RO_2 \quad (2)$$

$$RO_2 + NO \rightarrow RO + NO_2 \quad (3)$$

$$NO_2 + h\nu \rightarrow NO + O \quad (4)$$

$$O + O_2 + M \rightarrow O_3 + M \quad (5)$$

$$RO_2 + NO \rightarrow RONO_2 \quad (6)$$

In addition, VOCs have a wide range of atmospheric lifetimes (seconds to years), and are removed from the atmosphere by oxidation (OH, O_3, nitrate, halogens), photolysis, and/or deposition. Furthermore, several NMHCs (i.e., benzene, toluene, C_8 aromatics), OVOCs (i.e., formaldehyde, acetaldehyde), and halocarbons (i.e., tetrachloroethene) are classified as hazardous air pollutants by the U.S. Environmental Protection Agency because they are potential carcinogens and/or harmful to human health (U.S. EPA, 1998, 2008, 2010). Therefore, a complete, accurate, and quantitative description of the atmospheric VOC distribution is necessary for characterizing the air quality in a particular region, studying the oxidation capacity of the atmosphere, and evaluating air quality and climate change models. Prior research conducted at TF has found that the air quality of this semi-rural area of New England is influenced by a complex mixture of anthropogenic VOCs from local, regional and more distant source regions, as well as from substantial biogenic sources (forests, coastal seaweed/algae) (e.g., Russo et al., 2010a, 2010b; Sive et al., 2007; Talbot et al., 2005; White et al., 2008, 2009; Zhou et al., 2005, 2008). Unique spatial and diurnal VOC trends are exemplified by a study conducted at six different locations throughout the New Hampshire seacoast region in August 2003. During this one day study, several anthropogenic NMHCs exhibited large nighttime mixing ratio enhancements (White et al., 2008), the marine derived halocarbons exhibited a distinct spatial gradient from coastal to inland sites (Zhou et al., 2005), and the alkyl nitrates were uniformly distributed throughout the study area (Russo et al., 2010a). The distinct VOC trends observed in the continuous measurements at TF and from the August 2003 study led to a concerted effort to determine the sources and processes contributing to the VOC distribution over New England. We are aware of only one other detailed regional VOC measurement campaign conducted in the southwestern U. S. focused on examining the spatial variation of VOC mixing ratios and sources (Katzenstein et al., 2003). Similar types of studies are clearly needed. The objectives of this chapter are to discuss the sources and spatial and temporal trends of VOCs during four spatial surveys conducted throughout New England during 2006 and 2007 and to put the results in context with the overall atmospheric distribution of VOCs observed at the Thompson Farm field site in Durham, NH.

2. Methods

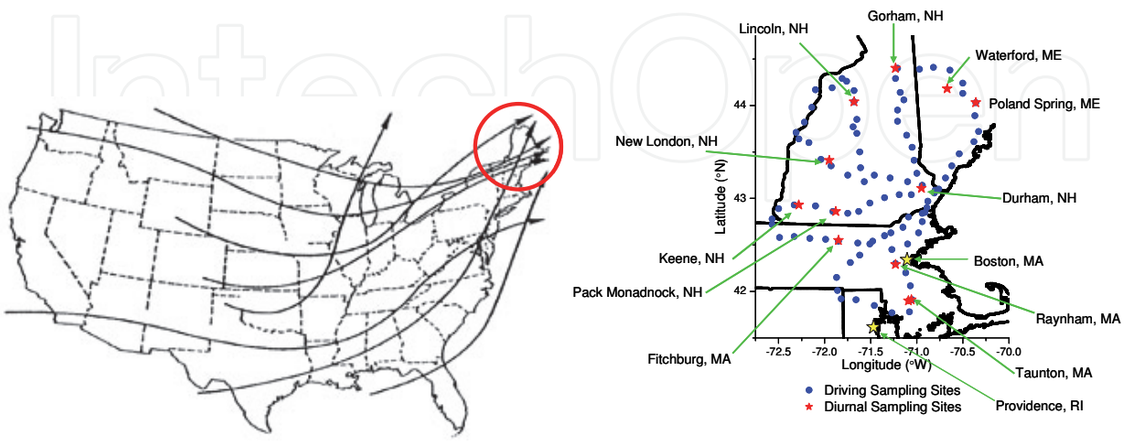
Spatial surveys were conducted on June 21, 2006, September 21-22, 2006, January 10-11, 2007, and May 22-23, 2007. Ambient air samples were collected in 2 liter canisters along four ~250-300 mile (~400-480 km) loops radiating out from UNH in Durham, NH and included portions of western Maine (ME), eastern Vermont (VT), northern and eastern Massachusetts (MA), extreme northeastern Connecticut (CT), and northern Rhode Island (RI) (Fig. 1b). During each survey, four pairs of researchers collected samples every 10-15 miles (16-24 km) for a total of 24 samples on each route. The time of sample collection and the geospatial coordinates were recorded at each sampling location using a global positioning sensor (GPS). The sampling sites were generally open areas (i.e., fields, public parks) upwind of major sources and were chosen during the first sampling trip (June 21, 2006) which was conducted during the daytime (~09:00-19:00 EDT). The three subsequent surveys were conducted at night (~19:00-05:00 EDT) when winds were predicted to be low (<5 m s^{-1}) to minimize the influence of photochemistry and to capture local nighttime emissions. The four sampling routes covered a wide geographic area that spanned considerable variation in altitude, land use, and population density. Moreover, the four surveys provide information on the seasonal variation of VOC sources.

In order to characterize the diurnal variation of VOCs throughout the region, hourly ambient canister samples were collected over 24 hour periods on September 8-9, 2006 in Waterford, ME, September 12-13, 2006 in Hinesburg, VT, September 27-28, 2006 at Pack Monadnock, NH and at six locations on January 13-14, 2007 and May 29-30, 2007 (Fig. 1b). These diurnal sampling sites were selected to cover a range of local housing and population densities and included public parks and private property where permission was granted from local authorities and landowners.

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. After each sampling campaign, the canisters were analyzed at UNH on a three gas chromatograph (GC) system equipped with two flame ionization detectors (FID), two electron capture detectors (ECD), and a mass spectrometer (MS) for C_2-C_{10} NMHCs, C_1-C_2 halocarbons, C_1-C_5 alkyl nitrates, OVOCs, and select reduced sulfur compounds (Sive et al., 2005; Zhou et al., 2005, 2008). The compounds discussed in this work are C_2-C_7 alkanes, C_2-C_3 alkenes, isoprene, ethyne, C_6-C_8 aromatics, monoterpenes (α-pinene, β-pinene), trichloroethene (C_2HCl_3), tetrachloroethene (C_2Cl_4), methyl iodide (CH_3I), dibromomethane (CH_2Br_2), bromoform ($CHBr_3$), methyl nitrate ($MeONO_2$), ethyl nitrate ($EtONO_2$), 2-propyl nitrate (2-$PrONO_2$), and 2-butyl nitrate (2-$BuONO_2$). 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 C_2-C_{10} NMHCs and 5-10% for the halocarbons and alkyl nitrates.

Hourly measurements from the automated in situ GC system at TF (Sive et al., 2005; Zhou et al., 2005, 2008) corresponding to the same time periods as the regional sampling surveys are also used to describe the diurnal variation of NMHCs and to calculate emission rates. Details of the custom designed four channel (2 FIDs, 2 ECDs) GC system, sample preconcentrator, sample trapping and splitting, calibrations, and instrument control are given in Sive et al. (2005) and Russo et al. (2010b). 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%. Additionally, measurements of O_3, CO_2, wind speed, and wind direction (e.g., Mao and Talbot, 2004a, 2004b; Talbot et al., 2005) at TF are included to further characterize the air mass composition and atmospheric dynamics during each survey.



(a) (b)

Fig. 1. (a) Location of New England (enclosed in circle) in the United States. (b) Sampling sites during the four regional spatial surveys (blue dots) and diurnal studies (red stars) conducted throughout Maine, New Hampshire, Vermont, Massachusetts, northeastern Connecticut, and northern Rhode Island.

3. Atmospheric distribution of VOCs throughout New England

3.1 Seasonal variation and general distributions

The general seasonal variation of C_2-C_8 NMHCs, C_2HCl_3, C_2Cl_4, and C_1-C_5 alkyl nitrates at TF during 2004-2008 is presented in detail in Russo et al. (2010a,b), but a brief discussion is given here. The dominant removal mechanism of NMHCs, C_2HCl_3, and C_2Cl_4 from the atmosphere is reaction with the hydroxyl radical (OH) which is produced following the photolysis of O_3. Hence, atmospheric OH concentrations in the Northern Hemisphere are highest during the summer and are lowest during winter (e.g., Logan et al., 1981; Spivakovsky et al., 2000). Furthermore, the rate of reaction between NMHCs and OH generally increases with increasing carbon number (e.g., Atkinson et al., 2006). Overall, the highest monthly mean C_2-C_8 NMHC, alkyl nitrate, and halocarbon mixing ratios were observed in winter (December, January, February) and decreased throughout the spring at TF (Russo et al., 2010b). The lowest mixing ratios were observed during middle to late spring through the summer corresponding to the time period when NMHC removal processes are fastest. Ethane is the longest lived NMHC in the atmosphere and was generally the most abundant. More specifically, ethane peaked in January-February (~2400 pptv; pptv = parts per trillion by volume) and was minimum in late summer (~900 pptv, August-September). The C_3-C_4 alkane mixing ratios decreased from December-January peak levels (propane ~1500 pptv, i-butane ~270 pptv, n-butane ~500 pptv) to minimum mixing ratios in May-September (propane ~400-600 pptv, i-butane ~50-75 pptv, n-butane ~100-120

pptv). The minimum monthly mean mixing ratios of the short-lived VOCs (C_5-C_6 alkanes, propene, toluene and C_2HCl_3) occurred in April-May and were factors of 2-4 lower than in winter. Their monthly mean mixing ratios increased in early summer and remained at similar levels through late summer (September). Benzene, ethyne, and ethene exhibited minimum monthly mean mixing ratios from late spring through summer. The monthly mean C_2Cl_4 mixing ratios were fairly uniform all year (~10-15 pptv). The total alkyl nitrate ($\Sigma RONO_2$ = sum of C_1-C_5 alkyl nitrates) mixing ratio was highest in late winter (February-March) and lowest in late summer. Methyl nitrate was relatively uniform (monthly mean ~3 pptv) all year. Ethyl nitrate was slightly lower in summer (mean ~2.2 pptv) than in winter (~2.7 pptv). 2-propyl and 2-butyl nitrate were the most abundant alkyl nitrates and exhibited the largest seasonal variation (monthly mean mixing ratios were factors of 1.5-3 higher in winter) (Russo et al., 2010a).

The spatial distributions of NMHC, halocarbon, and alkyl nitrate mixing ratios during the four driving sampling campaigns are shown in Fig. 2, and the statistics for each survey are given in Table 1. Most hydrocarbon mixing ratios were lower during June 2006 than during the overnight September 2006, January 2007, and May 2007 sampling campaigns reflecting more active photochemistry during the summer and the daytime (Table 1). The minimum NMHC, halocarbon, $MeONO_2$, and 2-$PrONO_2$ mixing ratios observed during each survey were highest in January and follow the general seasonal trend in background mixing ratios discussed in the preceding paragraph. In addition, the mean and median mixing ratios of i-butane, n-butane, ethyne, and benzene were higher during January than during the other three surveys (Table 1, Fig. 2). However, the distribution of VOCs throughout the atmosphere over New England during the four intensive spatial surveys exemplifies the influence of short-term pollution events and local emissions on the general VOC pattern.

Ethane was the most abundant compound measured throughout the region in June (mean ± standard deviation ~990±150 pptv), January (mean ~1970±170 pptv), and May (~1440±3650 pptv) (Fig. 2a, Table 1). Daytime propane levels during June were lower (390±370 pptv), with a few local hot spots above 1000 pptv. The highest mean and median mixing ratios of propane (mean 2150±2600 pptv), ethene (mean 580±480 pptv), propene (mean 175±150 pptv), and ethylbenzene (mean 60±50 pptv) were observed during the September 2006 survey (Table 1). During September 2006, propane was the most abundant NMHC followed by ethane (mean 1300±1300pptv). The major source of propane in New England is liquefied petroleum gas (LPG), while ethene and propene are minor components of LPG (Blake and Rowland, 1995; Chen et al., 2001; Jobson et al., 2004). These results suggest that LPG emissions had a significant influence on New England air quality on the night of September 21-22, 2006. Despite the high mean and median levels in September, the maximum propane, ethene, propene, and ethylbenzene mixing ratios, as well as ethane, ethyne, n-heptane, benzene, toluene, m+p-xylene, and o-xylene, were observed during May.

Furthermore, the C_5-C_7 alkanes exhibited comparable mean and median mixing ratios during September and May (mean i-pentane ~260 pptv, n-pentane ~120 pptv, n-hexane ~60 pptv, n-heptane ~40 pptv) (Table 1). Their mean and medians were slightly higher in May likely reflecting strong evaporative emissions. Moreover, the average toluene and xylene mixing ratios were highest in May. Overall, these results indicate that local emissions had a strong influence on alkane, alkene, and aromatic mixing ratios throughout New England

during the nighttime September and May sampling surveys. Interestingly, the highest maximum i-butane, n-butane, i-pentane, n-pentane, and n-hexane mixing ratios were observed during the daytime June trip at a site off of a major traffic route in Northern, MA. This likely reflects strong local fuel evaporation emissions.

		June 21, 2006	Sept. 21-22, 2006	Jan. 10-11, 2007	May 22-23, 2007
Ethane	Mean (SD)	989 (149)	1313 (1299)	1966 (113)	2384 (3657)
	Median (Range)	934 (889-1758)	933 (418-11545)	1951 (1739-2554)	1443 (1271-28634)
Propane	Mean (SD)	388 (367)	2145 (2619)	1075 (381)	1991 (3126)
	Median (Range)	266 (116-2690)	1196 (198-13782)	1025 (800-4486)	1134 (268-27537)
i-Butane	Mean (SD)	81 (332)	167 (242)	189 (27)	190 (383)
	Median (Range)	33 (12-3200)	99 (22-1664)	185 (144-371)	98 (23-2643)
n-Butane	Mean (SD)	155 (735)	212 (374)	334 (33)	267 (489)
	Median (Range)	49 (19-7048)	110 (35-3456)	332 (268-420)	171 (59-4618)
i-Pentane	Mean (SD)	185 (635)	257 (305)	133 (19)	264 (415)
	Median (Range)	66 (18-5867)	159 (23-2404)	127 (106-203)	168 (42-3861)
n-Pentane	Mean (SD)	79 (243)	120 (133)	81 (10)	126 (174)
	Median (Range)	33 (12-2306)	73 (7-1028)	80 (58-114)	80 (19-1194)
n-Hexane	Mean (SD)	24 (58)	64 (74)	26 (5)	62 (69)
	Median (Range)	11 (3-543)	39 (5-483)	25 (15-43)	43 (6-537)
n-Heptane	Mean (SD)	16 (14)	37 (38)	16 (4)	40 (46)
	Median (Range)	11 (3-72)	22 (4-215)	16 (7-30)	28 (8-377)
Ethyne	Mean (SD)	181 (113)	441 (529)	532 (123)	432 (432)
	Median (Range)	138 (101-805)	287 (103-3825)	503 (438-1510)	341 (192-4184)
Ethene	Mean (SD)	166 (144)	579 (488)	277 (132)	469 (770)
	Median (Range)	119 (42-819)	423 (42-2264)	241 (135-975)	299 (81-7035)
Propene	Mean (SD)	52 (42)	176 (150)	49 (26)	128 (235)
	Median (Range)	36 (13-218)	130 (13-691)	43 (20-201)	82 (28-2022)
Benzene	Mean (SD)	37 (28)	99 (90)	116 (19)	103 (230)
	Median (Range)	26 (4-129)	71 (11-620)	110 (96-230)	67 (29-2252)
Toluene	Mean (SD)	112 (121)	262 (256)	77 (26)	300 (452)
	Median (Range)	67 (16-746)	153 (21-1142)	69 (47-200)	191 (43-3872)

		June 21, 2006	Sept. 21-22, 2006	Jan. 10-11, 2007	May 22-23, 2007
Ethylbenzene	Mean (SD)	16 (22)	57 (47)	11 (4)	46 (82)
	Median (Range)	9 (3-159)	43 (3-262)	10 (5-27)	26 (8-561)
m+p-Xylene	Mean (SD)	47 (78)	121 (112)	25 (14)	156 (298)
	Median (Range)	22 (6-580)	79 (9-541)	22 (7-86)	90 (17-2190)
o-Xylene	Mean (SD)	17 (28)	45 (46)	12 (6)	63 (127)
	Median (Range)	9 (2-209)	29 (4-230)	10 (5-25)	31 (6-827)
Isoprene	Mean (SD)	791 (585)	68 (55)	-	33 (30)
	Median (Range)	623 (127-3468)	42 (5-229)	-	27 (5-200)
α-Pinene	Mean (SD)	116 (83)	344 (362)	16 (6)	377 (619)
	Median (Range)	91 (20-424)	263 (24-2598)	15 (6-32)	241 (21-5641)
β-Pinene	Mean (SD)	50 (54)	166 (157)	6 (2)	222 (317)
	Median (Range)	34 (2-300)	118 (18-921)	6 (5-8)	151 (4-2565)
C_2Cl_4	Mean (SD)	11 (13)	18 (26)	8 (2)	17 (11)
	Median (Range)	7 (5-115)	9 (2-205)	8 (6-22)	14 (5-65)
C_2HCl_3	Mean (SD)	2.3 (2.7)	4.5 (7.4)	2.5 (0.7)	7.4 (18)
	Median (Range)	1.3 (0.2-21)	1.2 (0.2-35)	2.3 (1.2-5.2)	1.9 (0.2-125)
CH_3I	Mean (SD)	1.5 (1.6)	0.93 (0.72)	0.97 (0.28)	0.94 (0.65)
	Median (Range)	0.76 (0.4-8.5)	0.76 (0.3-5.9)	0.91 (0.7-2.8)	0.71 (0.2-3.6)
CH_2Br_2	Mean (SD)	0.92 (0.2)	0.98 (0.1)	1.1 (0.1)	0.99 (0.3)
	Median (Range)	0.87 (0.7-1.7)	0.99 (0.6-1.5)	1.1 (0.9-1.7)	0.93 (0.7-2.6)
$CHBr_3$	Mean (SD)	1.8 (2.3)	3.4 (1.4)	3.7 (1.3)	2.7 (2.2)
	Median (Range)	0.95 (0.5-13.9)	3.0 (0.7-9.9)	3.5 (2.0-8.4)	2.1 (0.5-14.5)
$MeONO_2$	Mean (SD)	2.4 (0.4)	2.1 (0.4)	3.3 (0.2)	2.7 (0.5)
	Median (Range)	2.3 (2.0-3.5)	2.1 (1.2-3.3)	3.3 (2.9-3.6)	2.6 (1.8-4.2)
$EtONO_2$	Mean (SD)	1.9 (0.5)	1.4 (0.3)	2.7 (0.1)	4.3 (1.2)
	Median (Range)	1.6 (1.4-3.5)	1.4 (0.6-2.3)	2.7 (2.4-2.9)	3.8 (2.6-7.3)
$2\text{-}PrONO_2$	Mean (SD)	3.1 (1.5)	2.6 (1.5)	5.8 (0.3)	5.5 (2.2)
	Median (Range)	2.4 (1.7-7.9)	2.4 (0.9-3.4)	5.8 (4.2-6.5)	4.3 (3.2-11.3)
$2\text{-}BuONO_2$	Mean (SD)	2.1 (1.5)	2.2 (0.6)	7.8 (1.2)	5.1 (2.7)
	Median (Range)	1.4 (0.8-8.5)	2.0 (0.7-3.3)	8.1 (1.9-9.8)	4.0 (2.5-13.6)

Table 1. VOC statistics during the four regional surveys. Mixing ratios are in parts per trillion by volume (pptv). SD is the standard deviation.

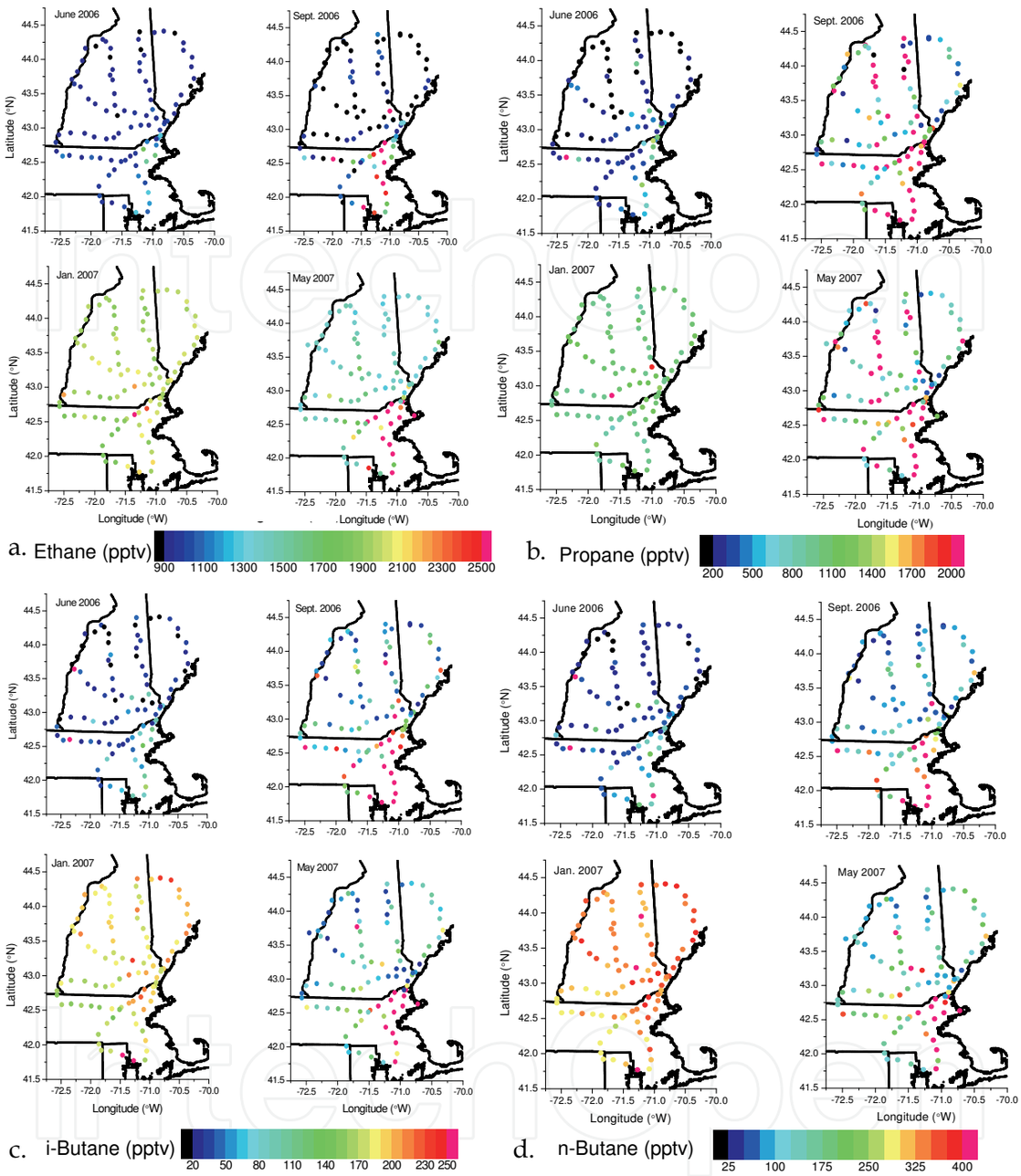


Fig. 2. Spatial variation of VOC mixing ratios (pptv) during the four regional sampling surveys conducted throughout New England. The four panels for each compound represent the four surveys. upper left panel-June 21, 2006; upper right panel- September 21-22, 2006; bottom left panel- January 10-11, 2007; bottom right panel- May 22-23, 2007. (a) ethane, (b) propane, (c) i-butane, (d) n-butane, (e) i-pentane, (f) n-pentane, (g) ethene, (h) propene, (i) ethyne, (j) benzene, (k) toluene, (l) α-pinene, (m) isoprene (not observed during January), (n) CH_3I, (o) C_2Cl_4, (p) C_2HCl_3, (q) CH_2Br_2, (r) $CHBr_3$, (s) $MeONO_2$, (t) $EtONO_2$, (u) $2\text{-}PrONO_2$, (v) $2\text{-}BuONO_2$.

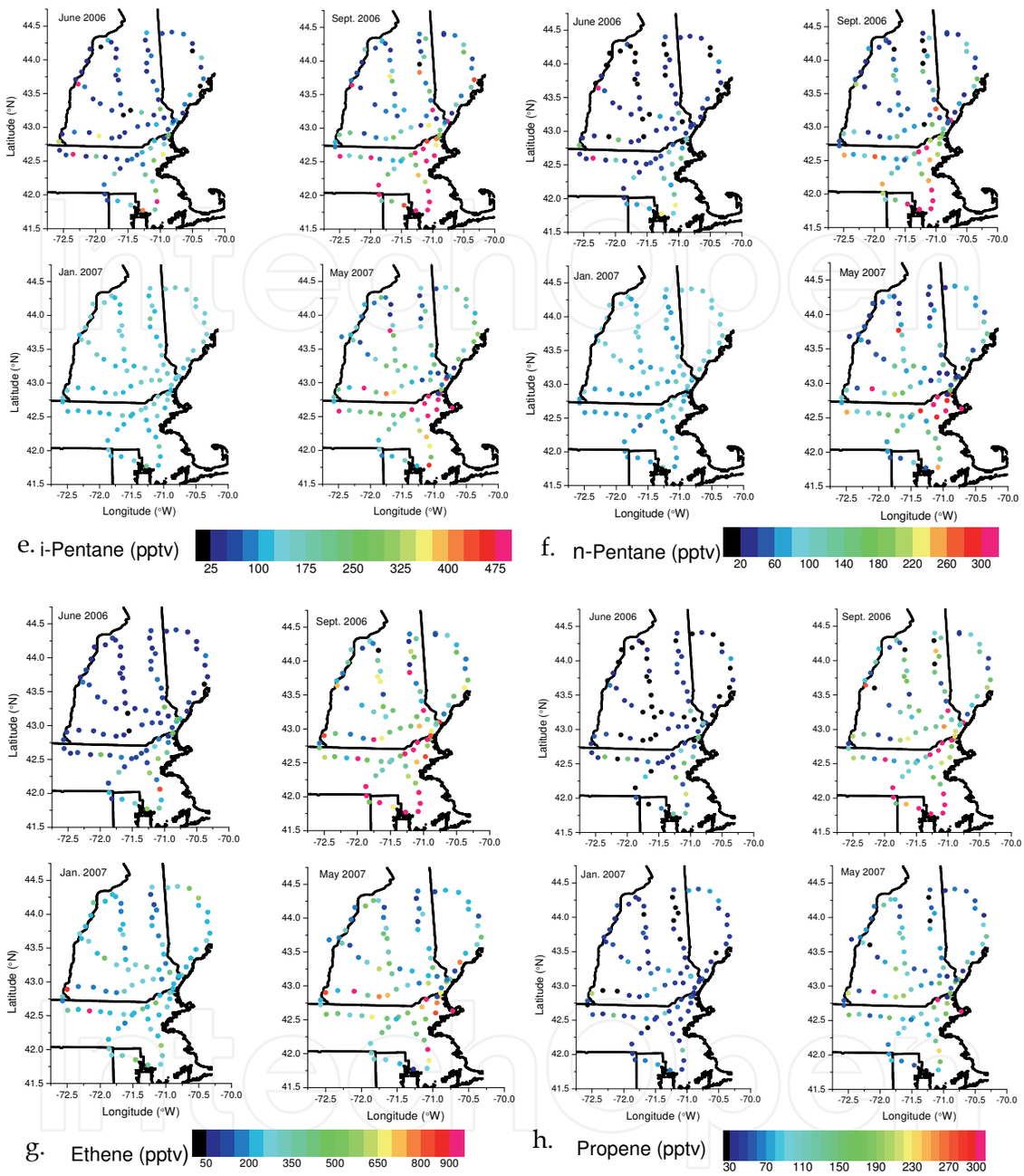
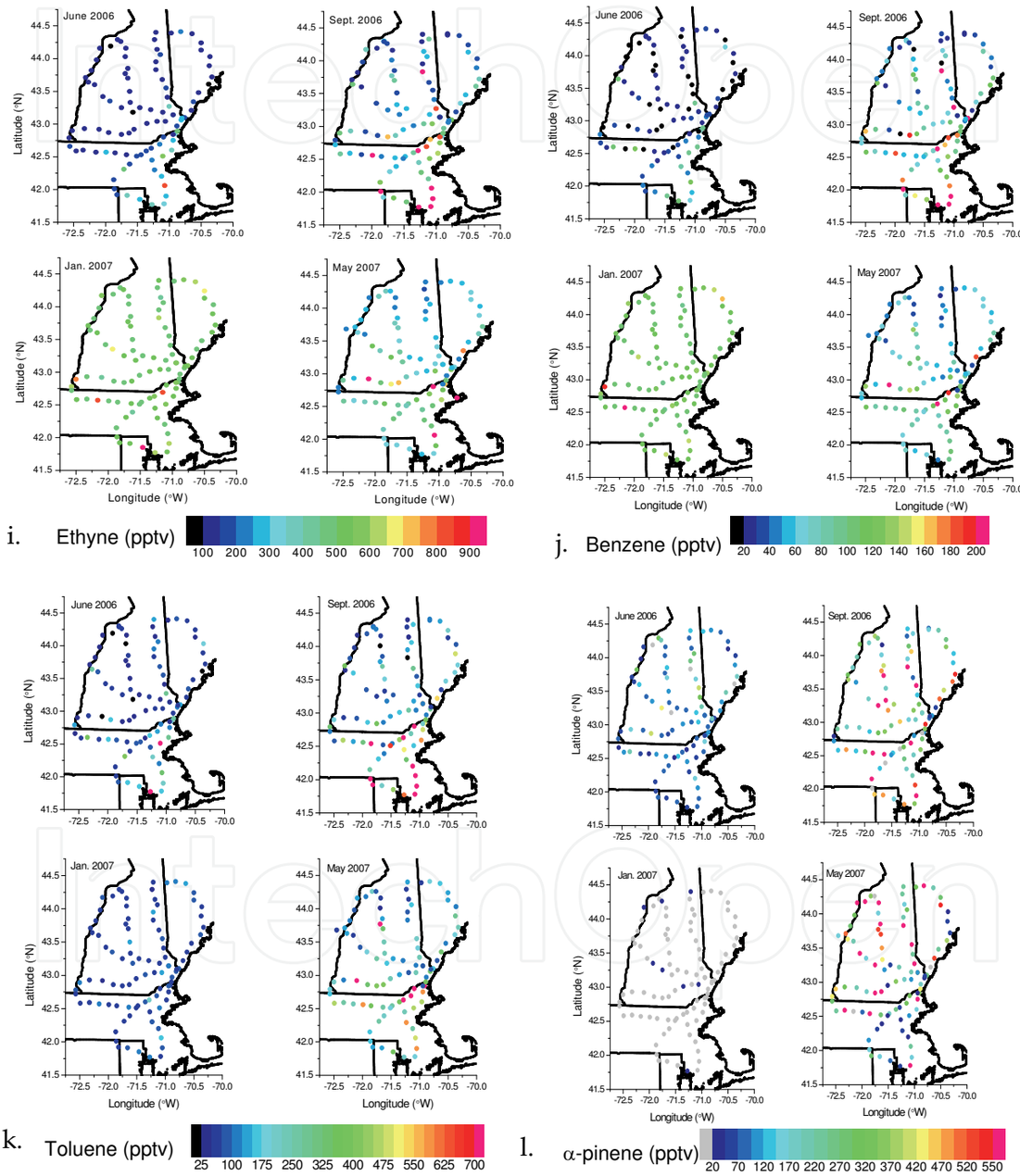


Fig. 2 continued

The biogenic NMHCs included in this analysis are isoprene and the monoterpenes, α-pinene and β-pinene. Isoprene and monoterpene emissions are dependent on both light and temperature (Guenther et al., 1995; Fehsenfeld et al., 1992). Isoprene is primarily emitted from deciduous vegetation and is detected in significant amounts when leaves are present (Guenther et al., 1995), specifically June-September at the TF site (Russo et al., 2010b). Thus, isoprene mixing ratios were highest during summer (Table 1). The mean isoprene mixing ratio was ~800±585 pptv, and isoprene was the second most abundant NMHC observed

following ethane in June. In contrast to isoprene, the monoterpenes were observed during all seasons. Alpha- and beta-pinene were lowest during January and were at comparable levels during September 2006 and May 2007 (mean and median ~120-380 pptv). Monoterpene mixing ratios were presumably lower in June compared to September and May because sampling was conducted during the day when removal rates were highest.



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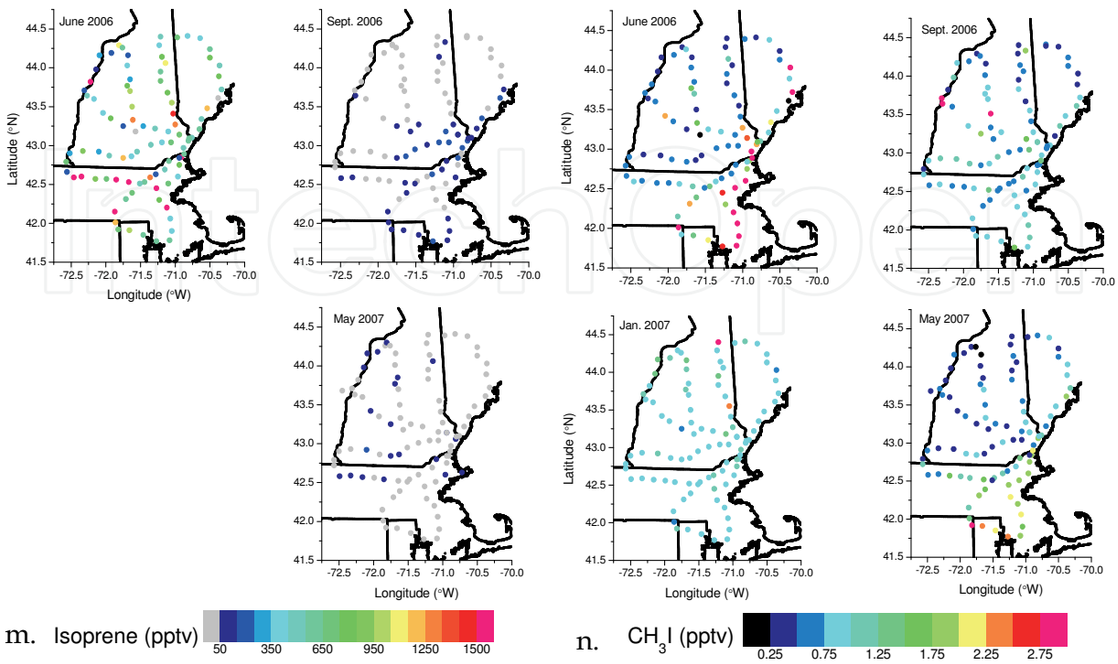

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Methyl iodide (photolysis lifetime of several days to ~1 week) is the dominant organic iodine compound in the atmosphere and is primarily emitted from oceanic sources (e.g., Bell et al., 2002). A recent study conducted in the eastern U.S. identified a significant terrestrial source of CH_3I as well (Sive et al., 2007). In addition to isoprene, CH_3I was the only compound with highest mean (~1.5±1.6 pptv) and maximum (8.5 pptv) mixing ratios during June (Table 1). At the TF monitoring site, CH_3I had a similar seasonal variation as isoprene (Sive et al., 2007). Overall, the range of CH_3I mixing ratios (~0.2-6 pptv) was comparable throughout New England during September, January, and May.

The anthropogenic halocarbons, C_2HCl_3 and C_2Cl_4, are primarily emitted from industrial sources (dry cleaning solvents, degreasing agents) (e.g., McCulloch and Midgley, 1996; Wang et al., 1995), and thus are excellent tracers of industrial emissions. The atmospheric distributions and budgets of C_2HCl_3 and C_2Cl_4 are of interest because they are (1) toxic air pollutants, (2) precursors to toxic oxidation products (phosgene, trichloroacetic acid) (e.g., Kindler et al., 1995), and (3) a potential source of chlorine atoms in the troposphere and stratosphere (Schauffler et al., 2003; Thompson et al., 2004). Similar to the pentanes and aromatics, the highest mean (7±18 pptv) and maximum (125 pptv) C_2HCl_3 was observed during May suggesting the influence of evaporative emissions (Table 1). This is consistent with results from the long-term measurements at TF which suggested that evaporative emissions from industrial sources contributed to the seasonal trend in ambient C_2HCl_3 (Russo et al., 2010b). Median C_2Cl_4 mixing ratios (14 pptv) were also highest in May, while mean (18±25 pptv) and maximum (205 pptv) C_2Cl_4 mixing ratios were observed in September (Table 1).

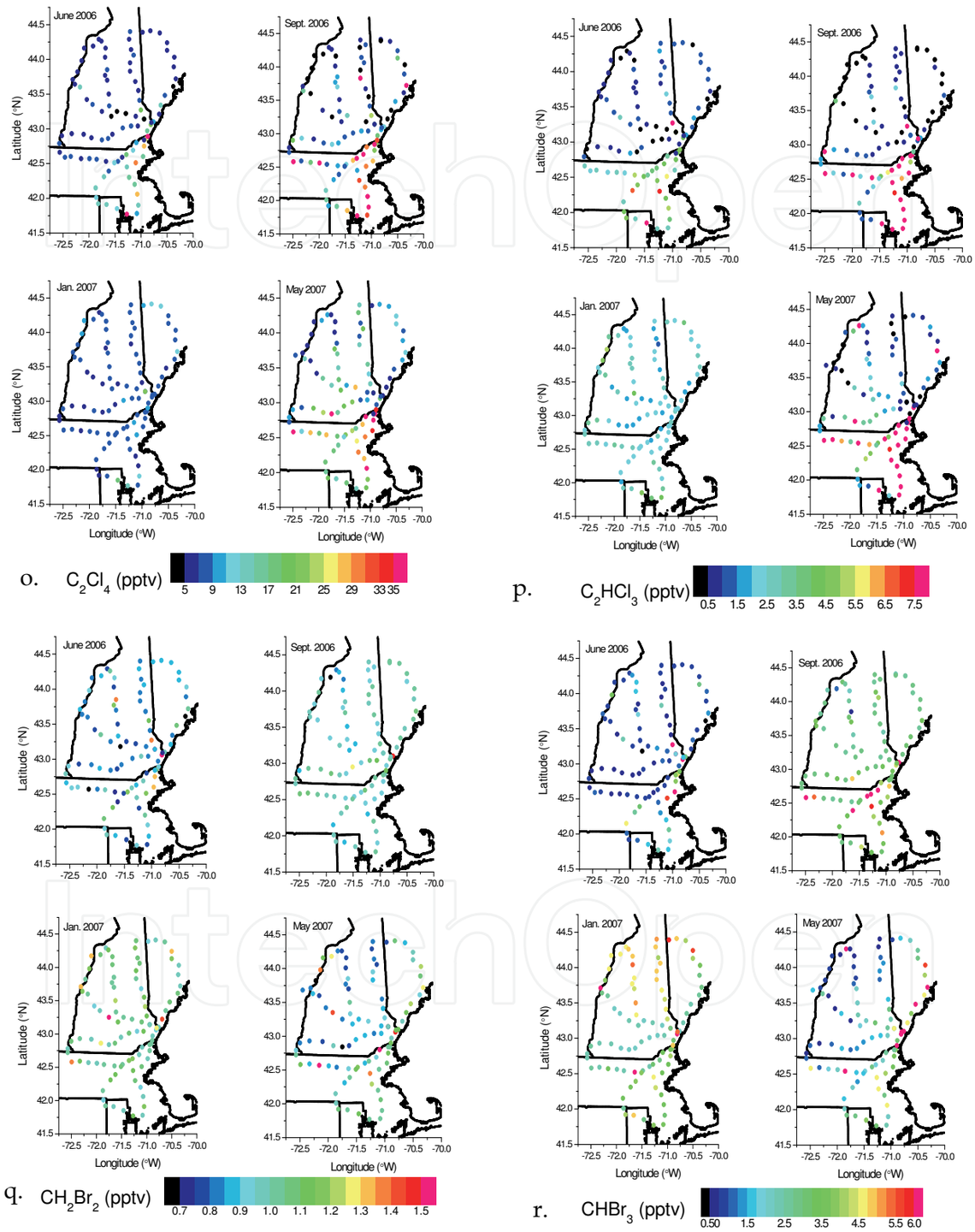

Fig. 2 .continued

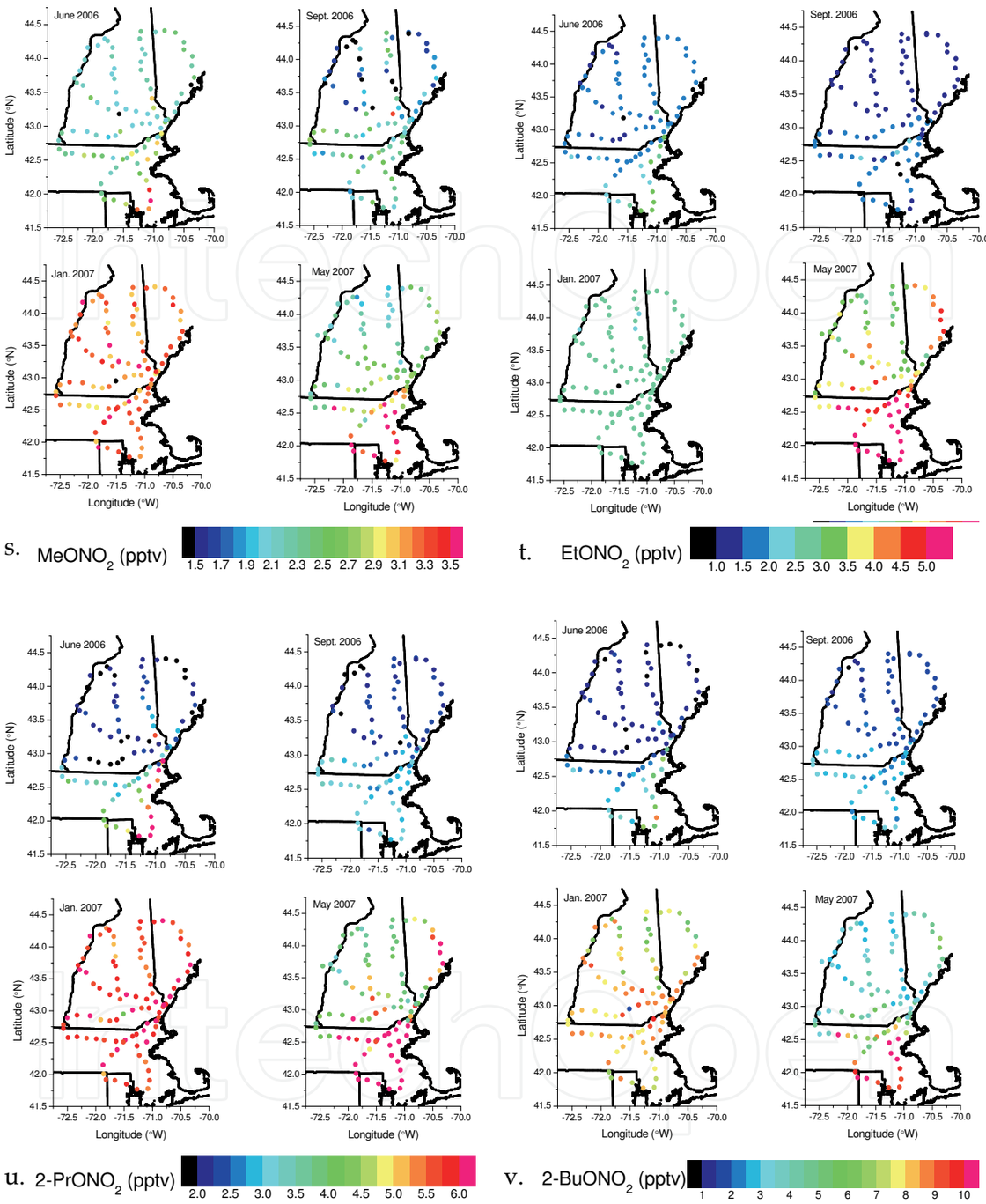

Fig. 2 continued

Short-lived brominated organic gases, such as bromoform ($CHBr_3$) (atmospheric lifetime 2-4 weeks) and dibromomethane (CH_2Br_2) (atmospheric lifetime several months), are the largest source of organic bromine to the atmosphere and are a potential source of bromine to the upper troposphere and stratosphere (e.g., Butler et al., 2007; Liang et al., 2010; Quack and Wallace, 2003). Consequently, the Br atoms and BrO radicals produced following the

photodissociation of organobromine compounds can impact catalytic O_3 destruction in the stratosphere (e.g., Schauffler et al., 1999). Organobromine compounds primarily originate from macroalgal and planktonic sources in surface seawater and enter the atmosphere through air-sea exchange processes. Anthropogenic sources (such as coastal power plants, chlorination of waste water and seawater, desalination) are minor (Quack and Wallace, 2003; Zhou et al., 2005). Coastal seawater and estuarine regions have been identified as a significant source of $CHBr_3$ and CH_2Br_2 to the atmosphere over New England (Zhou et al., 2005, 2008). Thus, $CHBr_3$ and CH_2Br_2 are useful tracers of marine emissions on New England air quality. Overall, the mean and median CH_2Br_2 mixing ratios were similar during the four surveys (~1 pptv) (Table 1). The median and mean $CHBr_3$ mixing ratios were comparable in September and January (~3.0-3.7 pptv) and higher than in June and May. However, both CH_2Br_2 and $CHBr_3$ had their highest peak mixing ratio in May. Furthermore, the highest $CHBr_3$ maximum mixing ratios and standard deviations were observed in June and May suggesting larger mixing ratio variability during the warmer months. This is consistent with the long-term TF data and may reflect variability in emission rates and/or the more rapid removal during summer (e.g., Zhou et al., 2005).

Alkyl nitrates are secondary compounds produced following the oxidation of their parent alkanes (i.e, methane, ethane, propane, n-butane) (Equations 1-6). The highest mean and median $MeONO_2$, 2-$PrONO_2$, and 2-$BuONO_2$ mixing ratios were observed in January, whereas $EtONO_2$ was highest in May (Table 1). The general distribution of the alkyl nitrates during the four spatial surveys was consistent with their long-term trends (Russo et al., 2010a). More specifically, 2-$PrONO_2$ (mean ~2.6-6 pptv) was the most abundant alkyl nitrate in June, September, and May while 2-$BuONO_2$ (~8 pptv) was dominant in winter.

3.2 Spatial variation and sources of VOCs

Specific NMHCs are primarily emitted by certain sources and thus can be used as tracers of those sources. The following source signature information is used to interpret and identify the various VOC sources in this work. The major sources of ethyne, benzene, and alkenes are incomplete combustion of fossil fuels, biomass burning, and vehicle exhaust emissions (e.g., Choi and Ehrman, 2004; Harley et al., 1992; 2001; McLaren et al., 1996). C_2-C_4 alkanes are emitted from natural gas, incomplete combustion, and unburned gasoline. Fuel evaporation emissions (caused by ambient temperature changes or residual engine heat during vehicle operation, resting, or refueling) are a dominant source of C_4-C_5 alkanes because of their high vapor pressures (Choi and Ehrman, 2004; Harley et al., 2001). The leakage of unburned liquefied petroleum gas (LPG) (during storage, distribution, or refilling) is a significant source of propane, i-butane, and n-butane and a minor source of alkenes (Blake and Rowland, 1995; Chen et al., 2001; Jobson et al., 2004). Aromatics are a major component of liquid gasoline and are often observed in vehicle exhaust because of incomplete combustion or leakage of unburned fuel (e.g., Harley et al., 2000, 2001; Kirchstetter et al., 1999). Toluene, ethylbenzene, m+p-xylene, and o-xylene are also emitted from fuel evaporation and industrial processes (i.e., painting, architectural coating, manufacturing, printing, degreasing solvents) (e.g., Monod et al., 2001). Furthermore, as mentioned in the preceding section, C_2Cl_4 and C_2HCl_3 are tracers of industrial/solvent emissions, CH_3I, CH_2Br_2, and $CHBr_3$ reflect the influence of marine emission sources, and alkyl nitrates are indicators of photochemical processing.

Typical summer daytime NMHC mixing ratios were prevalent throughout the majority of the study area during the June 2006 sampling campaign (with the exception of a few isolated sites with high propane, butane, and pentane mixing ratios). Furthermore, most VOCs exhibited a relatively uniform range of mixing ratios throughout ME, NH, eastern VT, and northern MA (Fig. 2). During the daytime, the atmosphere is well mixed which may have contributed to the low variability in mixing ratios throughout New England. A region of higher NMHC, C_2Cl_4, and C_2HCl_3 mixing ratios was observed in eastern MA and northern RI which was likely associated with increased urban activity near Boston, MA and Providence, RI (Fig. 2). This coincided with enhanced CH_3I (~3-8 pptv), $MeONO_2$ (2.5-3.5 pptv), and 2-$PrONO_2$ (4-8 pptv) mixing ratios which extended into southeast NH. In addition, in June, the highest $CHBr_3$ and CH_2Br_2 mixing ratios were observed in the seacoast region of NH and northeast MA, which likely reflects the influence of emissions from coastal algae (Fig. 2q, r).

Biogenic NMHCs had a persistent influence throughout New England during June, September, and May reflecting the highly forested nature of the region. Isoprene mixing ratios ranged from 130-3500 pptv during the daytime June survey (Fig. 2m). A corridor of elevated isoprene (>100 pptv) was located in southeastern NH during September. Sites with elevated α-pinene (range <50-5600 pptv) and β-pinene (range <50-2560 pptv) mixing ratios were distributed throughout New England overnight during September and May (Fig. 2l, Table 1).

An important feature of the VOC spatial distributions (Fig. 2) is the region of enhanced NMHC, C_2Cl_4, and C_2HCl_3 mixing ratios in eastern and northeastern MA particularly during September and May. This reflects strong anthropogenic emissions from the Boston, MA area, southeast NH, and the I-95 corridor which extends northeastward into Maine. The fact that VOCs which are tracers of different sources were all elevated in this region indicates that a complex mixture of emissions from natural gas, LPG, fuel evaporation, unburned gasoline, combustion, and industrial sources contributed to the air quality of the region.

Another notable observation is the region of enhanced propane mixing ratios (~2000-14000 pptv) in northern NH during both the September and May surveys indicating strong local emissions from LPG leakage (Fig. 2b). The absence of elevated ethane, ethyne, and i-pentane corresponding to the areas of high propane suggests that natural gas, combustion, and fuel evaporation sources were not important contributors to the high propane mixing ratios. Moreover, the high propane levels are noteworthy because they occurred during the warmer time of year (spring-fall) and thus are not likely associated with residential heating. Furthermore, in September, enhanced ethene (>500 pptv) and propene (>150 pptv) mixing ratios were colocated with sites exhibiting high propane providing additional evidence of an impact from LPG leakage (Fig. 2g, h).

A unique feature of the May regional survey is the corridor of enhanced $CHBr_3$ mixing ratios (~3-7 pptv) extending from southeast NH to the northeast along the Maine coast; CH_2Br_2 exhibited a similar, but less pronounced, trend with mixing ratios of ~1-1.2 (Fig. 2q,r). The elevated organobromine compound mixing ratios along the NH and ME coasts likely reflects the influence of marine emissions. Methyl iodide did not exhibit higher coastal mixing ratios illustrating the different marine sources or production mechanisms of brominated and iodinated halocarbons (e.g., Butler et al., 2007). Interestingly, high $EtONO_2$, 2-$PrONO_2$, and to a lesser extent $MeONO_2$, mixing ratios were colocated with several of the sites with enhanced $CHBr_3$ in southwest ME (Fig. 2). This is suggestive of a marine contribution to the alkyl nitrates (e.g., Atlas et al., 1993; Chuck et al., 2002) or the presence of an air mass containing a mixture of marine and photochemically processed emissions.

A significant feature of the January survey results is the uniform spatial distribution of VOC mixing ratios throughout the entire study area (Fig. 2). The low variability is illustrated by

the similar mean and median mixing ratios and the low standard deviations (Table 1). During the January 2007 sampling survey, the mean and median alkane, alkene, ethyne, benzene, toluene, ethylbenzene, C_2Cl_4, and C_2HCl_3 mixing ratios were lower than average (Russo et al., 2010b) indicating the presence of a clean air mass over New England. At TF, the wind direction was from the NW indicating the transport of clean, Canadian air to New England. The xylenes and alkyl nitrates were near typical January levels.

An interesting observation during the January survey is the elevated $CHBr_3$ (~4-6 pptv) and lower 2-$BuONO_2$ (~4-7 pptv) mixing ratios in northern NH and western ME compared to the rest of the region (Figure 2r, v). In contrast, throughout Massachusetts and southern NH, $CHBr_3$ and 2-$BuONO_2$ mixing ratios ranged from ~2-4 pptv and 6-10 pptv, respectively. It is unlikely that the elevated $CHBr_3$ in northern NH reflected marine emissions because the other marine tracers, CH_2Br_2 and CH_3I, do not exhibit a similar trend. This observation may reflect a local winter $CHBr_3$ source or a unique chemical signature from a source to the NW of New England and requires additional study.

3.3 Ambient ratios

In order to further characterize and identify the sources of VOCs in New England, ambient ratios were compared with emission ratios from the literature and from source samples collected near LPG refueling stations and gasoline storage containers throughout New Hampshire during summer 2004 and during the regional sampling trips. For example, typical ambient i-butane/n-butane ratios are ~0.2-0.3 for urban, fuel evaporation, and vehicle exhaust emissions, 0.46 for LPG emissions, and ~0.6 to >1 for natural gas (e.g., Barletta et al., 2002; Choi and Ehrman, 2004; Fujita, 2001; Goldan et al., 2000; Jobson et al., 1998, 2004; Lawrimore & Aneja, 1997; Mukerjee et al., 2004, Scheff and Wadden, 1993; B. Sive, unpublished data; Velasco et al., 2007; Watson et al., 2001). During the June and January surveys, the i-butane/n-butane ratio ranged from ~0.4-1.1 suggesting that a mix of vehicular, evaporative, LPG, and natural gas emissions influenced New England air quality (Fig. 3a). Higher i-butane/n-butane ratios were observed during September (range 0.4-2.9) and May (range 0.4-6) illustrating the influence of widespread liquefied petroleum and natural gas emissions. The highest mean (0.80) and median (0.72) i-butane/n-butane ratios were observed in September further supporting the presence of strong LPG emissions demonstrated by the high mean and median propane, ethene, and propene mixing ratios discussed in section 3.1.

The i-pentane/n-pentane emission ratios for several sources are fairly uniform with ranges of ~2.2-3.8 for vehicle exhaust, ~1.5-3 for liquid gasoline, and ~1.8-4.6 for fuel evaporation (e.g., Conner et al., 1995; Harley et al., 2001; Jobson et al., 2004; Lough et al., 2005; McGaughey et al., 2004; Mukund et al., 1996; Watson et al., 2001; Velasco et al., 2007). The mean and median i-pentane/n-pentane ratios during June, September, and May were similar at ~2.1 (range ~0.5-6.6) indicating the influence of emissions from exhaust, gasoline, and evaporative sources (Fig. 3b). The i-pentane/n-pentane ratio exhibits a seasonal variation at the TF site likely associated with enhanced fuel evaporation emissions of i-pentane in the summer (e.g., Rubin et al., 2006). Based on data from TF throughout 2004-2008, the i-pentane/n-pentane ratio is ~1.6 during the colder months (October-May) and increases to ~2.2 during the warmer months (June-September) (Russo et al., 2010b). The mean i-pentane/n-pentane ratio during the January regional survey was 1.6±0.1 which is consistent with the long-term measurements.

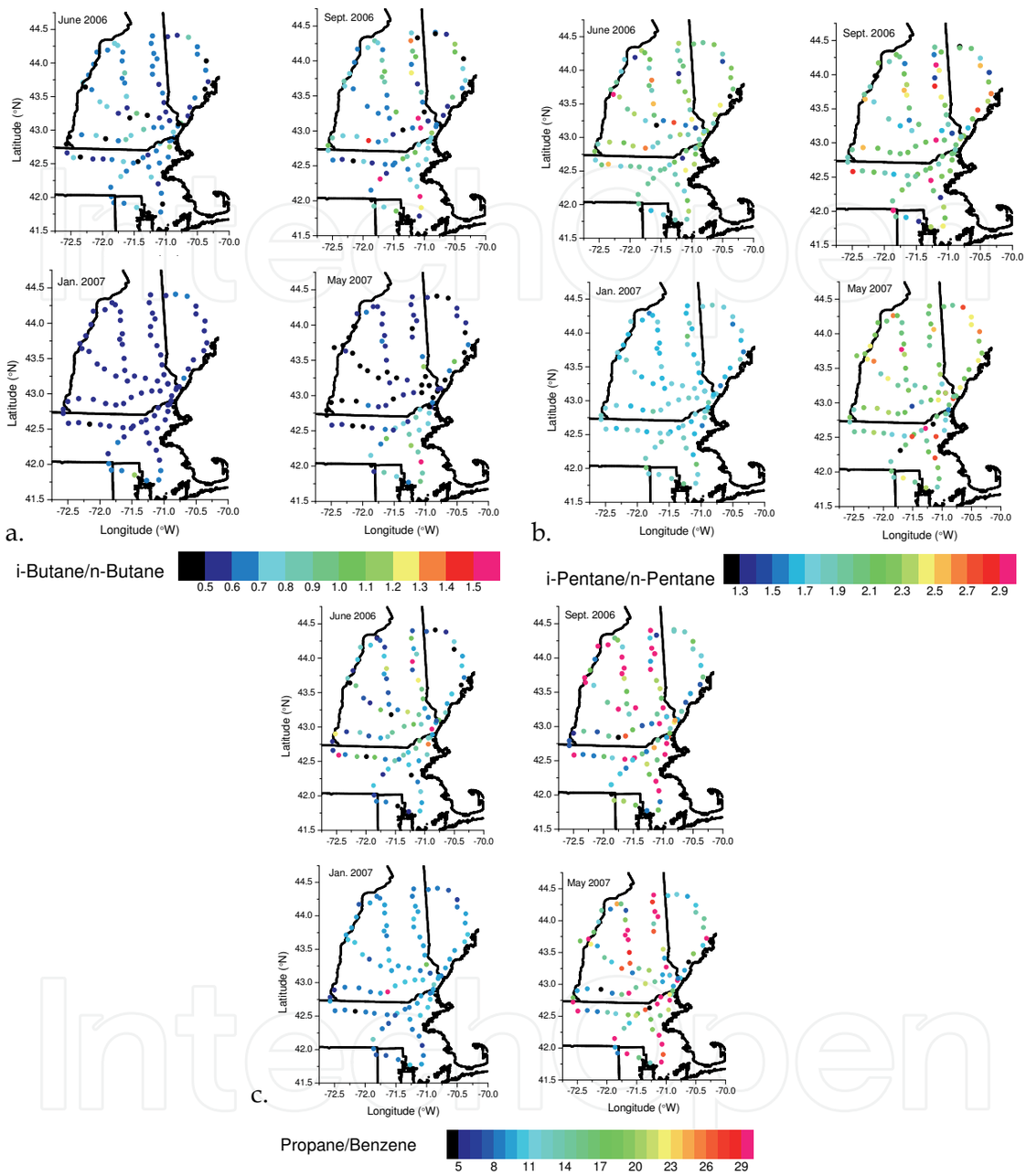

Fig. 3. Ambient NMHC ratios during the four regional surveys. The format is the same as in Figure 2. (a) i-butane/n-butane, (b) i-pentane/n-pentane, (c) propane/benzene.

A useful technique to characterize sources is to compare the ratio of two compounds with different sources but similar photochemical lifetimes. The ratio should remain relatively constant because neither compound will be removed preferentially during transport; thus the ratio can be assumed to equal the emission ratio (e.g., Parrish et al., 1998). An excellent

example is to compare ratios between propane, benzene, and ethyne because their rate constants for reaction with OH are similar to within ≤30% of each other (e.g., Atkinson et al., 2006). Propane is a tracer of liquefied petroleum gas while benzene and ethyne are tracers for vehicle exhaust and incomplete combustion. During the four regional surveys, the propane/benzene ratio ranged from 2-145 (with the exception of one site with a ratio of 0.3). The mean (~24) and median (~16) propane/benzene ratios were similar in September and May and higher than in June and January (mean ~9 and 13, respectively) (Fig. 3c). Similarly, the average propane/ethyne ratios were higher in September (5.6±6.1) and May (4.8±5.0) compared to June (2.2±2.2) and January (2.1±0.8). These results are additional evidence of the widespread influence from LPG leakage and refilling during all seasons throughout New England and indicate a stronger relative impact from LPG, natural gas, or evaporative emissions relative to combustion.

3.4 Regional emission rates

Ambient emission rates of speciated VOCs are required for developing regional budgets, implementing effective control strategies, and evaluating emission inventories and air quality models. However, emission rate estimates based on ambient data 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, emission rates are usually lumped into specific classes (i.e., alkane, alkene, aromatic, biogenic). A major reason for the lack of regional VOC emission rate estimates is the difficulty associated with differentiating between local, regional, and distant sources. In order to reduce this complication, we focused on measurements obtained when it was determined that air mass mixing was minimal.

In order to estimate speciated emission rates, 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 New England using measurements from the TF field site (i.e., Russo et al., 2010b; Sive et al., 2007; Talbot et al., 2005; White et al., 2008; Zhou et al., 2005). 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., Gusten et al., 1998; Hastie et al., 1993; Talbot et al., 2005). Therefore, advection and vertical mixing of air masses can be neglected. Under these conditions, we can assume that a change in NMHC mixing ratios reflects local sources or sinks. Two criteria were used for identifying nights when a stable inversion layer developed: (1) wind speeds <1 m s^{-1} and (2) O_3 < 10 ppbv. On both the nights of September 21-22, 2006 and May 29-30, 2007 at TF, O_3 decreased to less than 10 ppbv and the wind speed was stable at ~0.2 m s^{-1} demonstrating that a stable NBL developed (Figs. 4a and 5a). Another indication of a stable NBL is the significant increase in CO_2 mixing ratios. On both nights, CO_2 increased from background levels (~375 ppmv (parts per million by volume)) to near 440 ppmv reflecting local emissions from vegetation respiration or anthropogenic sources. Furthermore, the NMHC mixing ratios increased substantially compared to before the development of the NBL. For example, on September 21-22, propane mixing ratios were a factor of 6 higher and the butanes, pentanes, ethyne, and benzene were factors of 2-4 higher under the NBL compared to the 3 hours prior to sunset (~18:00 EDT) (Fig. 4b). Similarly, on May 29-30 at TF, propane, butanes, pentanes,

ethyne, and aromatic mixing ratios increased by factors of ~1.5-6 while α-pinene and β-pinene were factors of 13 and 20, respectively, higher under the NBL (Figs. 5b,c). Moreover, as demonstrated in Figure 5, the propane and α-pinene mixing ratios at TF are within the range observed at the five additional sampling sites indicating that the emission rates calculated using measurements at TF are representative of the region.

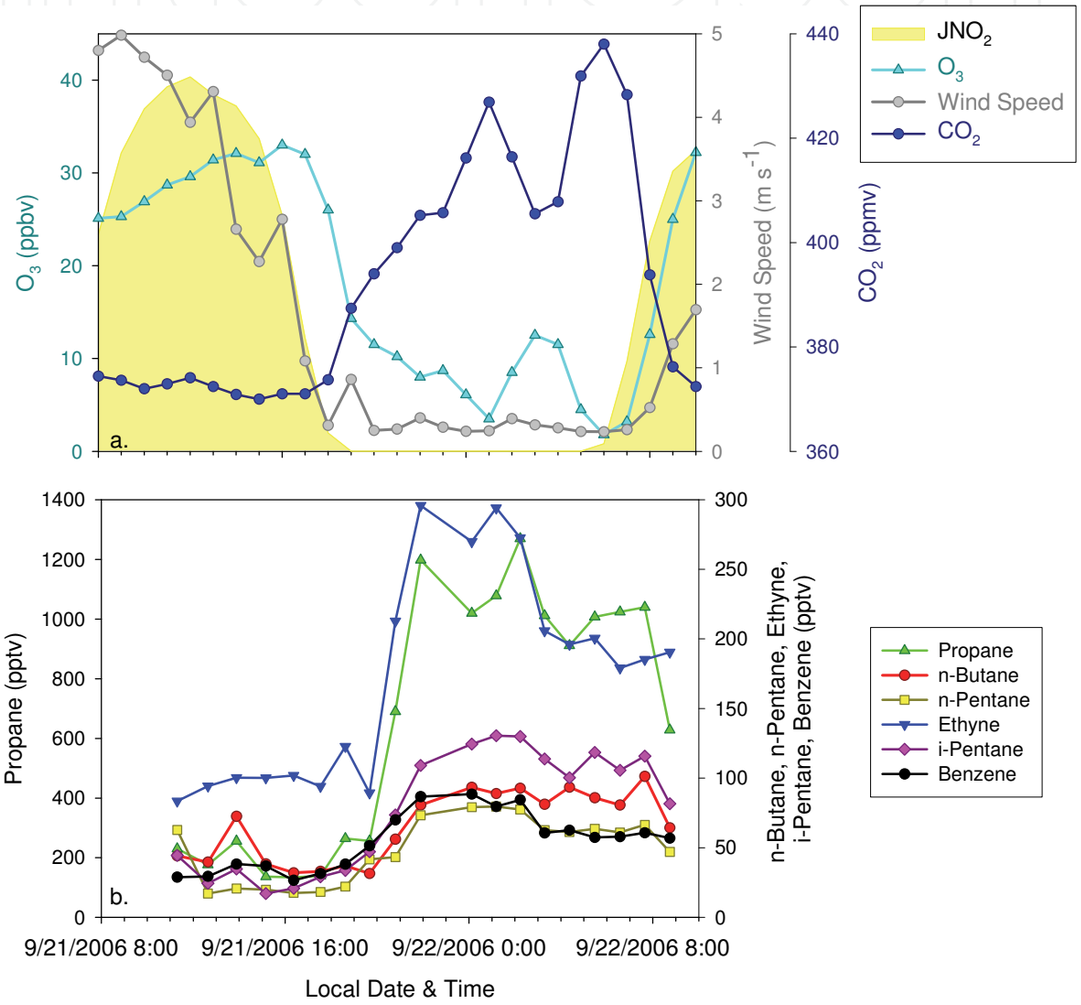

Fig. 4. Trace gas, wind speed, and nitrogen dioxide photolysis rate (J_{NO2}, indicator of when sunlight is available) between 08:00 September 21 to 08:00 September 22, 2006 (EDT) at the Thompson Farm field site in Durham, NH. (a) hourly average O_3 (ppbv), CO_2 (ppmv), and wind speed (m s^{-1}) and (b) propane (left axis), ethyne, n-butane, i-pentane, n-pentane, and benzene (right axis) (pptv).

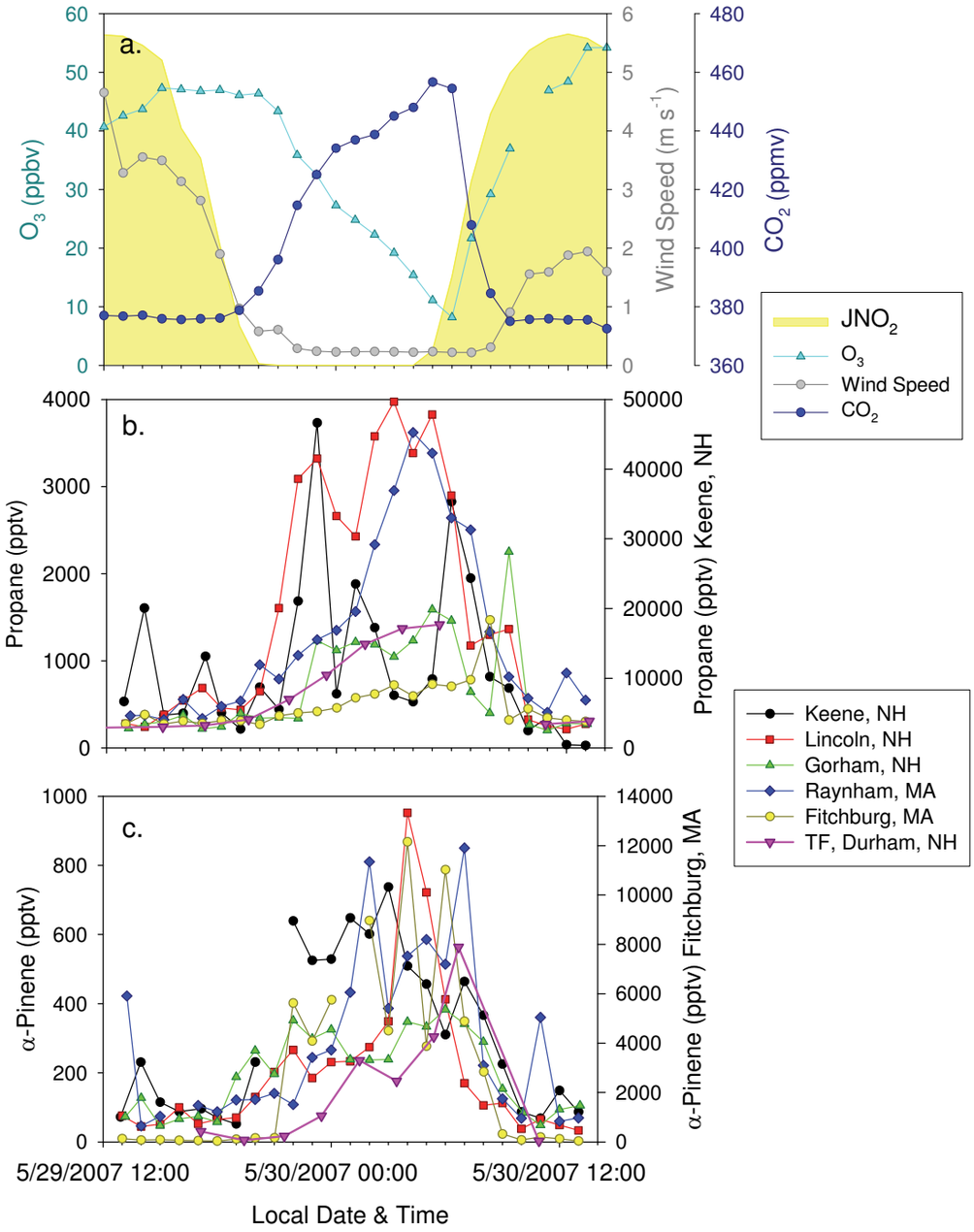

Fig. 5. (a) Hourly average O_3 (ppbv), CO_2 (ppmv), wind speed (m s^{-1}), and J_{NO2} at Thompson Farm 12:00 May 29 to 13:00 May 30, 2007 (EDT). (b) Propane mixing ratio (pptv) at six diurnal sampling sites throughout New Hampshire and Massachusetts. The right axis shows the propane mixing ratio at the Keene, NH site. (c) same as (b) but for α-pinene. The right axis shows the α-pinene mixing ratio in Fitchburg, MA.

Emission rates (ER) 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 hours) by the boundary layer height:

$$ER = \left[\frac{dC}{dt}\right] \times H \quad (1)$$

As shown by Eq. 1, the emission rate estimates are directly proportional to the nocturnal boundary layer height. Stable nocturnal boundary layer heights typically range from ~50-200 m at midlatitude continental locations and vary with meteorological conditions, time of day, and season (e.g., Gusten et al., 1998; Hastie et al., 1993; McKendry and Lundgren, 2000; Talbot et al., 2005; White et al., 2003); thus we chose 125 m as a representative value for the TF site (e.g., Mao et al., 2008; Sive et al., 2007; Talbot et al., 2005; White et al., 2008; Zhou et al., 2005). If H = 50 m or 200 m is used in Eq. 1, the emission rate estimates vary by ± 60%.

The emission rates of several NMHCs are shown in Table 2. During both September 2006 and May 2007, the propane emission rate (~18 x 10^9 molec. cm^{-2} s^{-1}) at TF was an order of magnitude larger than the other NMHCs ((~0.5-6) x 10^9 molec. cm^{-2} s^{-1}) on these calm nights reflecting local emissions rather than boundary layer dynamics or transport from a distant source. In fact, the propane emission rate may be larger than estimated here. For example, at the rural Lincoln, NH site in northwest NH, propane increased by ~1220 pptv/hour (from ~650 to 4000 pptv) whereas propane only increased by ~300 pptv/hour at TF (Fig. 5b). Furthermore, these results indicate that high propane emission rates from northern New England occur during each season. These large propane emission rates are significant, particularly because of the rural nature of this region. LPG use as a heating and cooking fuel is widespread throughout northern New England (e.g., EIA, 2005). Assuming the emission rate calculated for TF is applicable to all of New Hampshire, potentially over 20 tons of propane are emitted on a daily basis (Table 2); ~1-10 tons of C_4-C_5 alkanes, benzene, and toluene may be emitted per day. Because propane is relatively long-lived compared to other NMHCs, large inputs to air masses transported off of the continent and across the Atlantic Ocean could significantly impact tropospheric O_3 production, particularly in downwind locations, such as Europe.

Emission rates estimated using the same method during summers 2003 and 2004 (White et al., 2008) and winter 2006 (Russo et al., 2010b) are also included for comparison (Table 2). The emission rates calculated in this work are consistent with the summer and winter emission rates presented in White et al. (2008) and Russo et al. (2010b). Both the summer 2003 and 2004 ((3-20) x 10^9 molecules cm^{-2} s^{-1}) and May 2007 (~5 x 10^9 molecules cm^{-2} s^{-1}) emission rates illustrate the potential for significant monoterpene emissions from New England. Monoterpenes are extremely reactive in the atmosphere during spring and summer (lifetime of hours) and thus can contribute to O_3 production. Furthermore, the oxidation of monoterpenes produces low volatility products which can subsequently nucleate or condense onto preexisting aerosol particles and produce SOA (e.g., Atkinson and Arey, 2003; Hoffman et al, 1997).

The emission rates for a specific NMHC, which represent different seasons and years, agree within the given stated uncertainty (Table 2). This is an important result because it suggests that the emission rate of NMHCs from New Hampshire, and possibly all of New England, does not vary significantly with season or year. Thus, these emission rates may be useful for regional air quality modeling studies.

	Emission Rate (molecules cm^{-2} s^{-1}) x 10^9				New Hampshire Emission Rate (Mg/day)		
	Summers 2003 & 2004[a]	Winter 2006[b]	Sept. 21-22, 2006[c]	May 29-30, 2007[d]	Winter 2006[b]	Sept. 2006[c]	May 2007[d]
Propane	9-23	42±25	17±12	19±12	61±37	25±18	28±17
i-Butane	0.2-1	3.2±2.0	0.9±0.6	2.2±1.7	6.1±3.8	1.7±1.1	4.3±3.2
n-Butane	0.2-1.4	3.6±2.3	1.3±0.8	5.4±3.4	6.9±4.4	2.5±1.6	10.4±6.6
i-Pentane	2	2.4±1.5	1.9±1.2	2.3±1.5	5.8±3.6	4.5±2.8	5.5±3.6
n-Pentane		1.4±0.8	1.0±0.6	1.5±1.0	3.3±2.0	2.3±1.5	3.6±2.4
Ethyne		7.4±4.9	4.0±2.8		6.4±4.2	2.4±2.4	
Benzene		1.6±1.1	0.6±0.5	0.2±0.2	4.3±2.8	0.5±0.5	0.5±0.5
Toluene		2.7±1.7		1.8±1.2	8.2±5.3		5.6±3.7
m+p-Xylene		1.3±0.8		0.6±0.5	4.4±2.9		2.2±1.8
o-Xylene		0.5±0.3		0.2±0.2	1.8±1.1		0.8±0.6
α-Pinene	20			5.8±3.8			20.4±17
β-Pinene	3			5.3±3.5			18.6±16

[a]White et al. (2008), [b]Russo et al. (2010b), [c,d]This work

Table 2. Emission rates (molecules cm^{-2} s^{-1}) of C_3-C_{10} NMHCs calculated using data from the Thompson Farm field site on the nights of September 21-22, 2006 and May 29-30, 2007. The uncertainty was were calculated by propagating the standard error of the linear regression between the change in NMHC concentration per unit time and the assumed variation in nocturnal boundary layer height (125 m±75 m). Emission rates for summers 2003 and 2004 and winter 2006 were estimated in previous works and are included for comparison. Assuming the estimated emissions are representative of the region, the rates were extrapolated to the state of New Hampshire (Mg/day) using a land area of 2.3 x 10^{10} m^2.

4. Summary

The objective of this analysis was to present an overview of the VOC distribution (C_2-C_{10} nonmethane hydrocarbons, tetrachloroethene, trichloroethene, methyl iodide, dibromomethane, bromoform, methyl nitrate, ethyl nitrate, 2-propyl nitrate, 2-butyl nitrate) in the atmosphere over New England during four regional surveys (June 21, 2006, September 21-22, 2006, January 10-11, 2007, May 22-23, 2007). The seasonal and spatial variation of VOCs during the four surveys was discussed and put in context with the general seasonal trends of VOCs at the Thompson Farm field site in Durham, NH. Additionally, VOCs sources were identified and emission rates of several NMHCs were estimated. Future and ongoing research will include detailed analysis of the meteorological conditions on the days when regional surveys were conducted to determine the source regions more precisely and the influence of atmospheric dynamics on the VOC behavior, examination of additional trace gas (O_3, CO, NO, NO_y, SO_2) data from TF, estimation of

emission rates from diurnal sampling sites located throughout ME, NH, and MA, and in depth comparisons with emission ratios and the long-term continuous VOC data from TF.

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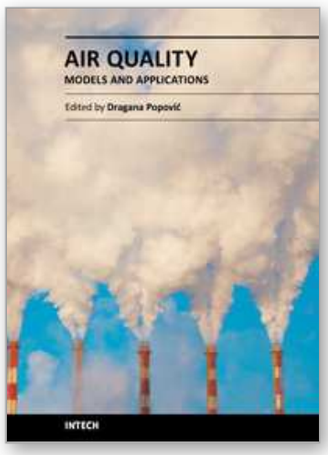

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