

Temporal variability, sources, and sinks of C₁-C₅ alkyl nitrates in coastal New England

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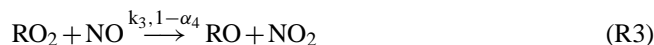
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Abstract. Seven C₁-C₅ alkyl nitrates were measured both on the mainland and off the coast of New Hampshire using gas chromatographic techniques. Five separate data sets are presented to characterize the seasonal and diurnal trends and the major sources and loss processes of these compounds. Based on in situ measurements conducted at the University of New Hampshire (UNH) Atmospheric Observing Station at Thompson Farm (TF) located in southeast NH during winter (January–February) 2002, summer (June–August) 2002, summer (July–August) 2004, and on daily canister samples collected at midday from January 2004–February 2008, the median total alkyl nitrate mixing ratio (ΣRONO_2) was 23–25 pptv in winter and 14–16 pptv in summer. During summers 2002 and 2004, MeONO₂ decreased overnight and reached minimum hourly average mixing ratios in the early morning. Comparison with wind speed and trace gas trends suggested that dry deposition contributed to the early morning MeONO₂ minimum which is a previously unaccounted for removal mechanism. The mean dry deposition rate and velocity of MeONO₂ was estimated to be $-0.5 \text{ nmol m}^{-2} \text{ hr}^{-1}$ and 0.13 cm s^{-1} , respectively. Results from ambient air and surface seawater measurements made onboard the NOAA R/V Ronald H. Brown in the Gulf of Maine during the 2002 New England Air Quality Study and from ambient canister samples collected throughout the Great Bay estuary in August 2003 are also presented. Comparisons between the alkyl nitrate trends with anthropogenic and marine tracers suggest that a marine source of alkyl nitrates is not significant in coastal New England. Given the apparent prominence of a secondary source, comparisons be-

tween observed and predicted alkyl nitrate/parent hydrocarbon ratios were made which demonstrated that background mixing ratios have a continuous and prevalent influence on the alkyl nitrate distribution.

1 Introduction

Alkyl nitrates are secondary products of hydrocarbon (RH) oxidation in the presence of nitrogen oxides ($\text{NO}_x = \text{NO} + \text{NO}_2$) and represent a link between the atmospheric carbon and nitrogen cycles (Reactions 1–4). The resulting alkyl radical (R) quickly reacts with O₂ to form an alkyl peroxy radical (RO₂). Further reaction with nitric oxide (NO) yields an alkoxy radical (RO) and nitrogen dioxide (NO₂) or an alkyl nitrate (RONO₂):



where k_1 , k_2 , k_3 , k_4 , and k_6 are reaction rate constants, J_5 is the photolysis rate constant, and α_1 and α_4 are the reaction branching ratios. The primary removal mechanisms from the atmosphere are photolysis and reaction with the hydroxyl



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radical (OH) (Reactions 5 and 6). Photolysis is dominant for the shorter-chain (C₁-C₃) alkyl nitrates while OH oxidation becomes a more important loss process for the larger alkyl nitrates (Roberts, 1990; Clemitshaw et al., 1997; Talukdar et al., 1997; Flocke et al., 1998). Reactions (1–4) demonstrate that alkyl nitrates share a common photochemical production mechanism with ozone (O₃), as O₃ formation follows the photolysis of the NO₂ formed in Reaction (R3). The formation of alkyl nitrates serves as a sink for NO_x and for the RO and RO₂ radicals, and therefore, impacts the O₃ production efficiency (Atkinson et al., 1982; Ranschaert et al., 2000). Alkyl nitrates may be transported long distances because of their long lifetimes and serve as a temporary reservoir for NO_x ultimately leading to O₃ production in remote regions (Clemitshaw et al., 1997; Flocke et al., 1998; Roberts et al., 1998).

Alkyl nitrates are a component of total reactive nitrogen (NO_y = NO_x + HNO₃ + NO₃ + N₂O₅ + organic nitrates), and their relative contribution to NO_y varies with location. It should be noted that the term organic nitrate refers to several types of compounds, including monofunctional alkyl nitrates, peroxyacetyl nitrates, and other multifunctional organic nitrate compounds. Some recent studies (i.e., Day et al., 2003; Perring et al., 2009) have used the term total alkyl nitrates (ΣRONO₂) to refer to nonspeciated measurements of several organic nitrate classes including isoprene nitrates, hydroxyalkyl nitrates, multifunctional organic nitrates, and the monofunctional alkyl nitrate compounds included in this work. In continental regions, the monofunctional alkyl nitrates typically comprise less than 10% of NO_y because of the close proximity to primary NO_x emissions (e.g., Shepson et al., 1993; Flocke et al., 1998; Thornberry et al., 2001; Simpson et al., 2006). In contrast, they may constitute a much larger proportion of NO_y in remote regions, such as the equatorial marine boundary layer (20–80%) (Talbot et al., 2000; Blake et al., 2003a) or the Arctic (~10–20%) (Muthuramu et al., 1994).

Characterizing alkyl nitrates may help explain imbalances in the atmospheric NO_y budget. Discrepancies between surface deposition rates determined from the sum of the individual NO_y compounds compared to the measured total NO_y deposition suggests that all the species contributing to the total deposition are not being accounted for (e.g., Nielsen et al., 1995; Lefer et al., 1999; Horii et al., 2006). The shortfall is often largest in photochemically processed air masses and is usually attributed to unidentified alkyl and multifunctional organic nitrates (e.g., Nielsen et al., 1995; Munger et al., 1998; Horii et al., 2006). Consequently, research on the contribution of organic nitrogen to atmospheric nitrogen deposition and the impact on ecosystem functioning has been gaining importance (Cornell et al., 2003).

In addition to their secondary photochemical source, primary emissions of light alkyl nitrates from the ocean (Atlas et al., 1993; Chuck et al., 2002; Moore and Blough, 2002; Blake et al., 2003a) and biomass burning have been observed

(Simpson et al., 2002). However, information on the relative influence of primary marine and secondary anthropogenic sources of alkyl nitrates in coastal regions is limited (e.g., Roberts et al., 1998; Chuck et al., 2002; Simpson et al., 2006). Recent modeling results suggest that the photolysis of alkyl nitrates emitted from the tropical Pacific Ocean, and the subsequent production of NO₂, may increase O₃ production by up to 20% (Neu et al., 2008). This demonstrates the importance of identifying alkyl nitrate sources and quantifying their mixing ratios in marine environments.

The seacoast region of New Hampshire is downwind of the heavily populated and urban northeastern US corridor and is in an excellent location for studying the chemical composition of air masses transported from the continental US to the North Atlantic. Previous research has shown that this area is influenced by marine, vegetative, and anthropogenic sources of nonmethane hydrocarbons (NMHCs) and halocarbons (Sive et al., 2007; Varner et al., 2008; White et al., 2008, 2009; Zhou et al., 2005, 2008) and is strongly impacted by boundary layer dynamics (Mao and Talbot, 2004a; Talbot et al., 2005). In this work, we characterize the seasonal and diurnal variability, sources, and sinks of C₁-C₅ alkyl nitrates at an inland site (Thompson Farm) and in coastal New England. A portion of the alkyl nitrate data was obtained as a component of the 2002 and 2004 New England Air Quality Studies (NEAQS). The objectives of NEAQS were to examine the transport, formation, and distribution of air pollutants in New England and the Gulf of Maine. Additionally, we incorporate data from a one day intensive study throughout the Great Bay estuary in August 2003 and daily canister samples collected during 2004–2008 at Thompson Farm in order to further describe the temporal variability and atmospheric distribution of alkyl nitrates.

2 Experimental

2.1 Thompson Farm gas chromatography system: 2002 and 2004

Measurements of C₂-C₁₀ NMHCs, C₁-C₂ halocarbons, and C₁-C₅ alkyl nitrates were made during winter (11 January to 1 March) and summer (1 June to 31 August) 2002 and summer (1 July to 15 August) 2004 at the University of New Hampshire Atmospheric Observing Station at Thompson Farm (TF) (43.11° N, 70.95° W, elevation 24 m) in Durham, New Hampshire (Fig. 1). TF is surrounded by a mixed forest and is located ~20 km inland from the Gulf of Maine, 5 km northwest of the Great Bay estuary, and ~100 km north of Boston, MA. Samples were analyzed onsite by an in situ automated gas chromatography (GC) system equipped with two flame ionization detectors (FID) for detecting NMHCs and two electron capture detectors (ECD) for measuring halocarbons and alkyl nitrates (described in detail by Zhou et al., 2005, 2008). The measurement precision for each of the

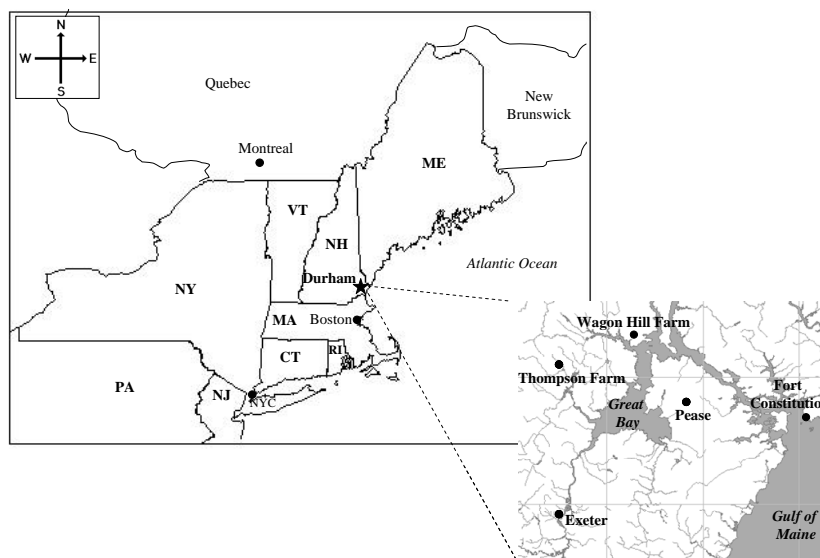


Fig. 1. Map detailing the location of Thompson Farm in Durham, New Hampshire, and (inset) the sampling sites used during the Great Bay experiment.

hydrocarbons, halocarbons, and alkyl nitrates ranged from 0.3–15%. Specifically, the alkyl nitrate measurement precision is conservatively 5% for mixing ratios above 5 pptv and 10% for mixing ratios below 5 pptv. The accuracy of the alkyl nitrate measurements is 10–20%, and their detection limit is 0.01 pptv. The alkyl nitrates discussed in this work are methyl nitrate (MeONO₂), ethyl nitrate (EtONO₂), 2-propyl nitrate (2-PrONO₂), 1-propyl nitrate (1-PrONO₂), 2-butyl nitrate (2-BuONO₂), 2-pentyl nitrate (2-PenONO₂), and 3-pentyl nitrate (3-PenONO₂). In this work, we define the total alkyl nitrate mixing ratio (Σ RONO₂) as the sum of the seven individual C₁-C₅ compounds measured at TF.

2.2 GC System on the NOAA R/V Ronald H. Brown

During 30 July to 6 August 2002, ambient air and surface seawater samples were collected onboard the NOAA Research Vessel Ronald H. Brown off the coasts of New Hampshire and Boston, MA. An automated in situ GC measured MeONO₂, 2-PrONO₂, and 2-BuONO₂ in addition to several hydrocarbons and halocarbons. Ambient air was sampled from ~15 m above the sea surface and traveled approximately 80 m to the GC located near the back of the ship. A portion of this air flow was drawn by the sample concentrator and a 1000 cc sample was cryogenically trapped. Water from the ship's clean seawater system flowed to a Weiss type equilibrator. Air was drawn from the equilibrator at 200 ccm for determining concentrations of the stripped gases from the surface seawater. After the ambient air or equilibrator sample was concentrated, it was injected to a two gas chromatograph system. One GC quantified halocarbons and alkyl nitrates with an ECD, and the other GC measured C₂-C₆ hydrocarbons by FID (Zhou et al., 2005).

2.3 Canister samples

2.3.1 Great Bay experiment

In addition to the routine measurements at TF (Sect. 2.1), an intensive study was conducted from 18:00 on 18 August to 19:00 on 19 August 2003 (local time) to examine the influence of marine derived halocarbons from the Great Bay estuary throughout southeast NH. The Great Bay is a 2140 hectare estuary located ~16 km inland from the coast of NH. The study area consisted of TF and 4 sites located in southern NH: Downtown Boat Launch, Exeter (42.98° N, 70.95° W), Fort Constitution (FC), Newcastle (43.07° N, 70.71° W), Pease Weather Station, Portsmouth (43.08° N, 70.82° W), and Wagon Hill Farm (WHF), Durham (43.13° N, 70.87° W) (Fig. 1 inset). At each of the four sites, an evacuated two-liter electropolished stainless steel canister was filled to ambient pressure each hour. The samples were returned to the laboratory at UNH for analysis on a three GC system equipped with 2 FIDs, 2 ECDs, and a mass spectrometer (MS). The laboratory GC system has been previously described in Sive et al. (2005), White et al. (2008), and Zhou et al. (2005, 2008). The FIDs were used for detecting C₂-C₁₀ NMHCs, and the ECDs measured C₁-C₅ alkyl nitrates and C₁-C₂ halocarbons. Oxygenated VOCs, sulfur compounds, halocarbons, and several NMHCs were detected by the MS. The measurement precision for each of the hydrocarbons, halocarbons, and alkyl nitrates ranged from 0.1–12%. The alkyl nitrate measurement precision for the canister samples is conservatively 3–4% for mixing ratios above 5 pptv and <10 % for mixing ratios below 5 pptv. The accuracy of the alkyl nitrate canister measurements is 10–20%, and the detection limit is 0.01 pptv.

2.3.2 Thompson Farm daily canister samples

Measurements of C₁-C₅ alkyl nitrates from daily canister samples collected throughout 12 January 2004 to 8 February 2008 are also presented. The ambient air samples were collected at approximately noon (local time) from the top of the 12 m tower at TF. The 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; fall: September, October, November. Note that the data includes five winter seasons (2004–2008) and four spring, summer, and fall seasons (2004–2007). The samples were analyzed in the lab at UNH every 1–3 months for a large suite of volatile organic compounds (C₂-C₁₀ NMHCs, C₁-C₅ alkyl nitrates, C₁-C₂ halocarbons, and selected oxygenated and sulfur compounds) using the same three GC system described in Sect. 2.3.1. The primary working standards for the canister analysis system were two calibrated whole air samples contained in 36 l electropolished low pressure pontoons (~350 psi). Due to overlapping periods when different working standards were being used throughout the four years, mixing ratios were verified and recalibrated (if/when necessary), and were cross referenced with other calibrated whole air and synthetic standards maintained by our laboratory. Furthermore, we have conducted several instrument intercomparison studies to verify that the measurements from the in situ TF GC and canister samples made over multiple years are comparable and to ensure the stability of VOCs within our canisters (see Sive et al., 2005; Zhou et al., 2008; Russo et al., 2010).

2.4 Ancillary measurements

Hourly average measurements of O₃, carbon monoxide (CO), carbon dioxide (CO₂), and NO_y made at TF during winter and summer 2002, summer 2004, and 18–19 August 2003 were also used in this analysis. The instruments used were a Thermo Environmental Instruments (TEI) model 49C-PS using ultraviolet spectroscopy at 254 nm for O₃, a custom modified TEI model 48CTL using absorption of infrared radiation at 4600 nm for CO, a Licor model 7000 differential infrared absorption instrument for CO₂, and a TEI model 42C using chemiluminescence measured NO_y (Mao and Talbot, 2004a, b; Talbot et al., 2005). Meteorological parameters (wind speed, wind direction, temperature) were measured with a Met One model 014A anemometer.

3 Temporal variation of alkyl nitrates at Thompson Farm

Three distinct data sets are combined to provide a robust characterization of the temporal variation of alkyl nitrates in New Hampshire. The continuous in situ measurements made at Thompson Farm during winter 2002 and summers 2002 and 2004 and the four years (2004–2008) of daily canister

samples allow both the short (diurnal to seasonal) and long (seasonal to interannual) term trends to be described (Figs. 2 and 3).

3.1 Seasonal variation

The hourly in situ GC data and the daily canister samples gave comparable seasonal statistics with mean (\pm standard deviation) total alkyl nitrate mixing ratios (Σ RONO₂= sum of individual C₁-C₅ alkyl nitrates) of 26 (\pm 7) pptv in winter and 19 (\pm 13) pptv in summer (Tables 1 and 2). The nearly 30% lower Σ RONO₂ mixing ratio in summer was driven by the reduced levels of C₃-C₅ alkyl nitrates which were typically highest in late winter-early spring (February–March) and exhibited a broad minimum from May–October (Fig. 3, Table 2). In contrast, the monthly mean and median mixing ratios of the longer-lived MeONO₂ and EtONO₂ were more uniform all year, particularly in 2004–2005, and both compounds exhibited low day-to-day variability in late fall-winter (Fig. 3a). Methyl and ethyl nitrate mixing ratios were lowest in mid-to-late summer through the fall (July–October) (Table 2).

The relative contributions of the individual C₁-C₅ alkyl nitrates to Σ RONO₂ were nearly the same in the continuous measurements and in the daily samples (Tables 1 and 2). 2-propyl nitrate was generally the most abundant, and 2-BuONO₂ was at comparable to slightly higher levels in winter-early spring. In all study years, 2-BuONO₂ exhibited the most pronounced seasonal variation with approximately a factor of 2–3 higher median mixing ratio in winter than in summer. While the relative contribution of 2-BuONO₂ to Σ RONO₂ decreased from winter to summer, the contributions from MeONO₂ and EtONO₂ increased. As a result, MeONO₂, EtONO₂, and 2-BuONO₂ made nearly equal contributions to Σ RONO₂ in summer (15–20%). The pentyl nitrates and 1-PrONO₂ were the least abundant components of Σ RONO₂ all year. Overall, the alkyl nitrate mixing ratios and distributions at TF were comparable to trends observed at other North American sites, such as Michigan (Ostling et al., 2001), Colorado and the eastern US (Stroud et al., 2001), the southeastern US (Bertman et al., 1995), Summit, Greenland (Swanson et al., 2003), Ontario, Canada (Shepson et al., 1993), Alert NW Territories, Canada (Muthuramu et al., 1994), and Chebogue Point, Nova Scotia (Roberts et al., 1998).

Two possible explanations for the seasonal variation of alkyl nitrates at TF are (1) their different tropospheric lifetimes throughout the year and (2) different regional scale transport patterns. The alkyl nitrate lifetimes are shorter in summer than in winter because of higher OH concentrations and faster photolysis rates which may explain the lower C₃-C₅ alkyl nitrate mixing ratios (winter lifetimes ~1–3 weeks, summer lifetimes \leq ~1 week) (Atkinson, 1990; Atkinson et al., 2006; Clemitshaw et al., 1997; Talukdar et al., 1997). In addition, the longer lifetimes of MeONO₂ and

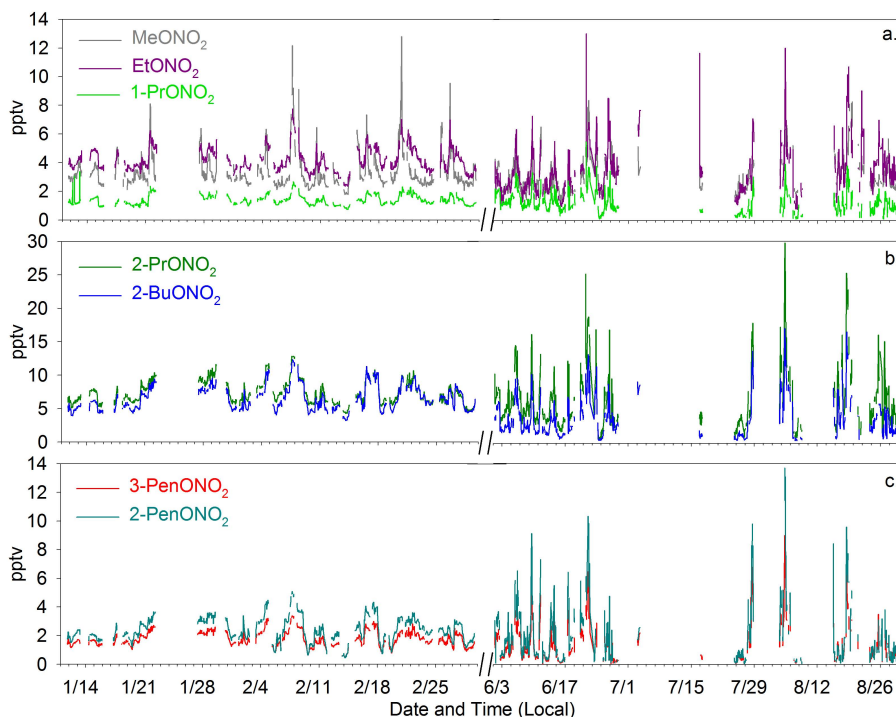


Fig. 2. Time series of (a) MeONO₂, EtONO₂, 1-PrONO₂, (b) 2-PrONO₂, 2-BuONO₂, and (c) 2-PenONO₂, 3-PenONO₂ (pptv) during winter (11 January–1 March) and summer (1 June–31 August) 2002. Note: there is a break in the x-axis during March–May 2002.

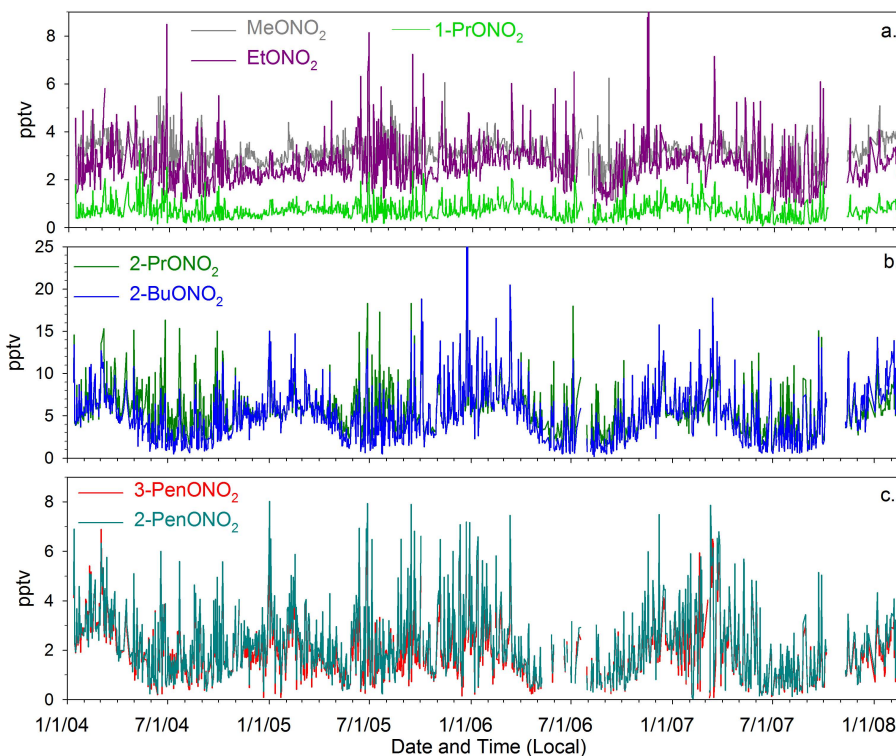


Fig. 3. Time series of (a) MeONO₂, EtONO₂, 1-PrONO₂, (b) 2-PrONO₂, 2-BuONO₂, and (c) 2-PenONO₂, 3-PenONO₂ (pptv) from daily canister samples collected at Thompson Farm during 12 January 2004 to 8 February 2008.

Table 1. Seasonal mean, standard deviation (SD), median, and number of samples (*N*) of alkyl nitrates at Thompson Farm during Winter (11 January–1 March) and Summer (1 June–31 August) 2002 (mixing ratios in pptv). % Σ RONO₂ is the median contribution of each alkyl nitrate to the total alkyl nitrate mixing ratio in both seasons. %NO_y is the median contribution of Σ RONO₂ to NO_y in both seasons (i.e., seasonal median value of Σ RONO₂/NO_y).

	Winter	Summer
MeONO ₂		
Mean (SD)	3.4 (1.3)	3.1 (1.3)
Median (<i>N</i>)	3.0 (735)	2.7 (775)
% Σ RONO ₂	12	17
EtONO ₂		
Mean (SD)	4.2 (0.8)	3.4 (1.6)
Median (<i>N</i>)	4.0 (720)	3.0 (773)
% Σ RONO ₂	16	19
2-PrONO ₂		
Mean (SD)	7.4 (1.7)	6.5 (4.7)
Median (<i>N</i>)	6.9 (731)	4.9 (771)
% Σ RONO ₂	27	30
1-PrONO ₂		
Mean (SD)	1.4 (0.3)	1.2 (0.8)
Median (<i>N</i>)	1.3 (716)	1.1 (783)
% Σ RONO ₂	5	6
2-BuONO ₂		
Mean (SD)	6.5 (1.8)	3.6 (3.1)
Median (<i>N</i>)	6.1 (739)	2.6 (768)
% Σ RONO ₂	24	16
3-PenONO ₂		
Mean (SD)	1.8 (0.5)	1.4 (1.4)
Median (<i>N</i>)	1.7 (738)	0.9 (697)
% Σ RONO ₂	7	5
2-PenONO ₂		
Mean (SD)	2.4 (0.8)	2.0 (2.1)
Median (<i>N</i>)	2.2 (735)	1.2 (671)
% Σ RONO ₂	9	7
Σ RONO ₂		
Mean (SD)	26.3 (6.9)	20.2 (13.6)
Median (<i>N</i>)	24.9 (748)	15.9 (797)
% NO _y	0.20	0.60

EtONO₂ likely contribute to their more homogeneous distribution throughout the year (winter lifetimes \sim 1 month, summer lifetimes \sim 1 week) (Figs. 2 and 3; Tables 1 and 2). Additionally, previous research has documented that the chemical composition of air masses transported to New England strongly depends on both the season and source region. For example, north-northwesterly winds typically transport clean, Canadian air masses to New England that contain low O₃, CO, NO_y, and hydrocarbon mixing ratios and that

are representative of background conditions (Munger et al., 1996; Moody et al., 1998; Shipham et al., 1998). This transport pattern is more frequent during the winter. In contrast, air masses containing enhanced levels of anthropogenic emissions are primarily observed during transport from the south and west. This air mass transport pathway occurs most frequently in summer (Moody et al., 1998; Fischer et al., 2004; Mao and Talbot, 2004b). Consequently, the seasonal variation in the dominant source region(s) of alkyl nitrates and their precursors may contribute to the seasonal trends in ambient alkyl nitrate mixing ratios observed at TF.

3.2 Diurnal variation

The chemical and physical processes controlling the atmospheric distribution of alkyl nitrates can be elucidated through examination of their diurnal trends. During winter and summer 2002, the hourly average (\pm standard error) C₁-C₅ alkyl nitrate mixing ratios were lowest at \sim 05:00 to 07:00 (local time), increased throughout the morning, and reached peak levels in the afternoon (Fig. 4a, only MeONO₂ summer data shown). The morning increase likely reflects a combination of vertical mixing, advection, and photochemical production. This is supported by comparison to the O₃, wind speed, and *J*_{NO₂} diurnal cycles (Fig. 4a). Following sunrise, surface heating causes the nocturnal boundary layer (NBL) to dissipate and air masses from the residual layer above the NBL are mixed toward the surface resulting in increased O₃ and alkyl nitrate mixing ratios. This illustrates that the development and dissipation of the NBL can contribute to the C₁-C₅ alkyl nitrate trends observed at TF in both winter and summer.

The finding of an early morning MeONO₂ minimum is particularly intriguing because its lifetime in the atmosphere is much longer than one day. For example, the lifetime of MeONO₂ resulting from oxidation and photolysis is \sim 5 days in summer and over one month in winter (assuming [OH] = 6×10^5 (winter) and 2×10^6 (summer) molecules cm⁻³; *k*_{OH-MeONO₂} = 2.3×10^{-14} cm³ molecule⁻¹ s⁻¹ (Atkinson et al., 2006); *J*_{MeONO₂} \sim 2.2×10^{-6} s⁻¹ in summer (Roberts, 1990), and 0.29×10^{-6} s⁻¹ in winter (<http://cprm.acd.ucar.edu/Models/TUV>)). However, the decrease in mixing ratios throughout the night indicates the predominance of removal processes occurring on a time scale \leq 1 day. Processes potentially contributing to the early morning minima include losses from chemistry, deposition, decomposition, or mixing with air masses having lower mixing ratios. Chemical reactions and decomposition can be neglected because the rates of reaction with oxidants potentially available at night, such as O₃ and the nitrate radical (NO₃), are insignificant for alkyl nitrates (Becker and Wirtz, 1989; Atkinson, 1990) and because alkyl nitrates are thermally stable at tropospheric temperatures (Roberts, 1990). Transport or mixing may play a role in regulating nighttime ambient mixing ratios. However, the observation of decreasing MeONO₂ on nights with

Table 2. Monthly mean, standard deviation (SD), median, and number of samples (*N*) from the daily canister samples collected at Thompson Farm throughout 12 January 2004–8 February 2008 (mixing ratios in pptv). % Σ RONO₂ is the median contribution of each alkyl nitrate to the total alkyl nitrate mixing ratio each month. %NO_y is the median contribution of Σ RONO₂ to NO_y in each month.

	Jan.	Feb.	March	April	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
MeONO₂												
Mean (SD)	3.0 (0.5)	3.4 (0.4)	3.4 (0.5)	3.2 (0.4)	3.2 (0.4)	3.1 (0.9)	3.0 (0.9)	3.0 (0.9)	3.0 (0.9)	3.0 (0.6)	3.2 (0.5)	3.1 (0.4)
Median (<i>N</i>)	3.3 (135)	3.4 (109)	3.4 (107)	3.2 (95)	3.2 (103)	3.0 (99)	2.9 (98)	2.9 (107)	2.9 (106)	2.9 (91)	3.1 (101)	3.1 (100)
% Σ RONO ₂	14	13	13	16	20	21	19	20	19	19	15	14
EtONO₂												
Mean (SD)	2.7 (0.6)	2.8 (0.6)	3.2 (0.9)	2.9 (0.7)	2.7 (0.8)	2.9 (1.5)	2.6 (1.2)	2.2 (1.0)	2.3 (1.1)	2.5 (0.8)	2.8 (1.2)	2.6 (0.6)
Median (<i>N</i>)	2.7 (136)	2.7 (108)	3.0 (107)	2.8 (95)	2.6 (103)	2.5 (99)	2.4 (92)	1.9 (105)	2.0 (111)	2.2 (92)	2.5 (102)	2.4 (102)
% Σ RONO ₂	11	11	12	14	16	17	15	14	14	14	12	11
2-PrONO₂												
Mean (SD)	6.2 (2.0)	6.8 (1.8)	7.7 (2.8)	6.2 (2.1)	4.9 (2.3)	5.0 (3.7)	5.4 (3.4)	4.6 (2.8)	4.9 (3.2)	5.1 (2.8)	5.9 (2.0)	6.3 (2.8)
Median (<i>N</i>)	5.8 (137)	6.4 (108)	6.8 (108)	5.6 (95)	4.1 (105)	3.6 (101)	4.6 (98)	3.7 (107)	4.0 (111)	4.0 (92)	5.4 (102)	5.4 (102)
% Σ RONO ₂	24	25	27	28	27	25	29	27	27	26	26	25
1-PrONO₂												
Mean (SD)	0.8 (0.3)	0.9 (0.3)	0.9 (0.3)	0.8 (0.3)	0.7 (0.5)	0.7 (0.5)	0.7 (0.4)	0.6 (0.3)	0.6 (0.4)	0.7 (0.4)	0.7 (0.3)	0.8 (0.4)
Median (<i>N</i>)	0.8 (137)	0.8 (108)	0.8 (108)	0.7 (94)	0.6 (105)	0.6 (101)	0.6 (98)	0.5 (107)	0.5 (109)	0.5 (92)	0.6 (102)	0.7 (102)
% Σ RONO ₂	3	3	3	4	4	4	4	4	4	3	3	3
2-BuONO₂												
Mean (SD)	7.2 (2.7)	7.5 (2.6)	7.7 (3.0)	5.2 (2.0)	3.2 (1.8)	3.2 (2.7)	3.1 (2.2)	2.9 (2.1)	3.6 (2.8)	4.5 (3.1)	6.1 (2.6)	7.0 (4.1)
Median (<i>N</i>)	6.8 (135)	6.8 (108)	6.9 (106)	4.7 (95)	2.8 (105)	2.1 (101)	2.7 (98)	2.3 (107)	2.7 (111)	3.2 (92)	5.1 (102)	5.7 (102)
% Σ RONO ₂	28	26	27	23	18	15	17	17	18	21	25	26
3-PenONO₂												
Mean (SD)	2.4 (1.1)	2.8 (1.2)	2.7 (1.6)	1.7 (0.9)	1.4 (1.0)	1.7 (1.5)	1.5 (1.0)	1.5 (1.0)	1.6 (1.2)	1.7 (1.0)	2.1 (0.9)	2.2 (1.2)
Median (<i>N</i>)	2.3 (132)	2.8 (105)	2.2 (105)	1.5 (95)	1.1 (96)	1.2 (83)	1.2 (96)	1.2 (103)	1.4 (105)	1.4 (89)	1.9 (101)	1.9 (98)
% Σ RONO ₂	9	11	9	8	7	8	8	8	9	9	9	9
2-PenONO₂												
Mean (SD)	2.8 (1.3)	3.0 (1.3)	3.0 (1.7)	1.9 (1.0)	1.5 (1.1)	2.1 (1.8)	1.6 (1.1)	1.7 (1.2)	1.9 (1.4)	1.8 (1.2)	2.5 (1.2)	2.6 (1.5)
Median (<i>N</i>)	2.6 (132)	3.0 (106)	2.6 (104)	1.7 (95)	1.3 (96)	1.4 (83)	1.3 (95)	1.5 (103)	1.5 (106)	1.4 (89)	2.2 (101)	2.3 (98)
% Σ RONO ₂	11	12	10	8	8	10	8	11	10	9	10	11
ΣRONO₂												
Mean (SD)	25.1 (7.6)	26.8 (7.3)	28.2 (10.0)	22.0 (6.5)	17.3 (7.2)	18.0 (11.7)	17.6 (9.4)	16.2 (8.7)	17.6 (10.5)	19.1 (8.9)	23.2 (7.8)	24.1 (9.4)
Median (<i>N</i>)	23.3 (134)	25.1 (109)	24.2 (108)	20.5 (95)	15.2 (105)	13.6 (101)	16.2 (98)	14.3 (107)	15.3 (111)	15.5 (92)	20.7 (102)	21.5 (101)
%NO _y	0.6	0.8	1.0	0.9	0.7	0.6	0.6	0.6	0.7	0.6	0.5	0.5

calm winds and a stable inversion layer is indicative of a process besides advection or vertical mixing of different air masses (Sect. 3.2.1). Additionally, it is typically thought that alkyl nitrates do not undergo wet and dry deposition because of their low solubility (e.g., Roberts, 1990, Shepson et al., 1996). However, wet deposition of alkyl nitrates has been reported in some studies (e.g., Hauff et al., 1998). Moreover, the Henry's Law constant of MeONO₂ (2.0 M/atm) is similar to peroxyacyl nitrates (PANs) (1–5 M/atm) (Kames and Schurath, 1992; Sander, 1999). Several factors, including surface wetness, contribute to the surface deposition of PANs (Schrimpf et al., 1996; Sparks et al., 2003; Doskey et al., 2004; Turnipseed et al., 2006). Therefore, it seems likely that surface deposition contributed to the MeONO₂ diurnal behavior at TF.

3.2.1 Evidence for MeONO₂ dry deposition

Two criteria were used to identify the nights when a stable NBL formed: (1) O₃ ≤ 5 ppbv and (2) wind speed < 0.5 m/s. During summer 2002, there were only 4 nights when concurrent measurements of alkyl nitrates, O₃, and wind speed

were available and the atmospheric conditions met these criteria. For example, on the evenings of 7 and 13 June 2002, O₃ decreased to ≤ 3 ppbv and the wind speed was near zero (Fig. 5). Both chemistry and surface deposition contribute to the nocturnal removal of O₃ at TF (Talbot et al., 2005). On both nights, MeONO₂ tracked O₃ suggesting a similar removal mechanism for both compounds. As discussed above, chemistry is an unlikely explanation for the decreasing MeONO₂ which points toward deposition as the cause of the MeONO₂ removal. Ozone and wind speed remained at low levels through ~ 07:00 on the following morning indicating that a stable nocturnal inversion layer had developed. Under these stable and calm conditions, the surface air was isolated from the air in the remnant boundary layer aloft which inhibits vertical mixing and advection (e.g., Hastie et al., 1993; Gusten et al., 1998; Talbot et al., 2005). Therefore, variations in trace gas mixing ratios reflect local sources or sinks. This is illustrated by the large increase in carbon monoxide (CO) and NMHC mixing ratios on both nights resulting from local petroleum, natural gas, vehicular, or combustion emissions (e.g., Talbot et al., 2005; White et al.,

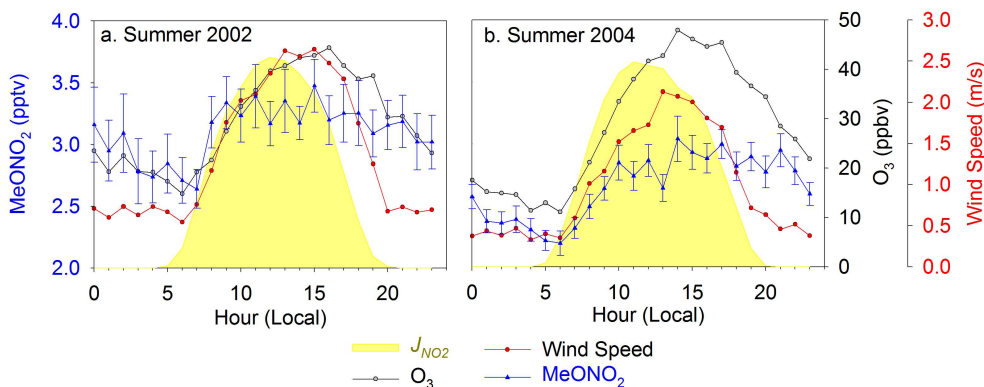


Fig. 4. Hourly average (local time) O₃ (ppbv), wind speed (m/s), J_{NO_2} (yellow shaded curve), and MeONO₂ (\pm standard error) (pptv) using all data during (a) 1 June to 31 August 2002 and (b) 1 July to 15 August 2004 at Thompson Farm.

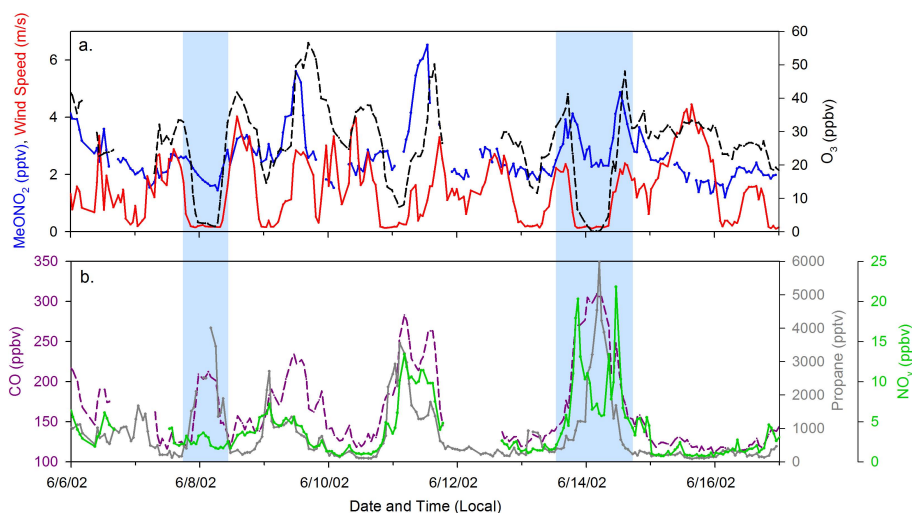


Fig. 5. Time series of (a) MeONO₂ (pptv), O₃ (ppbv) and wind speed (m/s) and (b) CO (ppbv), propane (pptv) and NO_y (ppbv) at Thompson Farm during 6–16 June 2002. Shaded regions are the nights of 8 and 14 June.

2008) (Fig. 5b; propane is shown as a representative example of the NMHC behavior). Additionally, NO_y decreased (Fig. 5b) mainly because of wet and dry deposition of HNO₃ and NO₂ (e.g., Munger et al., 1998). The slightly different NO_y trend on both nights is likely a combination of deposition and different air mass source regions. On 7–8 June, the wind direction shifted from easterly to southwesterly, whereas the wind was from the south-southwest throughout the entire day on 13 June and continuing into 14 June.

Additionally, measurements made at TF during summer (1 July–15 August) 2004 are included to provide further evidence for the surface deposition of MeONO₂. Similar to 2002, the hourly average MeONO₂ mixing ratios decreased overnight, were lowest during the early morning hours, and increased throughout the morning following the dissipation of the NBL (Fig. 4b). Based on our criteria, a strong NBL developed on nearly half of the nights during summer 2004. On approximately 80% of these nights, MeONO₂ decreased

concurrently with O₃ and wind speed (Fig. 6a, wind speed not shown). In addition, decreasing NO_y mixing ratios were observed on most of these nights. Non-depositing species, such as CO and NMHCs, exhibited the opposite trend with significantly increasing mixing ratios overnight and rapidly decreasing mixing ratios following dissipation of the NBL in the morning (Fig. 6b, propane and ethene are shown as representative examples of the CO and NMHC behavior).

It should be noted that our analysis is limited to MeONO₂ because the C₂-C₅ alkyl nitrates did not consistently exhibit nighttime depletion under the stable NBL. Methyl nitrate is more soluble (Henry's Law constant ~ 2.0 M/atm) than the C₂-C₅ alkyl nitrates (0.34–1.6 M/atm) (Kames and Schurath, 1992; Sander, 1999). Therefore, the greater solubility of MeONO₂ may explain the different behavior compared to the C₂-C₅ alkyl nitrates.

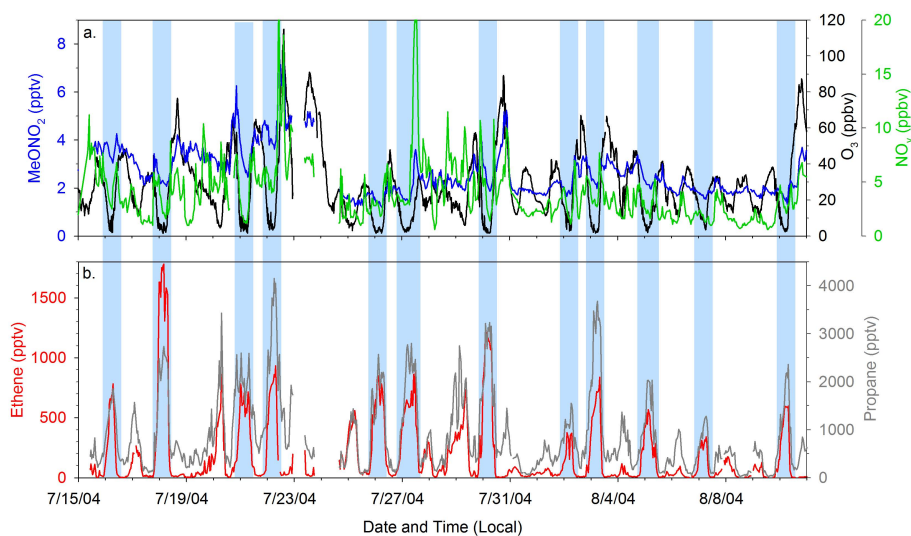


Fig. 6. Time series of (a) MeONO₂ (pptv), O₃ (ppbv), NO_y (ppbv) and (b) ethene and propane (pptv) at Thompson Farm during 15 July to 11 August 2004. Shaded regions are nights with O₃ ≤ 5 ppbv and wind speed < 0.5 m/s indicating that a strong and stable inversion layer had developed.

Table 3. Mean dry deposition flux ± standard deviation (SD) (nmol m⁻² hr⁻¹) and velocity ± SD (V_d) (cm s⁻¹) of MeONO₂. The range of dry deposition rates and velocities calculated for each night during summers 2002 and 2004 when a stable nocturnal boundary layer developed using the criteria that O₃ ≤ 5 ppbv and wind speed < 0.5 m/s are shown in parentheses. Fluxes were calculated from the linear regression between the change in MeONO₂ mixing ratios versus time (00:00 to 06:00, EDT=UTC-04:00). τ_d (=H/V_d) is the MeONO₂ lifetime (days) resulting from dry deposition. N is the number of nights included in the calculations for each summer.

	Flux ± SD (Range)	V _d ± SD (Range)	τ _d	N
Summer 2002	-0.51 ± 0.38 (-0.15 to -1.04)	0.13 ± 0.07 (0.04–0.20)	0.7–3.3	4
Summer 2004	-0.47 ± 0.32 (-0.17 to -1.2)	0.13 ± 0.07 (0.05–0.30)	0.5–2.6	16

The diurnal variation of MeONO₂ at TF provides evidence for a previously unaccounted for removal mechanism from the atmosphere and for a potential additional source of organic nitrogen to the surface. For each night when a stable NBL developed, the flux from the atmosphere to the surface and the dry deposition velocity (V_d) of MeONO₂ was estimated as follows:

$$\text{Flux} = \left[\frac{dC}{dt} \right] \cdot H = -C \cdot V_d \quad (1)$$

where *C* is the mean MeONO₂ concentration (molecules cm⁻³) between 00:00 to 06:00, *H* is the nocturnal boundary layer height, and (*dC/dt*) is the change in MeONO₂ concentration between 0:00 to 06:00. In these calculations, we assume a constant boundary layer height (*H*) of 125 m because it is a typical nocturnal boundary layer height for this site (e.g., Talbot et al., 2005; Sive et al., 2007; Mao et al., 2008; White et al., 2008; Zhou et al., 2005). However, it must be kept in mind that the resulting dry deposition flux and velocity estimates scale directly with the boundary layer

height which varies with meteorological conditions, time of day, and season (Talbot et al., 2005). The estimates of the dry deposition rate and velocity of MeONO₂ were similar during both summers and agree within the stated error bars suggesting that a relatively uniform amount of MeONO₂ is lost from the atmosphere to the surface (Table 3). The mean dry deposition rate of MeONO₂ was approximately -0.5 nmol m⁻² hr⁻¹ (range 0.18 to 1.47 g N ha⁻¹ yr⁻¹), and the dry deposition velocity was ~0.13 cm s⁻¹ (Table 3). To the best of our knowledge, these are the first estimates of the deposition rate and velocity of MeONO₂. Furthermore, the dry deposition lifetime (τ_d = H/V_d) of MeONO₂ was ~1–3 days (Table 3) which is shorter than the combined oxidation + photolysis lifetime (~5 days). The total lifetime of MeONO₂ resulting from deposition, oxidation, and photolysis is ~0.4–1.7 days in summer further illustrating that dry deposition is a likely explanation for the diurnal variation of MeONO₂ at TF.

3.2.2 Comparison with previous organic nitrogen dry deposition research

The MeONO₂ dry deposition flux and velocity values at TF are at the lower end of estimates compared to other organic nitrogen compounds at North American sites. For example, dry deposition velocities were estimated to be 0.65 cm s⁻¹ for isoprene nitrates (Giacopelli et al., 2005), 0.4 cm s⁻¹ for hydroxyalkyl nitrates (Shepson et al., 1996), and 0.1 to 0.6 cm s⁻¹ for peroxyacetyl nitrate (PAN) (Shepson et al., 1992; Schrimpf et al., 1996; Sparks et al., 2003; Doskey et al., 2004; Turnipseed et al., 2006; Wolfe et al., 2009). Additionally, nighttime V_d values for peroxyacetyl nitrate (MPAN) and peroxypropionyl nitrate (PPN) ranging from ~ 0.1 to 0.7 cm s⁻¹ with fluxes of -10 to -50 nmol m⁻² hr⁻¹, as well as PAN fluxes that were an order of magnitude larger (-140 to -260 nmol m⁻² hr⁻¹), have been observed over pine forests (Turnipseed et al., 2006; Wolfe et al., 2009).

Previous studies in the eastern US and Canada have discussed the potentially significant contribution from unmeasured organic nitrogen compounds to nitrogen deposition. For example, research conducted at Harvard Forest (HF) (a temperate deciduous forest ~ 110 km southwest of TF) concluded that the deposition of unmeasured organic nitrogen compounds could explain discrepancies between total NO_y and the sum of speciated NO_y compound measurements (Munger et al., 1996, 1998; Lefer et al., 1999; Horii et al., 2004, 2006). Additionally, studies conducted at several sites throughout Canada reported that "Other-NO_y" compounds (i.e., excluding HNO₃, NO₂, pNO₃⁻, PAN, PPN) contributed 9–38% to NO_y dry deposition (Zhang et al., 2009). Furthermore, measurements made at Duke Forest in North Carolina concluded that total dry nitrogen deposition (not including organic nitrate compounds) was potentially significantly underestimated (Sparks et al., 2008). Based on the total dry nitrogen deposition in eastern Canada (0.5–2.4 kg N ha⁻¹ yr⁻¹; Zhang et al., 2009) and at Duke Forest (7.9 kg N ha⁻¹ yr⁻¹; Sparks et al., 2008), as well as the MeONO₂ deposition rates estimated in this work, MeONO₂ contributes < 1% to the total N deposition. These results suggest that MeONO₂ constitutes a minor component of total N dry deposition. Nonetheless, our results provide supporting evidence that unaccounted for organic nitrogen compounds contribute to nitrogen dry deposition, and these compounds should be included in studies on the nitrogen budget in various ecosystems.

4 Sources of alkyl nitrates in coastal New England

The following discussion uses a combination of four separate VOC data sets, which are representative of three different environments, in order to identify the major source(s) of alkyl nitrates in southeastern New Hampshire by comparing their temporal and/or spatial distributions to characteristic source signatures and to NMHC and halocarbon trends.

4.1 Inland/coastal environment: Thompson Farm

The predominant source region and regional transport pathway of air masses to TF varies with season as discussed in Sect. 3.1. In order to determine whether the alkyl nitrate mixing ratios observed at TF depend upon the source region, the hourly average wind direction data from winter and summer 2002 was separated into four sectors (northeast (0–90°), southeast (90–180°), southwest (180–270°), and northwest (270–360°). In winter, the ΣRONO₂ mixing ratio was fairly uniform in the SW, NW, and NE sectors but was significantly higher ($p < 0.05$) in the SE sector, while in summer, the mean mixing ratio in both the SE and SW sectors was significantly higher ($p < 0.001$) than in the northern sectors (Table 4). It is not unexpected that enhanced mixing ratios would be observed during transport from the SE. Previous studies have shown that air masses that passed over east coast metropolitan areas and over the Atlantic Ocean can be transported inland to TF from the south-southeast by the sea breeze (Miller et al., 2003; Angevine et al., 2004; Mao and Talbot, 2004a; Zhou et al., 2008). Furthermore, in both seasons, the highest and lowest mean parent hydrocarbon (ethane, propane, *n*-butane, *n*-pentane) mixing ratios were observed in the southern and northern transport sectors, respectively (not shown). The high levels observed are consistent with the location of major urban and industrial regions to the west-southwest of New England. The sources of the precursor hydrocarbons observed at TF include fuel evaporation, vehicle exhaust, and natural and liquefied petroleum gas usage and leakage (White et al., 2008; Russo et al., 2010). These results point toward a continental source of alkyl nitrates which was most likely secondary production following hydrocarbon oxidation. Moreover, the highest mixing ratios of alkyl nitrates corresponded to events with enhanced mixing ratios of NMHCs and carbon monoxide. For example, the highest C₂-C₅ alkyl nitrate mixing ratios during winter 2002 were observed on 7 February under west-southwesterly winds (Fig. 2). Concurrent with the high alkyl nitrates were enhanced (above 90th percentile for winter) mixing ratios of CO (370–750 ppbv), ethane (4–7.2 ppbv), propane (5.7–11 ppbv), *n*-butane (1–3.7 ppbv), and *n*-pentane (0.3–0.5 ppbv).

The dominant and consistent contribution of 2-PrONO₂ and 2-BuONO₂ to ΣRONO₂ at TF over various years and time scales further corroborates that the major source of both alkyl nitrates was photochemical production from propane and *n*-butane, respectively (Tables 1 and 2). The C₃-C₄ alkanes are among the most abundant NMHCs at TF (Russo et al., 2010). Both 2-PrONO₂ and 2-BuONO₂ have been found to be the dominant alkyl nitrates at numerous continental locations (Ridley et al., 1990; Shepson et al., 1993; Ostling et al., 2001; Stroud et al., 2001; Blake et al., 2003b; Swanson et al., 2003; Simpson et al., 2003; 2006). This characteristic continental source signature reflects a balance between the increasing alkyl nitrate yield and the decreasing

Table 4. Mean (\pm standard deviation of the mean) mixing ratios of alkyl nitrates (pptv) in the northeast (NE, 0–90°), southeast (SE, 90–180°), southwest (SW, 180–270°), and northwest (NW, 270–360°) transport sectors during Winter and Summer 2002.

	Winter				Summer			
	NE	SE	SW	NW	NE	SE	SW	NW
MeONO ₂	3.6 ± 0.2	4.2 ± 0.2	3.2 ± 0.1	2.9 ± 0.1	2.4 ± 0.1	3.2 ± 0.1	3.4 ± 0.1	2.7 ± 0.1
EtONO ₂	4.2 ± 0.1	4.7 ± 0.1	4.0 ± 0.04	4.0 ± 0.1	2.6 ± 0.1	3.5 ± 0.1	3.6 ± 0.1	2.9 ± 0.1
2-PrONO ₂	7.3 ± 0.2	7.9 ± 0.1	7.1 ± 0.1	7.4 ± 0.1	4.2 ± 0.3	6.9 ± 0.4	7.3 ± 0.3	5.1 ± 0.3
1-PrONO ₂	1.5 ± 0.05	1.5 ± 0.03	1.3 ± 0.02	1.4 ± 0.02	1.0 ± 0.1	1.3 ± 0.1	1.4 ± 0.1	1.0 ± 0.1
2-BuONO ₂	6.4 ± 0.3	7.0 ± 0.1	6.3 ± 0.1	6.5 ± 0.1	2.1 ± 0.2	3.9 ± 0.2	4.2 ± 0.2	2.8 ± 0.2
3-PeONO ₂	1.8 ± 0.1	1.9 ± 0.04	1.7 ± 0.03	2.3 ± 0.05	0.7 ± 0.1	1.5 ± 0.1	1.6 ± 0.1	1.0 ± 0.1
2-PeONO ₂	2.4 ± 0.1	2.6 ± 0.1	2.3 ± 0.1	2.3 ± 0.1	0.9 ± 0.1	2.2 ± 0.2	2.5 ± 0.1	1.4 ± 0.1
ΣRONO ₂	26.2 ± 1.0	29.0 ± 0.6	25.5 ± 0.4	25.8 ± 0.5	13.3 ± 0.7	21.6 ± 0.0	22.6 ± 0.8	16.1 ± 0.9

lifetimes of both the parent alkane and alkyl nitrate with increasing carbon number (Atkinson et al., 1982; Flocke et al., 1991; 1998; Arey et al., 2001) as well as the distribution of parent hydrocarbons in a specific region. In contrast, in remote oceanic regions, the C₁-C₃ alkyl nitrates have been found to be supersaturated in the surface ocean (Chuck et al., 2002; Dahl et al., 2005) and positively correlated with marine halocarbons (Atlas et al., 1993; Blake et al., 1999, 2003a). Additionally, oceanic emissions of MeONO₂ were estimated to be a factor of $\sim 3-4$ larger than EtONO₂ in the Pacific (Blake et al., 2003a; Dahl et al., 2007) and Atlantic Oceans (Chuck et al., 2002). Although TF is often influenced by marine air masses originating from the SE and NE (Zhou et al., 2005, 2008), MeONO₂ and EtONO₂ were not correlated with marine halocarbons, and the year-round MeONO₂/EtONO₂ ratio averaged ~ 1 . This suggests that the MeONO₂ and EtONO₂ levels observed in seacoast New Hampshire were controlled by anthropogenic precursor source(s).

Furthermore, the C₃-C₅ alkyl nitrates were strongly correlated with each other in both winter and summer 2002 ($r^2 \sim 0.7-0.9$), and in all seasons throughout 2004–2008 ($r^2 \sim 0.60-0.96$). Ethyl nitrate exhibited slightly weaker correlations with the C₃-C₅ alkyl nitrates ($r^2 \sim 0.4-0.8$). In winter, MeONO₂ was poorly correlated with the other alkyl nitrates, whereas in summer 2002 and spring-fall 2004–2008, MeONO₂ was moderately correlated with the C₂-C₅ compounds ($r^2 \sim 0.3-0.6$). The weaker MeONO₂ and EtONO₂ correlations may be a consequence of their longer lifetimes or different sources. In addition, the C₁-C₅ alkyl nitrates tracked each other extremely well (Figs. 2 and 3) reflecting their similar photochemical and/or collocated hydrocarbon precursor sources.

4.2 Marine environment: measurements aboard the NOAA R/V Ronald H. Brown

Measurements of MeONO₂, 2-PrONO₂, and 2-BuONO₂ were made from ambient air and surface seawater samples collected onboard the NOAA R/V Ronald H. Brown during 30 July to 6 August 2002 as a component of the NEAQS 2002 campaign. Sampling occurred in Boston Harbor on 30–31 July and off the coast of New Hampshire from 1–6 August. 2-Propyl and 2-butyl nitrate were well correlated in air ($r^2 = 0.97$) and were positively, but weakly ($r^2 \sim 0.34$), correlated with MeONO₂ indicating that the alkyl nitrates shared a common source. In the air samples, MeONO₂, 2-PrONO₂, and 2-BuONO₂ ranged from 2–8, 4–30, and 2–16 pptv, respectively (Figs. 7a, c; 2-BuONO₂ not shown). In contrast, 2-PrONO₂ and 2-BuONO₂ mixing ratios in the surface seawater were lower and more uniform ($\sim 9-13$ pptv, 0.008–0.017 nmol L⁻¹ and 2–5 pptv, 0.002–0.006 nmol L⁻¹, respectively) (Fig. 7d). Methyl nitrate was more variable in the seawater but exhibited a similar range of mixing ratios ($\sim 1-6$ pptv, 0.007–0.051 nmol L⁻¹) as in the air samples (Fig. 7b). The saturation anomalies ((seawater concentration – air concentration/air concentration) * 100%) of MeONO₂, 2-PrONO₂, and 2-BuONO₂ ranged between $\pm 150\%$. The similar range of positive and negative saturation anomalies suggests that the New England coastal seawater was neither a net source nor sink of alkyl nitrates. These results are consistent with Chuck et al. (2002) and Reeves et al. (2007) who proposed that alkyl nitrates in northern hemisphere temperate waters were near equilibrium with the atmosphere. Similar to the TF results (Sect. 4.1), this limited data set from the Gulf of Maine during NEAQS 2002 does not provide conclusive evidence for a marine source of light alkyl nitrates in this region.

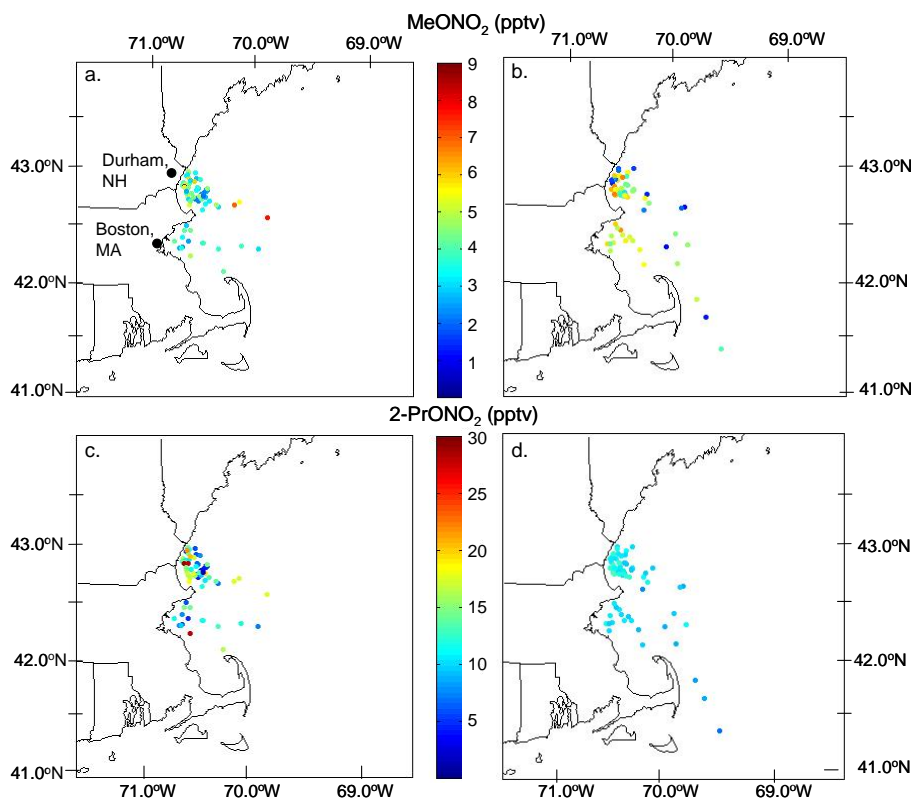


Fig. 7. Air and surface seawater samples (pptv) collected in the Gulf of Maine onboard the NOAA Ship Ronald H. Brown during NEAQS 2002 throughout 30 July–6 August 2002: (a) ambient air and (b) surface seawater mixing ratios of MeONO₂; (c) ambient air and (d) surface seawater mixing ratios of 2-PrONO₂.

4.3 Estuarine environment: Great Bay experiment

An intensive study focused on examining the spatial variability and sources of VOCs throughout the Great Bay estuary in seacoast New Hampshire was conducted from 18:00 18 August to 19:00 19 August 2003 (local time) (Fig. 1 inset). At TF, winds were from the south-southeast from noon on 18 August until early morning on 19 August when they shifted to the west-northwest (Fig. 8b). Three day back trajectories obtained from the NOAA HYSPLIT model (Draxler and Rolph, 2003) showed that air masses originated in eastern Canada and traveled along the Maine coastline before reaching NH from the east on the evening of 18 August. Furthermore, a strong nocturnal inversion layer developed between midnight and 07:00 on 19 August as demonstrated by decreases in O₃ and wind speed and by an increase in carbon dioxide (Figs. 8a, b).

The mixing ratios of each alkyl nitrate were remarkably uniform across the five sampling locations (Fig. 8c–i). The standard deviation of the mixing ratios at all five sites each hour was ≤ 0.2 pptv for MeONO₂, EtONO₂, 1-PrONO₂, 2-PeONO₂, and 3-PeONO₂ and ≤ 0.5 pptv for 2-PrONO₂ and 2-BuONO₂. The lack of a spatial variation in mixing ratios and a correlation with marine derived compounds sug-

gests that the source(s) of the alkyl nitrates was not associated with coastal emissions. In contrast, the marine halo-carbons (bromoform (CHBr₃), dibromomethane (CH₂Br₂), methyl iodide (CH₃I), and ethyl iodide (C₂H₅I)) exhibited a distinct spatial variation with higher mixing ratios at coastal sites (FC, WHF) compared to inland sites (TF, Pease, Exeter) (Zhou et al., 2005). For example, the elevated mixing ratios of CHBr₃ (> 10 pptv) reflect the influence of local coastal and estuarine emissions on the evening of 18 August (Fig. 8j). Additionally, NMHC mixing ratios increased significantly under the nocturnal boundary layer at each sampling location and decreased rapidly following the breakup of the inversion layer in the morning (White et al., 2008) (Fig. 8j). The slightly increasing alkyl nitrate mixing ratios on 19 August likely reflect processed continental emissions and/or the downward mixing of air from above the inversion layer in the morning. Overall, the different temporal and spatial distributions of the alkyl nitrates throughout the Great Bay estuary compared to tracers of anthropogenic and marine emissions is further evidence for their dominant secondary source.

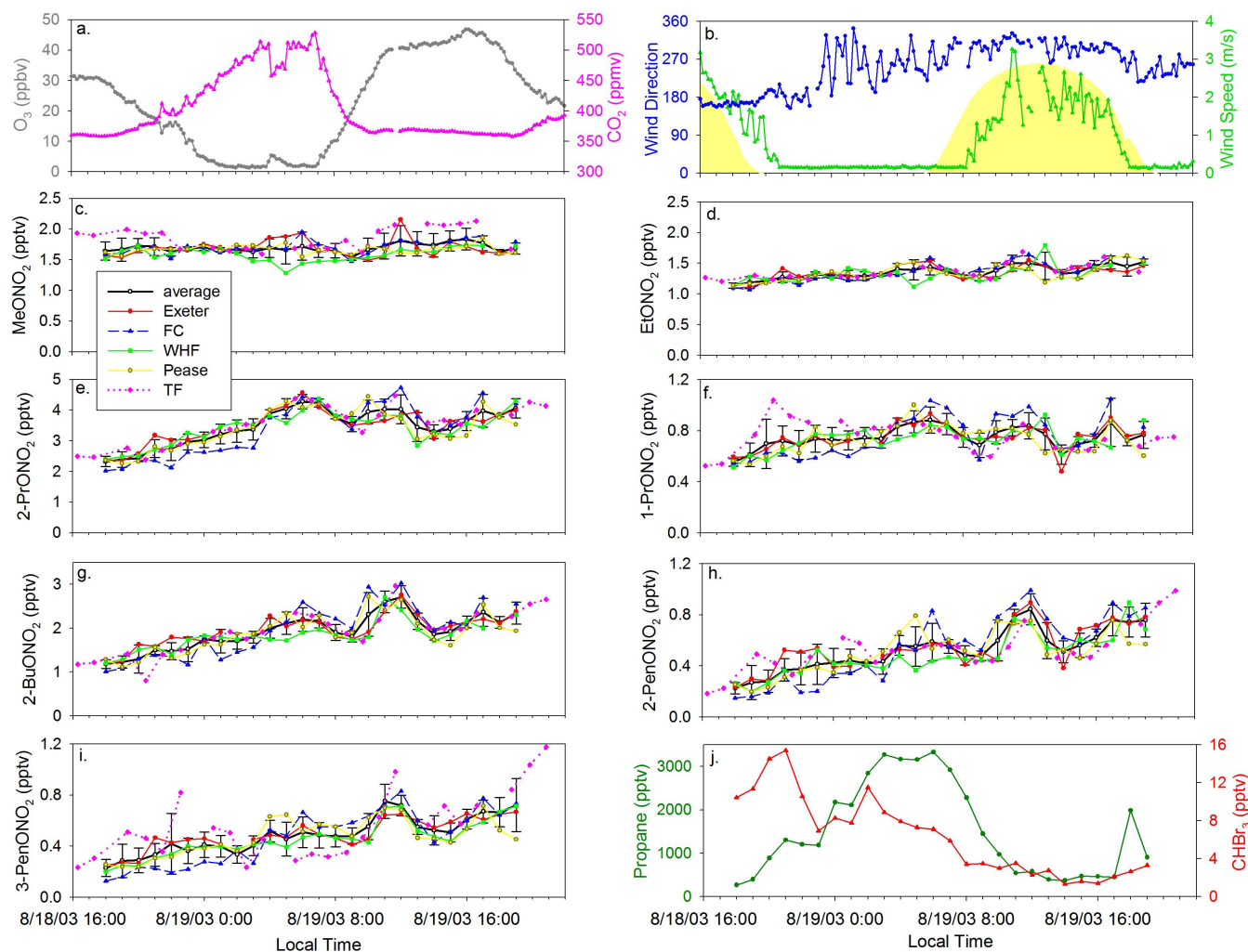
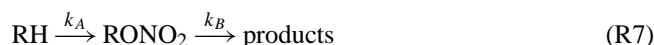


Fig. 8. (a) 10 min. average O₃ (ppbv) and CO₂ (ppmv) mixing ratios and (b) wind speed (m/s), wind direction, and J_{NO_2} (yellow shaded curve) at Thompson Farm from 18 August at 16:00 to 19 August 2003 at 22:00 (local time). Alkyl nitrate mixing ratios (pptv) at four sites throughout the Great Bay estuary and at Thompson Farm: (c) MeONO₂, (d) EtONO₂, (e) 2-PrONO₂, (f) 1-PrONO₂, (g) 2-BuONO₂, (h) 2-PenONO₂, (i) 3-PenONO₂, and (j) hourly average propane and CHBr₃ mixing ratios (pptv) for the five sampling sites. (c–i) The black line is the average \pm standard deviation mixing ratio of all 5 sites each hour.

5 Alkyl nitrate/parent hydrocarbon relationships

In the previous section, the analysis of four distinct data sets indicated that the dominant source of alkyl nitrates in the seacoast region of New Hampshire was photochemical production from hydrocarbons. Accordingly, the relationships with the parent hydrocarbons were further examined using a sequential reaction scheme. The production and loss reactions of alkyl nitrates summarized in Reactions (R1–R6) can be simplified as follows by assuming that Reaction (R1) between the parent hydrocarbon and OH is the rate-limiting step and that reaction with NO is the main reaction pathway for RO₂ radicals (R3 and R4) (i.e., no peroxy radical self-reactions):



The simplified kinetic equations lead to a differential equation, whose solution is a function only of time, and can thus be integrated to yield (Eq. 2) (see Bertman et al., 1995 for details on the derivation of Eq. 2):

$$\frac{(\text{RONO}_2)}{(\text{RH})} = \frac{\beta k_A}{(k_B - k_A)} (1 - e^{(k_A - k_B)t}) + \frac{(\text{RONO}_2)_o}{(\text{RH})_o} e^{(k_A - k_B)t} \quad (2)$$

where $k_A = k_1[\text{OH}]$, $k_B = k_6[\text{OH}] + J_5$, $\beta = \alpha_1\alpha_4$, and $(\text{RONO}_2)_o/(\text{RH})_o$ is the initial alkyl nitrate/parent hydrocarbon ratio (see Table 5 for parameter values). Based on a preliminary analysis, including a first-order removal rate constant for dry deposition ($k_D = V_d/H = 1/\tau_d$) in Eq. (2) did not

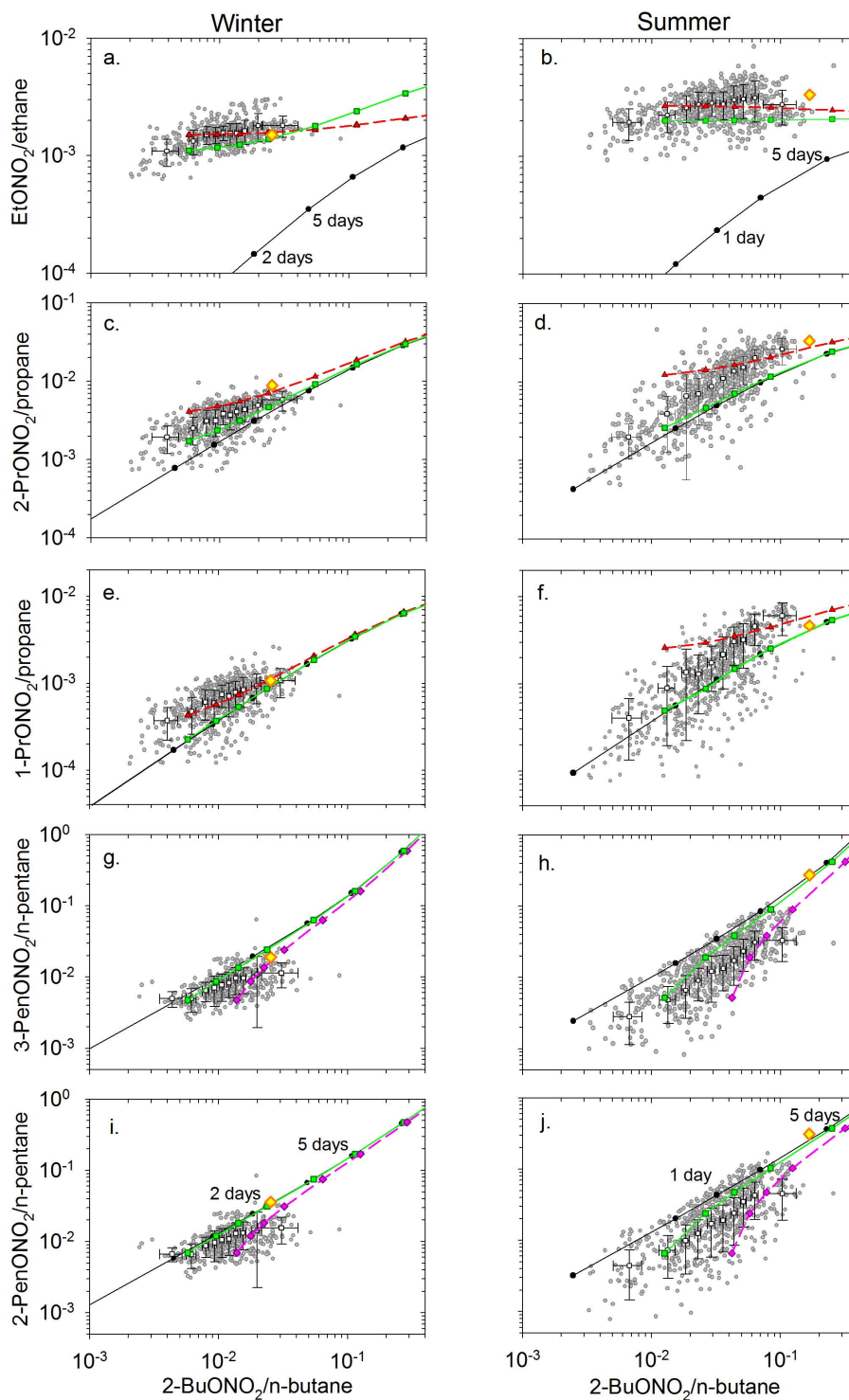


Fig. 9. Alkyl nitrate/parent hydrocarbon ratios versus 2-BuONO₂/n-butane for Winter (left) and Summer (right) 2002: (a) and (b) EtONO₂/ethane, (c) and (d) 2-PrONO₂/propane, (e) and (f) 1-PrONO₂/propane, (g) and (h) 3-PenONO₂/n-pentane, and (i) and (j) 2-PenONO₂/n-pentane. The white squares are averages each containing 10% of the data. Error bars represent ± 1 standard deviation of the 2-BuONO₂/n-butane ratio in the x-direction and ± 1 standard deviation of the RONO₂/RH ratio in the y-direction. Solid black line and circles: (RONO₂)_o/(RH)_o=0, the black dots correspond to the number of days since the parent alkane was emitted; (a–f) red dashed line with triangles: (RONO₂)_o/(RH)_o = seasonal mean and (2-BuONO₂)_o/(n-butane)_o=seasonal background; green lines with squares: (RONO₂)_o/(RH)_o and (2-BuONO₂)_o/(n-butane)_o=seasonal background; (g–j) pink dashed lines with diamonds: (PenONO₂)_o/(n-pentane)_o=seasonal background and (2-BuONO₂)_o/(n-butane)_o=seasonal mean. See Table 5 for initial ratio values. The yellow diamonds are (RONO₂)/(RH) ratios from samples collected at remote sites along the US west coast in December 2001 and June 2002.

improve agreement between the observations and the predicted RONO₂/RH trend. It is worth noting that the mean NO mixing ratios at TF were 2.5 and 0.35 ppbv in winter and summer 2002, respectively. These mixing ratios are sufficient (~0.04–0.1 ppbv) for reaction with NO to be the dominant reaction pathway for RO₂ radicals (e.g., Flocke et al., 1991; Roberts et al., 1998). Thus, we assume that the RO₂ + NO reaction is dominant at TF. If (RONO₂)₀/(RH)₀=0, the solution to Eq. (2) describes the time evolution of the alkyl nitrate/parent hydrocarbon (RONO₂/RH) ratio based solely on gas phase hydrocarbon chemistry (Bertman et al., 1995). Previous studies typically assumed that the initial alkyl nitrate mixing ratio is zero (Bertman et al., 1995; Roberts et al., 1998; Stroud et al., 2001; Simpson et al., 2003), while more recent studies included analyses using non-zero initial ratios (Reeves et al., 2007). Some studies have also attempted to quantify the influence of additional hydrocarbon precursors (e.g., Sommariva et al., 2008).

In order to examine the relationships between alkyl nitrates and their parent hydrocarbons, we compared the observed RONO₂/RH ratios to the values calculated when the initial (RONO₂)₀/(RH)₀ ratio equaled zero (pure photochemistry curve), the mean, and the background (10th percentile) ratio values at TF during winter and summer 2002 (Fig. 9, Table 5). Also included in Fig. 9 are the mean RONO₂/RH ratios from samples collected at several remote sites along the US west coast (34–47° N) during December 2001 and June 2002 (unpublished data, D. Blake, UCI). These samples are representative of background air masses and generally agree with the highest TF RONO₂/RH ratios (i.e., more aged air masses) in winter. The lower summer ratios at TF, compared to the west coast, likely reflect the influence of more recent emissions and higher parent hydrocarbon mixing ratios because of the closer proximity to anthropogenic sources. In fact, the samples collected on nights with a stable NBL, and thus representing local NMHC emissions and low RONO₂/RH ratios, largely correspond to the points on the lower left of the plots at the most recent processing times. In both winter and summer, air mass ages ranging from several hours to 5 days were observed at TF.

In both seasons, the EtONO₂/ethane ratios were factors of ~5–10 above the pure photochemistry curve (Fig. 9a, b). The trend toward the curve at the longest processing times is indicative of mixing with aged air masses containing lower ratios. Previous studies also observed large deviations of predicted EtONO₂/ethane ratios from the ambient ones (Bertman et al., 1995; Roberts et al., 1998; Simpson et al., 2003). The deviation has typically been interpreted as evidence of a primary source of EtONO₂ or of an additional source of the precursor ethyl peroxy radical from the decomposition of larger organic compounds, specifically alkoxy radicals (Bertman et al., 1995; Flocke et al., 1998). Interestingly, the mean and background initial ratio curves agreed with the TF observations very well in both the winter and summer over the entire range of measured ratios (Fig. 9a, b). Thus, the devia-

tion from the zero initial ratio curve may reflect background EtONO₂/ethane ratios in the atmosphere because of the sufficiently long lifetimes of EtONO₂ and ethane (~1 month and several months, respectively, in winter and ~1 week and 1–2 months, respectively, in summer). Bertman et al. (1995) and Reeves et al. (2007) also found better agreement between observed and predicted EtONO₂/ethane ratios at short processing times when an initial ratio was used. It should be noted that these results do not rule out a potential contribution from direct emissions or additional precursor sources of EtONO₂. Rather, these results provide an additional explanation for the discrepancy between observed and predicted ratios.

The 2-PrONO₂/propane and 1-PrONO₂/propane ratios were factors of 2–3 higher than the pure photochemistry curve at the shortest processing times in winter and trended toward the curve at longer times (Fig. 9c, e). In contrast, in summer, the propyl nitrate/propane ratios were factors of 0.5–0.9 above the pure photochemistry curve at all air mass ages (Fig. 9d, f). The small offsets above the curve at TF were much lower than observed by other studies conducted in North America (Bertman et al., 1995; Roberts et al., 1998; Stroud et al., 2001). The close agreement between the measured and predicted ratios and the similar behavior exhibited by both propyl nitrate/propane ratios indicates that 1-PrONO₂ and 2-PrONO₂ share a similar production mechanism following the oxidation of propane. This is in contrast to observations over the Atlantic Ocean (Reeves et al., 2007) and at Chebogue Point, Nova Scotia (Roberts et al., 1998) where the 2-PrONO₂/propane and 1-PrONO₂/propane ratios displayed different behavior which was attributed to the influence of different precursor compounds. Furthermore, the lifetimes of propane (weeks–months), 2-PrONO₂, and 1-PrONO₂ (days–weeks) are sufficiently long to sustain background propyl nitrate/propane ratios which may contribute to the deviations between ambient and predicted ratios. Overall, a significant amount of the data (~70–90%) in both seasons falls between the mean, background, and zero initial ratio curves further suggesting that precursor sources other than propane do not contribute to the propyl nitrate distribution observed at TF. Additionally, in Fig. 9a–f, the initial 2-BuONO₂/*n*-butane ratio was equal to its background values (Table 5) in order to highlight how well the predicted C₂-C₃ RONO₂/RH ratio curves encompass the observations.

The pentyl nitrate/*n*-pentane ratios were slightly (factors of 0.3–0.4) below the pure photochemistry curves except at the shortest reaction times in winter (Fig. 9g–j). Previous studies have also found the pentyl nitrate/*n*-pentane ratios to lie slightly below the predicted curve, but the cause of this unexpected behavior has remained unknown (Roberts et al., 1998; Stroud et al., 2001; Simpson et al., 2003). One possible explanation suggested by Reeves et al. (2007) was the fragmentation of *n*-pentane to alkyl radicals other than the 2-pentyl and 3-pentyl radicals. At TF, the slopes of the pentyl nitrate/*n*-pentane ratios were consistent with the

Table 5. Values used in Eq. (2) to produce the predicted photochemical evolution curves in Fig. 9. k_1 (10^{-12}) and k_6 (10^{-13}) are the rate constants ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) for the reactions between the parent hydrocarbon (R1) and alkyl nitrate (R6) with OH, respectively. α_1 and α_4 are the branching ratios of Reaction (R1) and Reaction (R4) producing the alkyl peroxy radical and alkyl nitrate, respectively. J_5 (10^{-6} s^{-1}) is the alkyl nitrate photolysis rate constant. $(\text{RONO}_2)_o/(\text{RH})_o$ is the initial alkyl nitrate/parent hydrocarbon ratio used in Eq. (2) and is equal to the seasonal mean (seasonal background) ambient ratios at TF. In Figs. 9a–f, $(2\text{-BuONO}_2)_o/(n\text{-butane})_o$ =seasonal background ratio. In Fig. 9g–j, $(2\text{-BuONO}_2)_o/(n\text{-butane})_o$ =seasonal mean ratio.

	$k_1^{\text{a,f}}$	α_1^{b}	α_4	$k_6^{\text{a,g}}$	J_5		$(\text{RONO}_2)_o/(\text{RH})_o$	
					Winter	Summer	Winter	Summer
EtONO ₂	0.24	1	0.006 ^{c,d}	1.8	0.33 ^h	1.5 ^h	0.002 (0.001)	0.003 (0.002)
2-PrONO ₂	1.1	0.7	0.039 ^d	2.9	0.43 ^h	1.6 ^h	0.004 (0.002)	0.012 (0.002)
1-PrONO ₂	1.1	0.3	0.02 ^e	5.8	0.58 ^h	2.2 ^h	0.0004 (0.0002)	0.003 (0.0004)
2-BuONO ₂	2.3	0.86	0.084 ^d	8.6	0.48 ⁱ	1.1 ^{j,k}	0.013 (0.005)	0.039 (0.01)
3-PenONO ₂	3.8	0.35	0.126 ^d	11	0.47 ⁱ	1.2 ^{j,k}	0.008 (0.004)	0.016 (0.003)
2-PenONO ₂	3.8	0.55	0.106 ^d	19	0.45 ⁱ	1.2 ^{j,k}	0.011 (0.006)	0.023 (0.003)

[OH]= 6×10^5 (winter) and 2×10^6 (summer) molecules cm^{-3} (Spivakovsky et al., 2000).

^a Atkinson et al. (2006); ^b Kwok and Atkinson (1995); ^c Ranschaert et al. (2000);

^d Arey et al. (2001); ^e Atkinson et al. (1987); ^f Atkinson (2003);

^g Atkinson (1990); ^h Clemitshaw et al. (1997); ⁱ Simpson et al. (2003);

^j Roberts (1990); ^k Bertman et al. (1995).

zero initial ratio curves, especially in summer, suggesting that photochemical production from *n*-pentane was the main source of both 2- and 3-PenONO₂. In contrast to the C₂-C₃ RONO₂/RH ratios, the mean initial ratio curves overestimated the observations in both seasons (not shown). For this case, plotting the mean initial 2-BuONO₂/*n*-butane ratio with the background pentyl nitrate/*n*-pentane ratios resulted in better agreement with the observations (pink lines in Fig. 9g–j). This result is likely because the C₅ compounds (*n*-pentane and pentyl nitrates) have shorter lifetimes and lower mean and background mixing ratios than for *n*-butane and 2-BuONO₂ (Tables 1, 2, 5).

6 Summary

Measurements of C₁-C₅ alkyl nitrates made at various locations throughout seacoast New Hampshire and spanning several years (2002–2008) were presented. The total C₁-C₅ alkyl nitrate mixing ratio was generally ~ 20 –30 pptv and constituted only a small component ($\leq 1\%$) of ambient NO_y at TF. This suggests that the C₁-C₅ alkyl nitrates are not likely to have a significant influence on the local O₃ or NO_y budget. However, owing to the high mixing ratios of precursor compounds (NO_x and NMHCs) emitted from the urban northeast US corridor, production of alkyl nitrates during trans-Atlantic transport is likely to occur and has been observed (e.g., Reeves et al., 2007). This may ultimately influence the NO_x and O₃ distributions of downwind regions, such as Europe, making it necessary to accurately quantify the distributions of precursors and secondary species originating in the northeastern US. Furthermore, the observation

of surface loss of MeONO₂ provides evidence that unaccounted for reactive nitrogen compounds contribute to NO_y deposition.

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