

RESEARCH ARTICLE

Seasonality, sources and sinks of C₁–C₅ alkyl nitrates in the Colorado Front Range

A. Abeleira*, B. Sive†, Robert F. Swarthout‡, Emily V. Fischer§, Y. Zhou§ and D. K. Farmer*

We describe observations of C₁–C₅ alkyl nitrates made at the Boulder Atmospheric Observatory in Northern Colorado in winter 2011, spring 2015, and summer 2015. Average mixing ratios of the alkyl nitrates are similar across the seasons, but increased diel variability in summer suggests increased production balanced by increased loss relative to winter and spring. We use a sequential production-destruction model based on ratios of alkyl nitrates to their parent alkanes to investigate seasonal sources and sinks of C₁–C₅ alkyl nitrates. We explore the role of uncertainties in the production and loss kinetic parameters on the interpretation of local atmospheric photochemical aging through the use of a photochemical clock based on the evolution of the ratios of alkyl nitrates to their parent alkanes over time. Photochemical age is typically consistent with hours from sunrise, suggesting that the site experiences well-mixed air masses dominated by daily photochemistry with little carry-over from the previous day or from other locations. Contrary to studies in other locations, we obtain good model-measurement agreement using a newer upper-bound ethyl nitrate branching ratios. This suggests that the efficiency of ethyl nitrate production from ethane oxidation has previously been underestimated, and decreases the relative importance of alkoxy radical decomposition versus ethane photochemistry on ethyl nitrate production. We estimate the dry deposition velocity of methyl nitrates is small and consistent with previous estimates, and that deposition velocities increase with carbon number for the C₂–C₅ RONO₂. Dry deposition is a small daytime sink relative to photolysis and reaction with OH for the alkyl nitrates, but improves the model-measurement comparison for methyl nitrate.

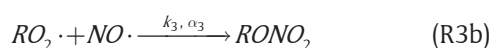
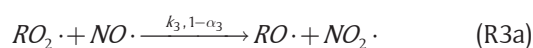
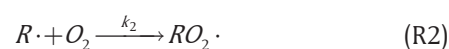
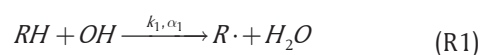
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1. Introduction

Short-chain alkyl nitrates (C₁–C₅ RONO₂) typically account for only a small fraction of both the organic nitrate (RONO₂) and NO_y budget (NO_y = NO + NO₂ + HNO₃ + HONO + 2N₂O₅ + HO₂NO₂ + RO₂NO₂ + NO₃ + RONO₂). However, the production and loss of C₁–C₅ RONO₂ still impacts tropospheric ozone, HO_x (RO₂ + HO₂), and NO_x (NO + NO₂) budgets. Ozone and RONO₂ are produced simultaneously in the atmosphere (**Figure 1a, b**), and the ratio of C₁–C₅ RONO₂ to their parent C₁–C₅ alkane can be used to determine the photochemical age of air masses (Bertman et al., 1995). However, uncertainties in the sources and sinks of

RONO₂ are substantial, and can lead to uncertainties in photochemical clock analyses (Simpson et al., 2003).

While direct emissions of C₁–C₂ RONO₂ have been observed from both the ocean (e.g. Atlas et al., 1993; Blake et al., 2003b; Blake et al., 1999; Chuck et al., 2002) and biomass burning (Simpson et al., 2011; Simpson et al., 2002), the dominant source of C₁–C₅ RONO₂ at continental mid-latitude sites is the photooxidation of anthropogenic precursors (R1–R3) (e.g. Bertman et al., 1995; Flocke et al., 1998b; Roberts, 1990; Roberts et al., 1998; Russo et al., 2010; Simpson et al., 2003; Worton et al., 2010) (**Figure 1a, b**):



* Department of Chemistry, Colorado State University, Fort Collins, Colorado, US

† National Park Service, Air Resources Division, Lakewood, Colorado, US

‡ Department of Chemistry, Appalachian State University, Boone, North Carolina, US

§ Department of Atmospheric Science, Colorado State University, Fort Collins, Colorado, US

Corresponding author: D. K. Farmer
(delphine.farmer@colostate.edu)



The fraction of proton abstraction (H-atom abstraction branching ratio) from the parent alkane (RH) at a particular carbon atom is α_1 (R1). Values for α_1 calculated from structural activity relationship studies are presented in Table S1 (Kwok and Atkinson, 1995). The formation of the peroxy (RO₂) radical is fast. In the presence of NO_x, RO₂ reacts with NO (R3); the minor pathway forms monofunctional C₁–C₅ RONO₂ (R3b, α_3). Thus, the fraction of reactions between the parent alkane and OH in the presence of NO that lead to RONO₂ formation is the product of α_1 and α_3 ($\beta = \alpha_1\alpha_3$), which we differentiate from the RONO₂ formation branching ratio as the integrated RONO₂ branching ratio.

Reaction with OH (R4) and photolysis (R5) are typically considered the major sinks of C₁–C₅ RONO₂ (Bertman et al., 1995; Perring et al., 2013; Roberts, 1990; Talukdar et al., 1997a; Talukdar et al., 1997b), although deposition may also be important (Russo et al., 2010) (**Figure 1c**). The

products of RONO₂ + OH depend on the size and structure of the RONO₂. The major (>50%) products from proton abstraction of C₃–C₄ linear and branched RONO₂ by OH are NO₂ and either aldehydes or ketones via the decomposition of intermediate alkoxy radicals (Aschmann et al., 2011). For example, the reaction of OH with linear 2-hexyl and 3-hexyl RONO₂ produces a variety of aldehydes and ketones including 2-hexanone, 3-hexanone, propanal, and butanal. A fraction of those reactions retain the nitrate functionality to produce multifunctional RONO₂, such as C₆-carbonyl nitrates, hydroxycarbonyl nitrates, and dinitrates (Aschmann et al., 2012):



Photolysis of C₁–C₅ RONO₂ releases the corresponding alkoxy radical and NO₂ (R5) (Roberts, 1990; Roberts and Fajer, 1989; Talukdar et al., 1997b):

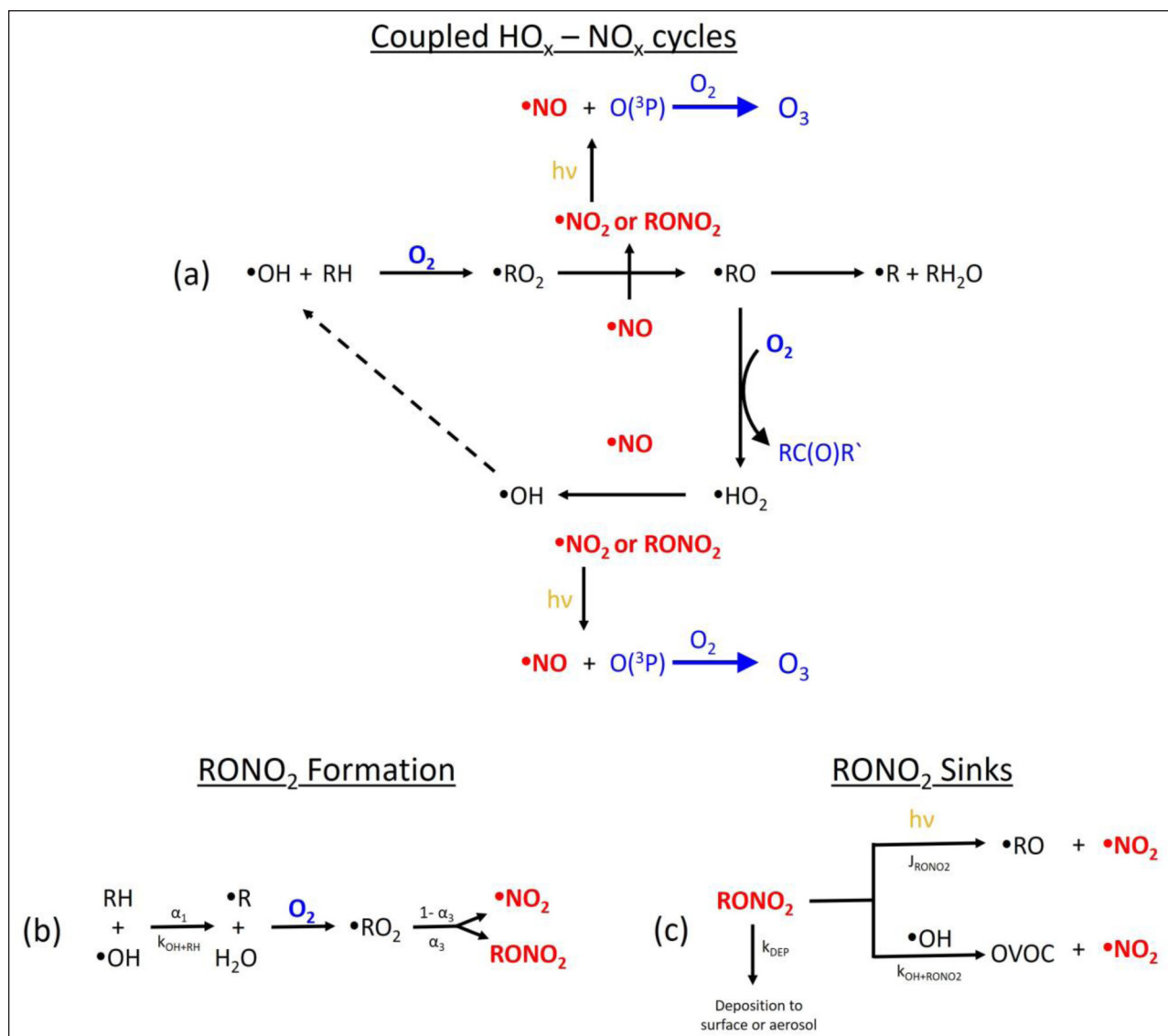
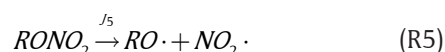


Figure 1: Coupled HO_x–NO_x reactions. (a) Ozone production cycle. (b) RONO₂ formation reactions. (c) RONO₂ sinks.

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Photolysis rates vary with RONO₂ structure, pressure (i.e. altitude), spectral radiance (intensity as a function of wavelength), and temperature. These photolysis rates are on the order of 10^{−7}–10^{−6} s^{−1} for C₁–C₅ RONO₂ at mid-latitude surface sites through all seasons, corresponding to lifetimes against photolysis of 6 for 2-butyl nitrate to 125 days for methyl nitrate (Bertman et al., 1995; Clemitshaw et al., 1997; Roberts, 1990; Roberts and Fajer, 1989; Simpson et al., 2003; Talukdar et al., 1997b; Wang et al., 2013; Worton et al., 2010).

Deposition and aerosol uptake are typically ignored as sinks of C₁–C₅ RONO₂ due to their low Henry's law constants (2.64 M atm^{−1} for MeONO₂; decreasing with increasing carbon number for mono-functional RONO₂ (Kames and Schurath, 1992)) and high vapor pressures (>3 torr (Fischer and Ballschmiter, 1998; Lim and Ziemann, 2005; Roberts, 1990)). Solubility of monofunctional RONO₂ is low, and hydrolysis is slow (10^{−5}–10^{−3} s^{−1}) (Robertson et al., 1982); water uptake is thus likely a small sink for C₁–C₅ RONO₂. However, the sum of all RONO₂ deposition accounts for ~3% of annual global nitrogen deposition of 92.9 Tg (Neff et al., 2002). Speciated oxidized nitrogen deposition rates are essential for accurate modeling of oxidized nitrogen deposition (Neff et al., 2002). Russo et al. (2010) report a dry deposition velocity of 0.13 cm s^{−1} for methyl nitrate (MeONO₂), which reduces the estimated summer lifetime of MeONO₂. The modeled global distribution of MeONO₂ is thus sensitive to the inclusion of dry deposition, which reduces the impact of long range transport of a HO_x + NO_x source to remote regions of the globe (Williams et al., 2014). To the best of our knowledge, Russo et al. (2010) provide the only observational estimate of speciated C₁–C₅ RONO₂ dry deposition.

Using measurements of speciated C₁–C₅ RONO₂, hydrocarbons, ozone, and other trace gases, we explore seasonal trends in C₁–C₅ RONO₂ observed at the Boulder Atmospheric Observatory in the Front Range of Northern Colorado from winter, spring, and summer measurement campaigns. The Front Range is an interesting region to study C₁–C₅ RONO₂ because the C₂–C₅ alkanes are abundant due to the high density of oil and natural gas operations (Abeleira et al., 2017; Gilman et al., 2013; McDuffie et al., 2016; Pétron et al., 2012; Pétron et al., 2014; Swarthout et al., 2013). Specifically, C₂–C₅ alkane mixing ratios are 5–300× higher than most other ground sites where speciated C₁–C₅ RONO₂ measurements have been reported (e.g. Bertman et al., 1995; Lyu et al., 2015; Russo et al., 2010; Swanson et al., 2003; Wang et al., 2010; Wang et al., 2013). The Front Range includes densely populated urban areas and high traffic interstate highways, and the region violates the National Ambient Air Quality Standard for ozone. Outside of Denver, the Front Range appears to be transitioning from a NO_x-saturated ozone production regime to peak production (Abeleira and Farmer, 2017). Here, we use a simple analytical model to explore the importance of – and uncertainties in – sources and sinks of C₁–C₅ RONO₂, and their impact on estimating the photochemical age of sampled air masses. This analysis includes estimates of dry deposition velocities of C₁–C₅ RONO₂, allowing us to investigate the relative importance of short-chain RONO₂ sinks.

2. Methods

2.1. Campaigns and site description

The C₁–C₅ alkyl nitrates, their parent alkane precursors, and other trace gases were measured at the NOAA Boulder Atmospheric Observatory (BAO) in Northern Colorado during winter 2011, spring 2015, and summer 2015. The winter 2011 measurements were part of the Nitrogen, Aerosol Composition, and Halogens on a Tall Tower (NACHTT) study from 18 February 2011 to 13 March 2011 (Brown et al., 2013; Swarthout et al., 2013). The spring 2015 measurements were associated with the Shale Oil and Natural Gas Nexus (SONGNETX) study from 20 March 2015 to 17 May 2015 (Abeleira et al., 2017; NOAA, 2017). The summer 2015 measurements occurred from 24 July 2015 to 29 August 2015 (Abeleira et al., 2017). BAO was in a semirural region with major urban centers to the south (Denver, 35 km), west (Boulder, 30 km), north (Fort Collins, 65 km), and northeast (Greeley, 65 km), but has since been decommissioned. The site is located on the edge of the Wattenberg natural gas field in the Denver-Julesburg basin, an area of extensive oil and natural gas exploration and extraction. (Abeleira et al., 2017; Brown et al., 2013; Gilman et al., 2013; McDuffie et al., 2016; Swarthout et al., 2013).

2.2. Measurements

We measured methyl nitrate (MeONO₂), ethyl nitrate (EtONO₂), 1-propyl nitrate (1-PrONO₂), 2-propyl nitrate (2-PrONO₂), 2-butyl nitrate (2-BuONO₂), 2-pentyl nitrate (2-PeONO₂), and 3-pentyl nitrate (3-PeONO₂) along with their parent alkanes (methane, ethane, propane, n-butane, and n-pentane) during all three campaigns, with the exception of methane, which was not measured during winter 2011. During winter 2011, the whole air samples were collected hourly by a canister sampling system, and analyzed off-line with a multi-channel gas chromatography system (Swarthout et al., 2013). The analytical precision was 1–8% for the parent alkanes and 3–8% for the alkyl nitrates. During spring and summer 2015, the alkyl nitrates and parent alkanes (except methane) were measured with a similar 4-channel online chromatography system, but instead utilized a cryogen-free system to pre-concentrate ambient samples on 1 mm silica beads at −180°C for *in situ* measurement. The inlet was 22 m above ground level (agl) for the 2011 measurements, and 6 m agl for the 2015 measurements. The measurements, calibrations, and 4-channel online chromatography system are detailed in (Abeleira et al., 2017); the analytical precision for the parent alkanes and alkyl nitrates was 1–10%. A Picarro 6401 commercial Cavity Ring-Down Spectrometer measured methane during spring and summer 2015 (6% precision).

Fixed-height temperature and wind-speed measurements were located on the 300 m BAO tower at 10, 100, and 300 m agl (NOAA, 2017). Average daytime 10 m height temperatures were 5°C (winter 2011), 15°C (spring 2015), and 25°C (summer 2015). Vertically resolved temperature and wind-speed measurements between 0–270 m agl were made during the winter 2011 study from an instrument enclosure mounted to a carriage on the tower (Brown et al., 2013).

2.3. Estimating photochemical age from RONO₂/RH

The evolution of RONO₂ with air mass age can be described by a sequential reaction system in which the reaction of *A* to *B* represents the production of RONO₂, and *B* to *C* represents the loss pathways (R6).



Bertman et al. (1995) described the evolution of RONO₂/RH as a function of air mass photochemical age (E1).

$$\frac{[\text{RONO}_2]}{[\text{RH}]} = \frac{\beta k_A}{(k_B - k_A)} \left(1 - e^{(k_A - k_B)t} \right) + \frac{[\text{RONO}_2]_0}{[\text{RH}]_0} e^{(k_A - k_B)t} \quad (\text{E1})$$

The ratio of RONO₂/RH is calculated as a function of time (seconds) using laboratory kinetic parameters. Because OH must be assumed, this time can be considered an ‘OH equivalent’ photochemical age – the time at an average OH concentration required to reach a given RONO₂/RH ratio. The production (or source) term (*k_A*) is *k₁*[OH] and, in conjunction with β, represents the production of RONO₂. Seasonal temperature and pressure adjusted integrated RONO₂ branching ratios (β = α₁α₃) are in **Table 1**. Details of those calculations can be found in supplemental section 2. The destruction (or sink) term (*k_B*) is *k₄*[OH] + *J₅*, and represents the loss of RONO₂ via oxidation and photolysis. The units of *k_A* and *k_B* are s^{−1}. Calculated values of *k_A* and *k_B* for each season are reported in **Tables 2** and **3**

Table 1: Seasonal integrated RONO₂ branching ratios accounting for pressure and temperature dependence^a. DOI: <https://doi.org/10.1525/elementa.299.t1>

RONO ₂	Seasonal integrated RONO ₂ branching ratios (β = α ₁ α ₃)		
	winter 2011	spring 2015	summer 2015
MeONO ₂	0.0093 ± 0.0005		
EtONO ₂	0.038	0.034	0.028
1-PrONO ₂	0.005	0.005	0.004
2-PrONO ₂	0.40	0.036	0.030
2-BuONO ₂	0.086	0.078	0.065
2-PeONO ₂	0.010	0.086	0.068
3-PeONO ₂	0.060	0.053	0.042

^a Integrated RONO₂ branching ratios are calculated from H-atom abstraction values in Table S1 and RONO₂ formation branching ratios in Tables S2 and S3. Details of the RONO₂ formation branching ratio temperature and pressure dependent calculations can be found in the section 2 of the supplemental. We determine uncertainty in MeONO₂ β by propagating the stated error in SI E5 in quadrature. Equation SI E4 used to calculate the EtONO₂ formation branching ratios did not have errors associated with it. Errors have not been reported with calculated RONO₂ formation branching ratios from SI E1–E3 (Arey et al., 2001; Carter and Atkinson, 1989), but the two least-squares standard deviations of the Δ[RONO₂]/Δ[n-alkane] relationships used to derive the falloff expression parameters for C₃–C₅ RONO₂ are typically <20%. We use 20% as a conservative error estimate for these integrated RONO₂ branching ratios.

Table 2: Kinetic parameters for the formation of RONO₂ at BAO. DOI: <https://doi.org/10.1525/elementa.299.t2>

RONO ₂	<i>k_A</i>			
	<i>k₁</i> ^a	winter 2011	spring 2015	summer 2015
	× 10 ^{−12} cm ³ molec. ^{−1} s ^{−1}	× 10 ^{−6} s ^{−1}		
MeONO ₂	0.0064	0.004–0.014	0.010–0.024	0.026–0.051
EtONO ₂	0.248	0.189–0.566	0.420–1.05	0.99–1.98
1-PrONO ₂	1.1	0.93–2.80	1.98–4.94	4.98–8.75
2-PrONO ₂	1.1	0.93–2.80	1.98–4.94	4.98–8.75
2-BuONO ₂	2.36	2.11–6.32	4.37–10.97	9.43–18.89
2-PeONO ₂	3.8	3.44–10.31	7.13–17.82	15.21–30.42
3-PeONO ₂	3.8	3.44–10.31	7.13–17.82	15.21–30.42

^a (Atkinson and Arey, 2003). The values of *k₁* are for 298 K and 760 torr. Units of *k₁* are × 10^{−12} cm³ molecule^{−1} s^{−1}. Values of *k_A* are calculated as *k₁*[OH] with temperature dependent parameters from Atkinson and Arey (2003) using average daytime (08:00–18:00) 10 m agl temperatures (5°C, 12°C, and 25°C for winter 2011, spring 2015, and summer 2015) and seasonal Northern Colorado OH concentration ranges (details in section 3.2.1). Units of *k_A* are × 10^{−6} s^{−1}.

respectively. Modeling RONO₂/RH with E1 assumes the following: (1) The OH + RH reaction is the rate limiting step in the production of RONO₂; (2) The evolution of RONO₂/RH is a result of gas phase hydrocarbon chemistry only (Bertman et al., 1995); (3) RO₂ reacts with NO only (*i.e.* no RO₂ self-reactions), which is expected in an urban/suburban 'high-NO_x' environment with NO > 0.1 ppbv (Flocke et al., 1991; Roberts et al., 1998); and (4) The only sinks of RONO₂ are reaction with OH and photolysis (Bertman et al., 1995; Roberts, 1990; Talukdar et al., 1997a; Talukdar et al., 1997b).

RONO₂/RH ratios for a given alkyl nitrate/parent hydrocarbon are typically plotted against 2-BuONO₂/n-butane because 2-BuONO₂ often exhibits the highest mixing ratios in polluted areas, is dominated by photochemical production (Bertman et al., 1995; Lyu et al., 2015; Wang et al., 2013; Worton et al., 2010), and has no reported primary sources (Atlas et al., 1993; Simpson et al., 2002). Additionally, in the first 24 hours of photochemical aging, 95% of 2-BuONO₂ is produced via oxidation of n-butane (Sommariva et al., 2008). Plotting RONO₂/RH against 2-BuONO₂/n-butane enables comparison of ambient data to these models without *a priori* knowledge of the absolute aging timescale of the ambient data (Bertman et al., 1995). This approach provides not only a quantitative metric of photochemical age, but also useful context for exploring the sources and sinks of alkyl nitrates.

3. Results and discussion

3.1. Seasonal and diel trends in C₁–C₅ RONO₂

Despite the relatively high hydrocarbon mixing ratios at BAO, average MeONO₂, EtONO₂, and 1-PrONO₂ mixing ratios at BAO are similar to previous measurements from rural and remote sites (*i.e.* Roberts et al., 1998; Russo et al., 2010; Swanson et al., 2003), while 2-PrONO₂ and the C₄–C₅ RONO₂ were more representative of polluted urban

sites (*i.e.* Lyu et al., 2015; Wang et al., 2013; Worton et al., 2010) (**Table 4**).

Seasonal averages of 2-PrONO₂ and C₄–C₅ RONO₂ deviate little from winter 2011 to summer 2015 at BAO (**Table 4**). For example, 2-BuONO₂ decreases from 30 pptv during winter 2011 to 20 pptv during summer 2015, but remains within the average ± standard deviation for all seasons. Average mixing ratios of MeONO₂, EtONO₂, and 1-PrONO₂ do not change seasonally. Measurements at other ground sites and during flight campaigns have shown greater contrasts in seasonal variation for C₁–C₅ RONO₂, and these differences have been attributed to meteorology, transport, and OH abundances (Beine et al., 1996; Blake et al., 2003a; Lyu et al., 2015; Russo et al., 2010; Simpson et al., 2004; Swanson et al., 2003; Wang et al., 2013). Maxima in C₁–C₅ RONO₂ in the winter and minima in the summer are typically observed at remote sites (Beine et al., 1996; Blake et al., 2003a; Swanson et al., 2003) resulting from increased photochemical removal of

Table 4: Average alkyl nitrate mixing ratios (ppbv) at BAO for winter 2011, spring 2015, and summer 2015. DOI: <https://doi.org/10.1525/elementa.299.t4>

RONO ₂	winter 2011	spring 2015	summer 2015
Average mixing ratios (standard deviation), pptv			
MeONO ₂	4 (1)	4 (1)	3 (1)
EtONO ₂	4 (1)	4 (1)	3 (2)
1-PrONO ₂	2 (1)	2 (1)	1.3 (0.9)
2-PrONO ₂	16 (8)	13 (6)	11 (6)
2-BuONO ₂	30 (20)	20 (10)	20 (10)
2-PeONO ₂	10 (10)	6 (5)	8 (7)
3-PeONO ₂	7 (6)	4 (4)	5 (5)

Table 3: Kinetic parameters for the loss of RONO₂ at BAO. DOI: <https://doi.org/10.1525/elementa.299.t3>

RONO ₂	J ₅				k _B		
	k ₄	winter 2011	spring 2015	summer 2015	winter 2011	spring 2015	summer 2015
	×10 ⁻¹² cm ³ molec. ⁻¹ s ⁻¹	×10 ⁻⁶ s ⁻¹					
MeONO ₂	0.04 ^a	0.07–0.50	0.19–0.79	0.30–0.94	0.11–0.62	0.27–0.99	0.46–1.26
EtONO ₂	0.218 ^b	0.11–0.82	0.32–1.32	0.49–1.52	0.33–1.47	0.76–2.41	1.36–3.26
1-PrONO ₂	0.597 ²	0.17–1.10	0.47–1.75	0.70–1.99	0.77–2.89	1.66–4.74	3.09–6.68
2-PrONO ₂	0.302 ^c	0.13–0.92	0.30–1.30	0.53–1.60	0.47–1.83	0.90–2.91	1.74–4.02
2-BuONO ₂	0.86 ^b	0.12–0.98	0.31–1.55	0.48–1.99	0.98–3.56	2.03–5.85	3.92–8.87
2-PeONO ₂	1.84 ^d	0.07–0.62	0.18–1.00	0.75–1.60	1.95–6.14	3.86–10.20	7.58–16.30
3-PeONO ₂	1.13 ^d	0.07–0.62	0.18–1.00	0.75–1.60	1.18–4.00	2.44–6.66	4.74–10.68

^a Preferred values from the Master Chemical Mechanism, MCM v3.3 ((Jenkin et al., 1997; Saunders et al., 2003)) via <http://mcm.leeds.ac.uk/MCM>, ^b(Morin et al., 2016), ^c(Romanias et al., 2015), ^d(Atkinson, 1990). The values of k₄ are for 298 K and 760 torr. Units of k₄ are ×10⁻¹² cm³ molecule⁻¹ s⁻¹. Selection and calculation of J₅ is detailed in the SI. Values of k₈ are calculated as k₄[OH] + J₅ with temperature dependent parameters from Atkinson and Arey (2003) using average daytime (08:00–18:00) 10 m agl temperatures (5°C, 12°C, and 25°C for winter 2011, spring 2015, and summer 2015) and seasonal Northern Colorado OH concentration ranges (details in section 3.2.1).

$RONO_2$ during summertime without an increase in production because of low precursor abundances (Swanson et al., 2003). In contrast, summer maxima were observed in polluted air masses outside of Freiburg, Germany (Flocke et al., 1998b).

The diel cycles of 2-PrONO₂ and C_4 – C_5 RONO₂ have more pronounced diel variability in summer 2015 compared to the winter or spring campaigns (Figure 2b, 2c). During winter 2011, average 2-BuONO₂ increases by a factor of 1.3 from 24 to 31 ppt_v between 04:00 and 14:00 (local time); during summer 2015, 2-BuONO₂ increases by a factor of 2.5 from 13 to 33 ppt_v (Figure 2e). A distinct summer maxima occurs earlier in the day between 10:00–12:00, unlike the broad afternoon maxima observed during winter and spring. In contrast, MeONO₂ exhibits little diel variability in all seasons, while EtONO₂ and 1-PrONO₂ exhibit small increases from 10:00 to 14:00 during summer 2015 (Figure 2a). Although daytime winter 2011 and summer 2015 mixing ratios were similar for 2-PrONO₂ and C_4 – C_5 RONO₂, the rapid decrease to lower background

mixing ratios in the summer is consistent with increased removal of the more reactive RONO₂. The diel cycles of 2-PrONO₂ and C_4 – C_5 RONO₂ are thus consistent with both increased summer photochemical sources from higher OH and increased summer losses from higher OH and photolysis rates. Diel cycles for the parent alkanes are presented and discussed in-depth in Swarthout et al. (2013) for winter 2011 and Abeleira et al. (2017) for spring and summer 2015.

3.2. Uncertainties in the $RONO_2$ /RH model

Uncertainties in RONO₂ formation branching ratios and the choice of OH concentration are the main sources of uncertainty that affect the agreement between modeled and measured RONO₂/RH and the estimation of the photochemical age from RONO₂/RH. The use of an initial RONO₂/RH value when modeling RONO₂/RH also impacts the agreement, particularly at lower photochemical ages. We investigate these uncertainties by comparing modeled and observed MeONO₂/methane, EtONO₂/ethane, and

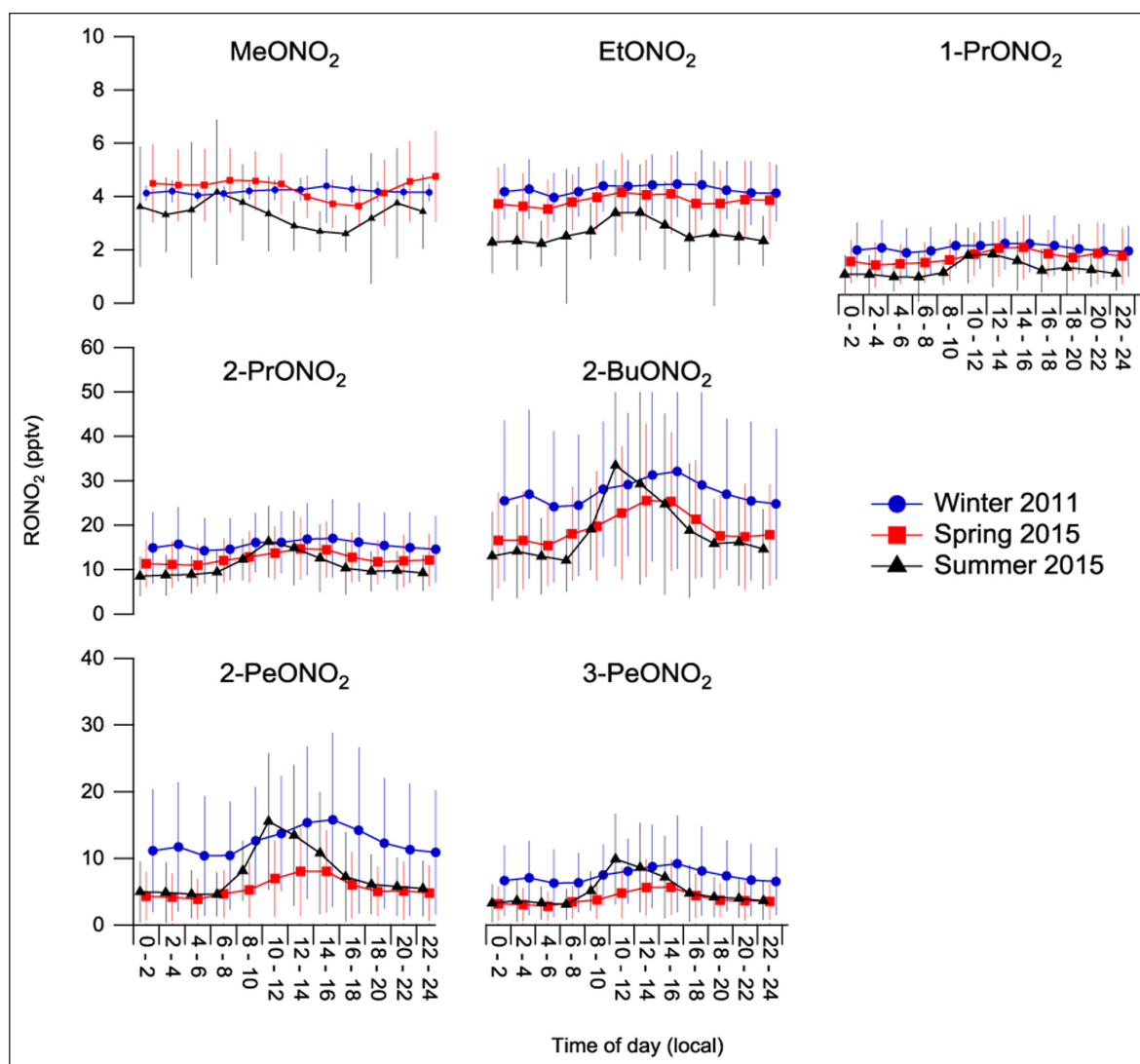


Figure 2: Average seasonal C_1 – C_5 RONO₂ diel cycles. Average diel cycles in mixing ratio for (a) MeONO₂, (b) EtONO₂, (c) 1-PrONO₂, (d) 2-PrONO₂, (e) 2-BuONO₂, (f) 2-PeONO₂ and (g) 3-PeONO₂ for the winter 2011 (blue circles), spring 2015 (red squares), and summer 2015 (black triangles) measurement campaigns. Error bars represent ± 1 standard deviation from the mean of each 2-hour time bin. DOI: <https://doi.org/10.1525/elementa.299.f2>

2-BuONO₂/n-butane ratios for the spring 2015 campaign. These uncertainties also impact the interpretation of RONO₂ sources and RONO₂ sinks.

3.2.1. OH concentration

The chosen OH concentration used for photochemical age estimation from the RONO₂/RH model should accurately represent the average OH encountered by an air mass. A limitation of this technique is that the use of a single OH concentration to model RONO₂/RH does not capture fluctuations in OH concentration that an air mass may experience. OH is responsible for not only initiating RONO₂ production via oxidation of the parent alkanes (i.e. the source, k_A), but also removing RONO₂ (i.e. a key sink, k_B). This interplay between source and sink dictates the rate at which RONO₂ increases and RH decreases, and subsequently controls the rate of increase of RONO₂/RH (Figure 3). Tables 2 and 3 list k_A and k_B calculated for a range of OH concentrations. We use an OH range of (1–3) × 10⁶ molecule cm⁻³ for winter 2011 based on co-located, simultaneous OH measurements (Kim et al., 2014). We use an average daytime range of (4–8) × 10⁶ molecule cm⁻³ for the summer 2015 campaign based on aircraft OH measurements from summer 2014 in the Northern Colorado Front Range (Ebben et al., 2017). We use (2–5) × 10⁶ OH molecule cm⁻³ for the spring 2015 campaign.

We illustrate the impact of OH concentration on RONO₂/RH with a high, low and base OH case (OH = 5, 2 and 3.5 × 10⁶ molecule cm⁻³) for spring 2015 (Figure 3). The rate

of RONO₂ production and RH consumption increases with increasing OH concentration (Figure 3a, b); overestimating OH causes an under-estimation of photochemical age. The reactivity of n-butane to OH ($k_{OH + n-butane} = 2.36 \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹) is greater than 2-BuONO₂ to OH ($k_{OH + 2-BuONO_2} = 0.86 \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹), causing a higher rate of increase in RONO₂/RH in the high OH versus low OH case. The opposite is true for EtONO₂ and ethane, where the reactivity of EtONO₂ with OH ($k_{OH + EtONO_2} = 0.218 \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹) is greater than that of ethane ($k_{OH + Ethane} = 0.248 \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹). The ratio of RONO₂ destruction to production (k_B/k_A) is a useful metric for predicting how RONO₂/RH will increase or decrease over time. For example, this ratio for 2-BuONO₂ is 0.70 for low OH, and decreases to 0.49 for high OH. This corresponds to a faster rate of consumption of the parent alkane and production of RONO₂, which is balanced by a smaller increase in the rate of removal of RONO₂ in the high OH case because 2-BuONO₂ has a lower reactivity than n-butane. Increasing OH causes higher RONO₂/RH ratio values to occur with less aging. For example, the EtONO₂/ethane versus 2-BuONO₂/n-butane value at 2 days of aging in the high OH case is not reached until 5 days of aging in the low OH case.

3.2.2. Selection of RONO₂ branching ratio

Branching ratios for the formation of some RONO₂ from RO₂ + NO are poorly constrained (Tables 5–6; Supplemental section 1), and the uncertainties propagate to the

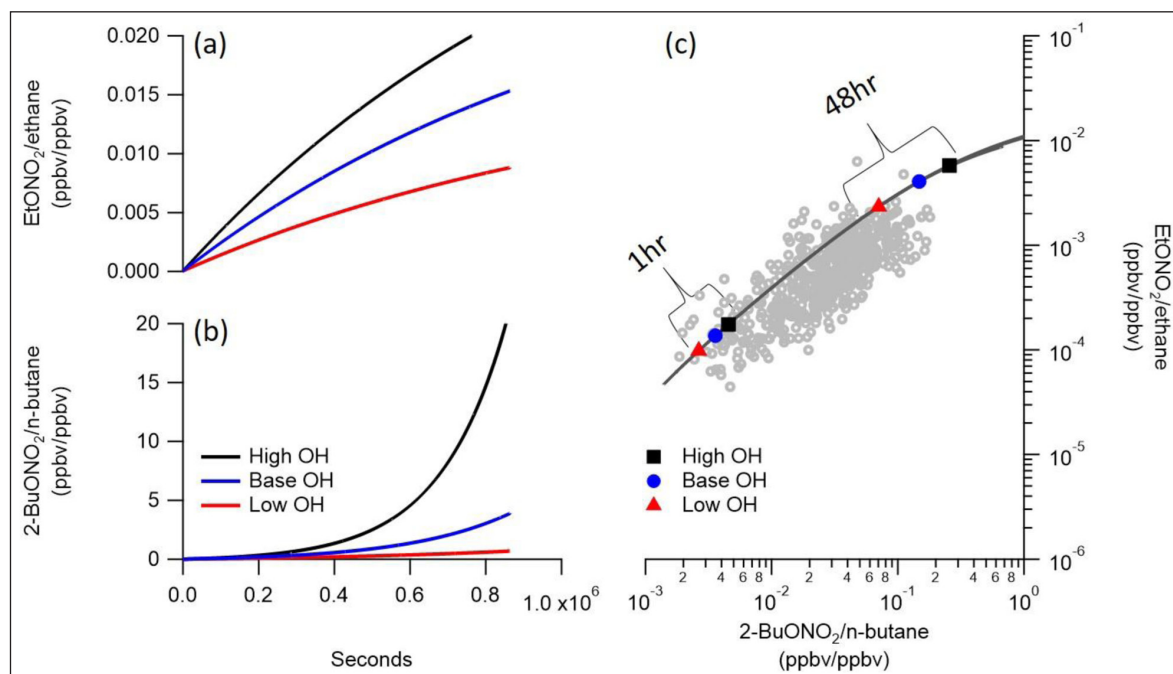


Figure 3: Impact of OH concentration on modeled EtONO₂/ethane. Modeled RONO₂/RH ratios for (a) EtONO₂/ethane and (b) 2-BuONO₂/n-butane vary with the assumed concentration of OH. The rate of production from OH + RH (k_A) and rate of destruction from OH and photolysis (k_B) are calculated for each OH case. The high, low and base OH cases are modeled with OH values of 5, 2 and 3.5 × 10⁶ molecule cm⁻³ respectively. Photolysis rates are spring averages (Table 3). Branching ratios are 0.034 (EtONO₂) and 0.078 (2-BuONO₂). (c) Observed (grey circles) and modeled (line, for each OH case) EtONO₂/ethane ratios are plotted against 2-BuONO₂/n-butane for the daytime (08:00–18:00) spring data (grey circles, c). Markers for 1 and 48 hours of photochemical aging for the three OH cases are overlaid on the modeled curves. DOI: <https://doi.org/10.1525/elementa.299.f3>

Table 5: C₃–C₅ RONO₂ formation branching ratios. DOI: <https://doi.org/10.1525/elementa.298.t5>

Reference	Type ^a	RONO ₂ formation α				Conditions		
		1-PrONO ₂	2-PrONO ₂	2-BuONO ₂	2-PeONO ₂	3-PeONO ₂	Temp. (k)	Press. (torr)
Atkinson 1982 ^{1,b}	exp.		0.036 ± 0.005	0.077 ± 0.009		0.117 ± 0.019	299 ± 2	735
Atkinson 1983 ^{2,b}	exp.		0.036 ± 0.005	0.077 ± 0.009		0.125 ± 0.003	299 ± 2	735
	calc.		0.039	0.07		0.121		
Atkinson 1984 ³	exp.	0.020 ± 0.009	0.043 ± 0.003	0.090 ± 0.009	0.129 ± 0.014	0.118 ± 0.016	299 ± 2	735
Carter 1985 ⁴	exp.	0.020 ± 0.009	0.042 ± 0.003	0.090 ± 0.008	0.129 ± 0.016	0.131 ± 0.016	299 ± 2	735
					0.134 ± 0.016	0.146 ± 0.016		
Atkinson 1987 ⁵	calc.	0.018	0.046	0.083	0.135		299–300	735–740
Carter 1989 ⁶	calc.	0.019	0.047	0.083	0.126	0.126–0.128	299–300	735–740
Arej 2001 ⁷	exp.	0.016	0.039 ± 0.002	0.084 ± 0.009	0.106 ± 0.018	0.126 ± 0.018	296–300	735–740
Chow 2003 ⁸	exp.		0.006				298	100
Aschmann 2006 ⁹	exp.				0.096 ± 0.009	0.116 ± 0.009	297 ± 1	737 ± 4
Cassanelli 2007 ¹⁰	exp.					0.11 ± 0.02	298	750
Butkovskaya 2010 ¹¹	exp.		0.038 ± 0.002				298	760
Jenkin 1997 ¹²	MCM	0.020	0.042	0.090	0.129	0.131	298	760

¹(Atkinson et al., 1982), ²(Atkinson et al., 1983), ³(Atkinson et al., 1984), ⁴(Carter and Atkinson, 1985), ⁵(Atkinson et al., 1987), ⁶(Carter and Atkinson, 1989), ⁷(Arej et al., 2001), ⁸(Chow et al., 2003), ⁹(Aschmann et al., 2006), ¹⁰(Cassanelli et al., 2007), ¹¹(Butkovskaya et al., 2010b), ¹²(Jenkin et al., 1997). ^aThe type designations are experimental for “exp.”, estimated for “est.”, preferred values at 298 k and 760 torr from the Master Chemical Mechanism for MCM, and “calc” for calculated isomeric branching ratios from a generalized falloff expression fitted to experimental branching ratios as reported in the individual references. ^bThe branching ratios are derived from the combined yields of 1-RONO₂ + 2-RONO₂ determined from $\Delta[\text{RONO}_2 + 2\text{-RONO}_2]/\Delta[\text{n-alkane}]$ in the reported kinetics studies. Errors are typically two least-squares standard deviations of $\Delta[\text{RONO}_2]/\Delta[\text{n-alkane}]$ or $\Delta[\text{reference product}]/\Delta[\text{reference product}]$ relationship for experimental data. Details of the other referenced experiments and calculations will be discussed in the text (section 2.3.).

Table 6: MeONO₂ and EtONO₂ formation branching ratios. DOI: <https://doi.org/10.1525/elementa.299.t6>

Reference	Type ^h	RONO ₂ formation α		Conditions	
		MeONO ₂	EtONO ₂	Temp. (k)	Press. (torr)
Atkinson 1982 ^a	exp.		<0.014	299 ± 2	735
Flocke 1998 ^b	est.	1.5–3.0 × 10 ⁻⁴		Lower troposphere ^k	
Scholtens 1999 ^c	est.	<0.03		295	100
Butkovskaya 2012 ^d	exp.	0.0107 ± 0.0014 ⁱ		298	760
Ranschaert 2000 ^e	exp.		0.007 ± 0.003	298	100
Butkovskaya 2010 ^f	exp.		0.03 ± 0.01 ^j	298	760
Jenkin 1997 ^g	MCM	0.001	0.009	298	760

^a(Atkinson et al., 1984), ^b(Flocke et al., 1998a), ^c(Scholtens et al., 1999), ^d(Butkovskaya et al., 2012), ^e(Ranschaert et al., 2000), ^f(Butkovskaya et al., 2010a), ^g(Jenkin et al., 1997). ^hThe type designations are experimental for “exp.”, estimated for “est.”, and preferred values at 298 k and 760 torr from the Master Chemical Mechanism for MCM. ^{i,j}Calculated from the temperature and pressure dependent branching ratio equations for 298 k and 760 torr reported within each reference. ^kEstimated branching ratio for the lower troposphere from lower stratospheric MeONO₂ observations. Errors are typically two least-squares standard deviations of $\Delta[\text{RONO}_2]/\Delta[\text{n-alkane}]$ or $\Delta[\text{RONO}_2]/\Delta[\text{reference product}]$ relationship for experimental data.

integrated RONO₂ branching ratio (β). For instance, the sole experimentally-derived formation branching ratio of MeONO₂ of 0.0107 ± 0.0014 (298 K, 760 torr) (Butkovskaya et al., 2012) is an order of magnitude higher than the commonly used value of 0.001 (Master Chemical Mechanism; (Jenkin et al., 1997) and almost two orders of magnitude greater than the observationally constrained estimate of 1.5 × 10⁻⁴ (Flocke et al., 1998a). EtONO₂ formation branching ratios at 298 K and 760 torr vary from 0.009 (Master Chemical Mechanism) to 0.03 ± 0.01 (direct experiment; (Butkovskaya et al., 2010a)). Similarly, 2-PeONO₂ has a reported experimental range of 0.096 ± 0.009 (Aschmann et al., 2006) to 0.134 ± 0.016 (Carter and Atkinson, 1985). In contrast, 2-PrONO₂ branching ratios have a very narrow range of experimental values at 298–300 K and 735–760 torr: 0.038 ± 0.002–0.043 ± 0.002 (Arey et al., 2001; Atkinson et al., 1987; Butkovskaya et al., 2010a; Carter and Atkinson, 1985). The selection or calculation of the formation branching ratios for these RONO₂ is important for interpreting the agreement or disagreement between modeled and observed RONO₂/n-alkane. Disagreement between modeled and observed RONO₂/n-alkane has typically been attributed to alkoxy radical chemistry that is not captured by these relatively simple models (Bertman et al., 1995; Reeves et al., 2007; Simpson, 2003).

In **Figure 4**, we compare the modeled and observed EtONO₂/ethane versus 2-BuONO₂/n-butane using seasonal temperature and pressure dependent integrated RONO₂ branching ratios, a commonly used value of 0.014 from Atkinson et al. (1982), and a value of 0.009 from the Master Chemical Mechanism (Jenkin et al., 1997). The temperature and pressure dependent EtONO₂ formation branching ratio calculations yield integrated branching ratio values (β) of 0.038, 0.034, and 0.028 for winter 2011, spring 2015, and summer 2015 respectively (**Table 1**). Seasonal temperature and pressure integrated RONO₂ branching ratios for 2-BuONO₂ are calculated with values

of 0.086, 0.078, and 0.065 for winter 2011, spring 2015, and summer 2015 respectively (**Table 1**).

In winter 2011, the temperature and pressure dependent EtONO₂ branching ratio (β = 0.038) agrees well with observed values with a small underprediction of 9–13% (**Figure 4a, d**). In contrast, the branching ratio values of 0.009 and 0.014 lead to model underpredictions of 39–76%, with larger underpredictions at higher photochemical aging (**Figure 4a, d**). However, in spring 2015 the temperature and pressure dependent branching ratio (β = 0.034) overpredicts observations by 37–111%, with greater overpredictions at longer photochemical aging (**Figure 4b, e**). Better agreement is found with the 0.014 branching ratio (model underprediction of 11–31%), especially at higher photochemical ages. Similarly, during summer 2015 the temperature and pressure dependent branching ratio (β = 0.028) overpredicts observations by 11–83%. As the photochemical age increases past 3 hours, we find better agreement between modeled and observed values with the 0.014 branching ratio. In contrast, we note that previous studies often use lower branching values for EtONO₂ of 0.006 to 0.014, and report model underpredictions for EtONO₂/ethane of >200% (Bertman et al., 1995; Russo et al., 2010; Simpson et al., 2003; Wang et al., 2013; Worton et al., 2010).

Similar model overpredictions are observed with 3-PeONO₂, though the reported range of the 3-PeONO₂ formation branching ratio value is much narrower than EtONO₂. The winter 2011 comparison (β = 0.060) is the best of the three seasons with overpredictions of 7–63%, with larger overpredictions after 3 hours of aging. The spring and summer 2015 (β = 0.053, 0.042) measurements are severely overpredicted with values of 91% to 320% for both seasons. The same temperature and pressure calculation method has been reported with parameters that lead to lower C₅-RONO₂ branching ratios (spring β = 0.044, summer β = 0.036) (Aschmann

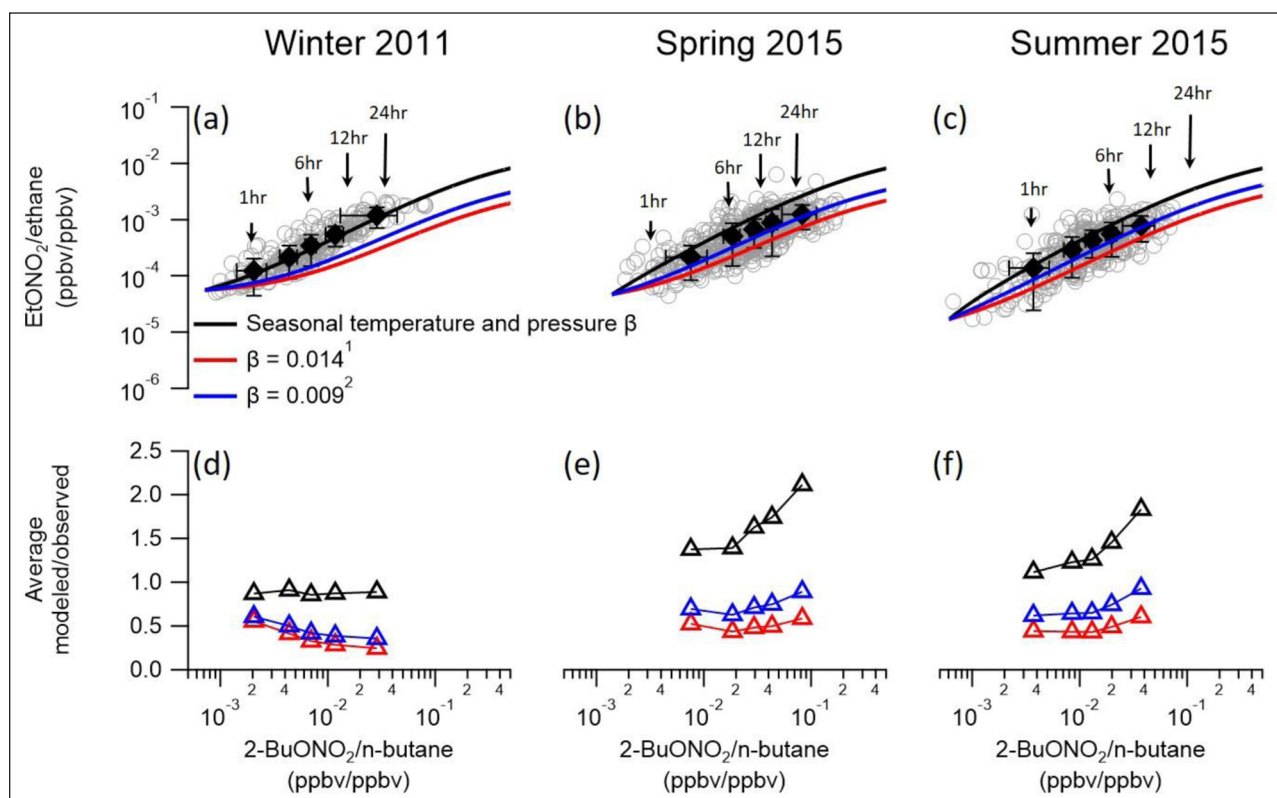


Figure 4: Seasonal EtONO₂/ethane model-measurement comparisons. Daytime (08:00–18:00) EtONO₂/ethane ratios are plotted against 2-BuONO₂/n-butane (grey circles) for (a) winter 2011, (b) spring 2015 and (c) summer 2015. Modeled ratios are calculated using branching ratios adjusted for seasonal pressure and temperature (solid blue line; see text for description), with an older value ($\beta = 0.014$) at 298 K and 760 torr¹(Atkinson et al., 1982), and with the preferred MCM value ($\beta = 0.009$) at 298 K and 760 torr²(Jenkin et al., 1997). Error bars represent one standard deviation around the bin averages. Modeled/observed ratios are shown for (d) winter 2011, spring 2015 (e) and summer 2015 (f) for the temperature-adjusted branching ratio versus average branching ratio scenarios. Photochemical ages derived from E2 for the model scenarios are listed above the models. DOI: <https://doi.org/10.1525/elementa.299.f4>

et al., 2006), but these values produce branching ratios that still severely overpredict the spring and summer 3-PeONO₂/n-pentane observations by 61–270%. Overpredictions of 3-PeONO₂/n-pentane ratios have been previously reported (Bertman et al., 1995; Russo et al., 2010; Simpson et al., 2003; Stroud et al., 2001; Worton et al., 2010). The implications of these comparisons will be discussed later in section 3.4.

3.2.3. Selection of initial conditions

RONO₂ is often assumed to be absent if no photochemistry has occurred in an air mass (Bertman et al., 1995; Roberts, 1990), although observations suggest this is not always the case. A non-zero initial RONO₂/RH ratio accounts for non-zero RONO₂/RH ratios during periods with no photochemistry in air masses impacted by marine and biomass burning RONO₂ emissions (Atlas et al., 1993; Blake et al., 1999; Simpson et al., 2002). Non-zero RONO₂/RH ratios in the absence of photochemistry are also common for the less reactive C_1 – C_2 RONO₂ (Bertman et al., 1995; Russo et al., 2010). Continental ground sites removed from oceanic sources and biomass burning plumes, including the BAO site, exhibit small non-zero RONO₂/RH values in the morning prior to sunrise, often attributed to carryover from the previous days'. Although the RONO₂/RH values

prior to sunrise are typically low, it has become common practice to use a non-zero initial RONO₂/RH ratio when applying the RONO₂/RH model (Russo et al., 2010; Wang et al., 2013). Accounting for initial RONO₂ concentrations yields better model-measurement agreement, particularly at photochemical ages <6 hours (Figure S1). The one exception is MeONO₂/methane, likely because the initial ratio is not only small due to high methane concentrations, but also consistent because of the low reactivity of both MeONO₂ ($k_{OH + MeONO_2} = 4 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) and methane ($k_{OH + methane} = 6.4 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). Thus, despite accounting for an initial MeONO₂/methane ratio, the model overpredicts observations >6 hours of photochemical aging. One explanation for this poor model-measurement comparison is a missing RONO₂ loss process.

3.3. Dry deposition

MeONO₂/methane exhibits the largest model-measurement discrepancy of all the measured RONO₂/RH pairs (Figures 5, S3). The observed trends in spring and summer 2015 MeONO₂/methane are not captured by modeled values when a pressure dependent MeONO₂ branching ratio ($\beta = 0.0093$) is used (Figure 5). Butkovskaya et al. (2012) note that the calculated pressure dependent branching

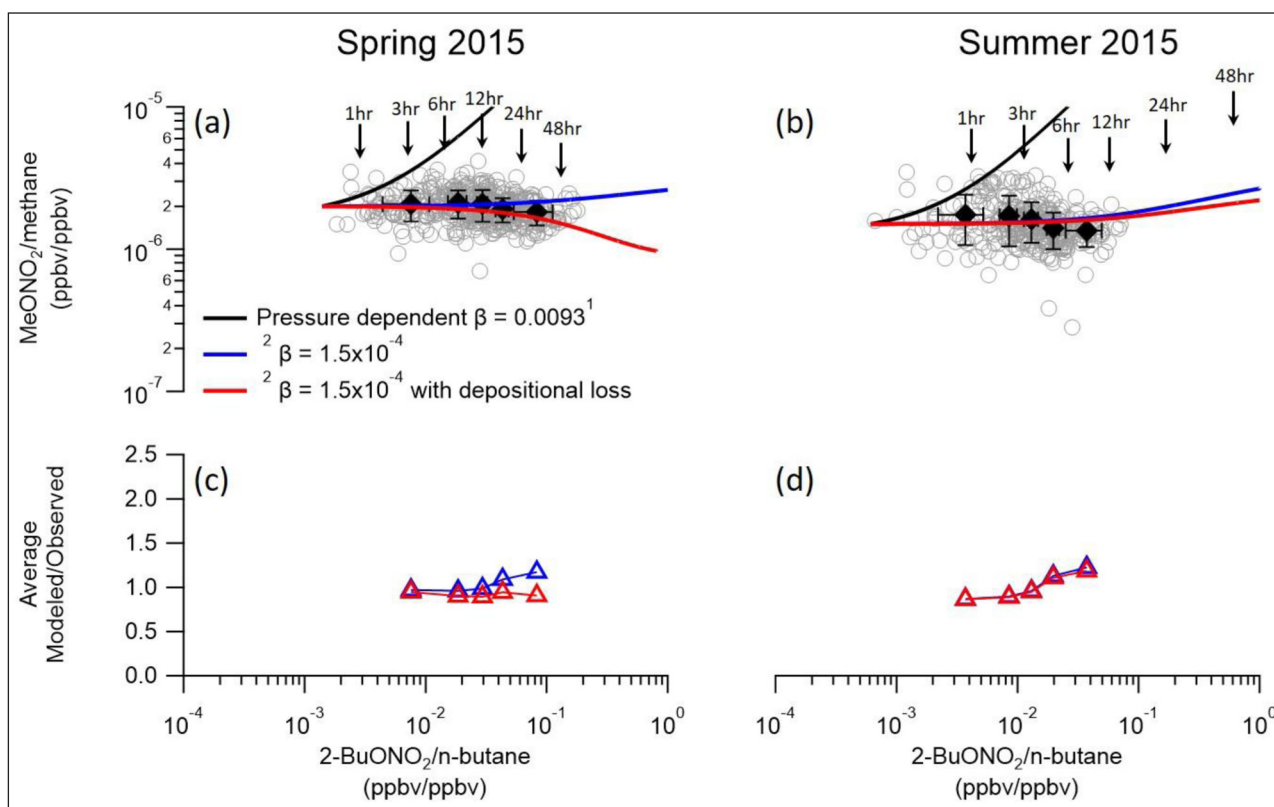


Figure 5: Seasonal MeONO₂/methane model-measurement comparisons. Observed MeONO₂/methane was plotted against 2-BuONO₂/n-butane for spring 2015 (grey circles, **a**) and summer 2015 (grey circles, **b**). Model ratios are shown that exclude loss by dry deposition (black and blue lines), and include dry deposition determined from nighttime data (red). Dry deposition loss rates of $1.7 \times 10^{-6} \text{ s}^{-1}$ and $0.87 \times 10^{-6} \text{ s}^{-1}$ were estimated for spring and summer 2015. ¹A pressure dependent MeONO₂ branching ratio at 298 K of 0.0093 was used for both spring and summer (black line). A low branching ratio estimate of 1.5×10^{-4} was used for spring and summer (red and black lines) (Flocke et al., 1998a). All models use upper J_{RONO₂} values for each RONO₂ (Table 2). Black diamonds are average MeONO₂/methane versus 2-BuONO₂/n-butane averaged into five bins of equal number of points ($n = 110/\text{bin}$ for spring 2015 and $n = 69$ for summer 2015). Error bars represent one standard deviation around the bin averages. Modeled/observed ratios are plotted for spring 2015 (**c**) and summer 2015 (**d**) for each scenario. Photochemical ages derived from the model scenarios are indicated. DOI: <https://doi.org/10.1525/elementa.299.f5>

ratio at leads to calculated steady-state MeONO₂ concentrations 2–5 higher than upper troposphere observations. Use of a smaller MeONO₂ branching ratio (*i.e.* $\beta = 1.5 \times 10^{-4}$, Flocke et al. (1998a)) provides better agreement in spring and summer 2015, but the model predicts an increase in MeONO₂/methane at higher photochemical ages. Observed MeONO₂/methane does not increase with increasing 2-BuONO₂/n-butane during either spring or summer 2015, and instead exhibits a constant ratio with averages of $(2.0 \pm 0.4) \times 10^{-6}$ and $(1.6 \pm 0.6) \times 10^{-6}$ ppbv/ppbv during spring and summer 2015, respectively (**Figure 5**).

Deposition is rarely considered for the alkyl nitrates. Russo et al. (2010) report dry deposition velocities (V_d) for MeONO₂ from summer observations in rural New Hampshire of $0.13 \pm 0.07 \text{ cm s}^{-1}$. Following their approach, we estimate a similar V_d of 0.09 cm s^{-1} from a single night in winter 2011. Briefly, Russo et al. (2010) calculated dry deposition fluxes from the nighttime decay rate of RONO₂ (change in concentration over a given time, pptv s⁻¹) multiplied by the nocturnal boundary layer height (H). Dividing the flux by the average concentration and multiplying by

–1 gives a deposition velocity (V_d , converted to cm s⁻¹). A negative flux and positive deposition velocity indicate a flux from the atmosphere to a surface. The loss rate from dry deposition (k_{dep}) is calculated as V_d/H , where H is the boundary layer height. See SI for detailed description of calculation, assumptions, and selection criteria.

Including dry deposition in the $\beta = 1.5 \times 10^{-4}$ case results in good model-measurement agreement, avoiding the modeled increase in MeONO₂/methane at higher photochemical ages that was not observed. Due to the lack of statistics of our singular dry deposition value, we use the value of 0.13 cm s^{-1} from Russo et al. (2010) for further analysis. We estimate a dry deposition loss rate for MeONO₂ in spring 2015 of $1.7 \times 10^{-6} \text{ s}^{-1}$ (assuming daytime boundary layer height of 750 m). The loss of MeONO₂ (k_b) for spring 2015 is calculated to be $0.62 \times 10^{-6} \text{ s}^{-1}$ from reaction with OH and photolysis (**Table 3**). Thus, the inclusion of dry deposition in spring 2015 increases the loss rate by nearly 4-fold, and improves the model-measurement agreement (**Figure 5a, c**). However, the inclusion of MeONO₂ loss by dry deposition during summer 2015 only minimally improves the model-measurement

agreement (**Figure 5b, d**). The estimated summer 2015 MeONO₂ dry deposition loss rate for an estimated daytime 1500 m boundary layer is $0.86 \times 10^{-6} \text{ s}^{-1}$, and the calculated k_b from OH + MeONO₂ and photolysis is $0.86 \times 10^{-6} \text{ s}^{-1}$. However, we note that by increasing the loss rate to $4 \times 10^{-6} \text{ s}^{-1}$ we can generate a model that does not exhibit increasing MeONO₂/methane at higher photochemical ages (not shown). This indicates that loss from dry deposition during summer is underestimated with this method, or that there is an additional major unaccounted for MeONO₂ loss process. Loss from dry deposition has little or no impact on the model-measurement agreement of the C₂–C₅ RONO₂, which is not surprising since loss of RONO₂ from OH+RONO₂ becomes more important as the number of carbon increase (Figure S4).

We note a trend of increasing deposition velocity with larger RONO₂ species (Table S7); while the lack of statistically robust values prevents us from investigating this pattern in great detail, we note that the increasing deposition velocity follows increasing vapor pressure, suggesting that the observed removal could be due to a temporary nighttime partitioning of the gases to the surface.

3.4. C₂–C₅ RONO₂ model-measurement comparison

In section 3.2.2, we note discrepancies among the three seasons regarding which EtONO₂ branching ratio provides the best model-measurement agreement. In winter 2011, the temperature and pressure dependent value of 0.038 provides a near 1:1 agreement with the observations. In spring and summer 2015, a value between the temperature and pressure dependent branching ratios (spring $\beta = 0.034$, summer $\beta = 0.028$) and 0.014 (Atkinson et al., 1982) provides the better model-measurement agreement at photochemical ages <24 hours. The model typically underpredicts observed EtONO₂/ethane by factors of 2 or more (Bertman et al., 1995; Russo et al., 2010; Simpson et al., 2003; Wang et al., 2013; Worton et al., 2010). However, those studies used a lower branching ratio ($\beta = 0.014$) (Bertman et al., 1995; Russo et al., 2010; Simpson et al., 2003; Wang et al., 2013; Worton et al., 2010). This underprediction was attributed to additional sources of ethyl radicals from the decomposition of larger alkoxy radicals (Bertman et al., 1995; Roberts et al., 1998; Worton et al., 2010). For example, Sommariva et al. (2008), with the Master Chemical Mechanism EtONO₂ branching ratio of 0.009, suggest that OH+ethane reaction only accounts for 15% of EtONO₂ in the first 24 hours of processing, while decomposition of alkoxy radicals from larger alkanes account for the rest. This is a reasonable explanation since alkoxy radical decomposition is known to occur (Atkinson, 1997; Atkinson and Carter, 1991; Orlando et al., 2003). However, the Master Chemical Mechanism EtONO₂ branching ratio value of 0.009 is much lower than the temperature and pressure dependent value range of 0.028–0.038 for the three seasons in this study. Alternatively, the winter 2011 model-measurement agreement with $\beta = 0.038$ and the spring and summer 2015 agreement with $\beta = 0.014$ –0.034 could be consistent with the original branching ratios (*i.e.* $\beta = 0.009$ –0.014) being too low, thereby underestimating the efficiency of EtONO₂

production from ethane in air masses with <24 hours of processing. Production of EtONO₂ from the decomposition of larger alkoxy radicals could still be important at longer processing times. However, with the current analysis we cannot definitively evaluate these arguments, and further work using a more detailed mechanistic model with a range of branching ratio values is warranted.

Modeled and observed 2-PrONO₂/propane are in good agreement for the winter and summer campaigns (7–29% underprediction, within the standard deviation of averaged observations), and fair agreement in spring 2015 with overpredictions of 34–59%. As noted in section 3.2.2, winter 2011 model-measurement comparisons are within the standard deviation of observed values for 3-PeONO₂, while the spring and summer 2015 models severely overpredict observed 3-PeONO₂/n-pentane. The same pattern is observed for 2-PeONO₂ for the three seasons. The use of the lowest calculated 2-PeONO₂ branching ratio, as described in section 3.2.2, slightly reduces the severe model overprediction for 2-PeONO₂ during spring and summer 2015. The lower C₅-RONO₂ branching ratios provide excellent model-measurement agreement for winter 2011, especially at photochemical ages <12 hours. The lack of model-measurement agreement in the spring and summer seasons is consistent with previous studies (*e.g.* Russo et al., 2010; Simpson et al., 2003; Sommariva et al., 2008; Worton et al., 2010). Reeves et al. (2007) attributed comparable model over-prediction to decomposition of C₅ peroxy radicals before reacting with NO, though no mechanism or evidence was put forth. As discussed previously, alkoxy radical decomposition of larger alkoxy radicals to smaller alkyl radicals that form peroxy radicals is well established. However, this pathway would not reduce the available pool of peroxy radicals as those alkoxy radicals would have already been converted from the pool of peroxy radicals before decomposition, and would be captured by the formation branching ratio. Alternatively, the formation branching ratios of the C₅ RONO₂ may be too high. However, without better constraints on the RONO₂ formation branching ratios it is difficult to reconcile these model-measurement discrepancies.

3.5. Photochemical age at BAO

We use the 2-PrONO₂/propane and 2-BuONO₂/n-butane ratios to derive photochemical ages during summer 2015 at BAO (OH = $6 \times 10^6 \text{ molecules cm}^{-3}$, $\beta_{2\text{-PrONO}_2} = 0.030$, $\beta_{2\text{-BuONO}_2} = 0.065$, and average summer k_A and k_B values from **Tables 2** and **3**). The alkyl nitrate photochemical clock captures daily photochemistry: *i.e.*, 89% of daytime data at BAO exhibit photochemical ages <12 hours and align with hours since sunrise during summer months (Figure S4). This consistency between hours since sunrise and derived photochemical age suggest that BAO typically experiences a fresh, well-mixed airmass with little influence from long-term transport or day-to-day carryover, and that 2-PrONO₂ and 2-BuONO₂ sources and sinks are typically well-described by the model. However, there are exceptional days when the assumption that photochemical age increases with

simultaneously increasing RONO₂ and decreasing RH is not met (Figure S5). For example, on 21 August 2015, calculated photochemical age increases through the afternoon despite decreasing 2-PrONO₂ resulting from a rapid decrease in propane relative to 2-PrONO₂ (Figure S5c). In Figure S5b photochemical age increases on 22 August 2015 between 06:00 and 10:00, and begins decreasing after 10:00 as a result of increasing propane concentrations that decrease RONO₂/RH. Because this event fails to meet the model assumptions, the subsequent calculation results in a decreasing photochemical age through the day. These examples from late August 2015 coincide with smoke intrusion into the Front Range from wildfires in the Washington and Idaho (Lindaas et al., 2017) – although we note that most other summer 2015 days designated as smoke-impacted do not show this anomalous 2-PrONO₂/propane trend.

4. Conclusions

Uncertainties in selection of OH concentration, RONO₂ branching ratios, and rates of RONO₂ photolysis and oxidation all impact modeled RONO₂/RH and thus photochemical age. However, OH concentration is the most sensitive factor when estimating photochemical age of a sampled air mass using the RONO₂/RH model. Incorporation of seasonal temperature and pressure dependent branching ratios reduces model-measurement discrepancies for EtONO₂/ethane.

Dry deposition is a loss process for RONO₂, but has little effect on photochemical models of these compounds with the exception of methyl nitrate. However, because reaction of RONO₂ with OH releases NO₂ and RO₂ radicals, their production and export can both hinder local ozone production and contribute to downwind production of ozone, and potentially HNO₃ or aerosol nitrate. Thus, deposition mitigates the impact on ozone of long-range transport of MeONO₂ out of the source region (Williams et al., 2014). Further work investigating the mechanisms of deposition for the volatile RONO₂ species is thus warranted.

Data Accessibility Statement

The data used in this manuscript can be found in a repository hosted by the National Oceanic and Atmospheric Administration for SONGNEX (<http://esrl.noaa.gov/csd/groups/csd7/measurements/2015songnex/>) and NACHTT (<https://www.esrl.noaa.gov/csd/groups/csd7/measurements/2011NACHTT/>).

Supplemental Files

The supplemental files for this article can be found as follows:

- **Table S1.** OH + alkane H-atom abstraction branching ratio. (Page 9). DOI: <https://doi.org/10.1525/elementa.299.s1>
- **Table S2.** Calculated temperature and pressure dependent C₃–C₅ RONO₂ formation branching ratios. (Page 9). DOI: <https://doi.org/10.1525/elementa.299.s1>
- **Table S3.** Calculated temperature and pressure dependent EtONO₂ and pressure dependent MeONO₂

formation branching ratios. (Page 9). DOI: <https://doi.org/10.1525/elementa.299.s1>

- **Table S4.** Equation SE1–SE3 parameters used to calculate temperature and pressure dependent C₃–C₅ RONO₂ formation branching ratios. (Page 10). DOI: <https://doi.org/10.1525/elementa.299.s1>
- **Table S5.** Average alkyl nitrate parent alkane mixing ratios (ppb_v) at BAO. (Page 10). DOI: <https://doi.org/10.1525/elementa.299.s1>
- **Table S6.** Seasonal lifetime ranges in days of C₁–C₅ RONO₂ at the BAO site in respect to OH oxidation ($\tau_{\text{OH}} = 1/k_4$), photolysis ($\tau_{\text{hv}} = 1/J_5$), and OH + photolysis ($\tau_{\text{OH} + \text{hv}} = 1/k_5$). (Page 10). DOI: <https://doi.org/10.1525/elementa.299.s1>
- **Table S7.** Fluxes and dry deposition velocities calculated from 22:00 06 March 2011 – 06:00 07 March 2011. (Page 11). DOI: <https://doi.org/10.1525/elementa.299.s1>
- **Figure S1.** RONO₂/RH is modeled using E2 for (a) MeONO₂/methane and (b) 2-BuONO₂/n-butane using initial RONO₂/RH ratios of zero and non-zero values for spring 2015 conditions and branching ratios of 0.078 for 2-BuONO₂ and 0.0093 for MeONO₂. Non-zero RONO₂/RH initial ratios are defined as the 5th percentile of RONO₂/RH during morning (00:00 – 06:00) hours for spring 2015. (c) MeONO₂/methane is plotted against 2-BuONO₂/n-butane for the daytime (08:00 – 18:00) spring 2015 data. Observations are in grey circles, while model results are in lines with markers indicating photochemical age. (Page 12). DOI: <https://doi.org/10.1525/elementa.299.s1>
- **Figure S2.** RONO₂ and meteorological data for dry deposition velocity calculations from the winter 2011 campaign for 06 March 2011–07 March 2011. (a) RONO₂ versus time for C₁–C₅ RONO₂. (b) Individual vertical profiles of potential temperature and wind speed that show the formation of a nocturnal boundary layer ceiling at 22:18. (c) Temperature and wind speed measurements made at 10 m (black), 100 m (blue), and 300 m (red) on the tower at the BAO site. (Page 13). DOI: <https://doi.org/10.1525/elementa.299.s1>
- **Figure S3.** Observed daytime (08:00 – 18:00) RONO₂/RH was plotted against 2-BuONO₂/n-butane (grey circles) for winter 2011 (left), spring 2015 (middle) and summer 2015 (right). Modeled RONO₂/RH were generated with E2 using average campaign k_A and k_B values from Table 2 and Table 3, and seasonal pressure and temperature dependent branching ratios (Table 1). Models were generated with non-zero initial ratios (black solid lines) defined as the 5th percentile value of RONO₂/RH between 00:00 – 06:00 for all days during each respective campaigns. Dashed red lines are modeled RONO₂/RH including loss by dry deposition (k_{dep} , Table S7). Solid blue circles are average RONO₂/RH versus 2-BuONO₂/n-butane values with an equal number of points per averaging bin ($n = 46$ for winter 2011, 110 for spring 2015, and 69 for summer 2015). Error bars are one standard deviation of the EtONO₂/ethane and 2-BuONO₂/n-butane averages. (Page 14). DOI: <https://doi.org/10.1525/elementa.299.s1>

- **Figure S4.** RONO₂/RH is modeled using E2 for 2-PrONO₂/propane and 2-BuONO₂/n-butane. Branching ratios are averages from Table 1 ($\beta_{2\text{-PrONO}_2} = 0.030$; $\beta_{2\text{-BuONO}_2} = 0.068$). Observed (circles) and modeled (line) 2-PrONO₂/propane are plotted against 2-BuONO₂/n-butane for the daytime (08:00 – 18:00) SONGNEX-summer data. Observations are colored by hours from sunrise for each data point. Markers for 1, 3, 6, 12, and 24 hours of photochemical aging for the two models are overlaid on the modeled curves. (Page 15). DOI: <https://doi.org/10.1525/elementa.299.s1>
- **Figure S5.** (a, b) Photochemical age, (c, d) 2-PrONO₂ concentration, and (e, f) propane concentration for 21 August 2015 and 22 August 2015 at the BAO site. Observed photochemical age is estimated by comparing ambient 2-PrONO₂/propane and 2-BuONO₂/n-butane values to modeled values. (Page 15). DOI: <https://doi.org/10.1525/elementa.299.s1>

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Competing interests

The authors have no competing interests to declare.

Author contributions

- Contributed to conception and design: AA, DFK, EF
- Contributed to acquisition of data: AA, DFK, EF, BS, BS, YZ
- Contributed to analysis and interpretation of data: AA, DFK, EF
- Drafted and/or revised the article: AA, DFK, EF
- Approved the submitted version for publication: AA, DFK, EF, BS, BS, YZ

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