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On the role of monoterpene chemistry in the remote continental boundary layer

E. C. Browne^{1,*}, P. J. Wooldridge¹, K.-E. Min^{2,**}, and R. C. Cohen^{1,2}

¹Department of Chemistry, University of California Berkeley, Berkeley, California, USA

²Department of Earth and Planetary Sciences, University of California Berkeley, Berkeley, California, USA

* now at: Department of Civil and Environmental Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, USA

** now at: NOAA Earth System Research Laboratory and Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, Colorado, USA

Correspondence to: R. C. Cohen (rccohen@berkeley.edu)

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Abstract. The formation of organic nitrates (RONO₂) represents an important NO_x (NO_x = NO + NO₂) sink in the remote and rural continental atmosphere, thus impacting ozone production and secondary organic aerosol (SOA) formation. In these remote and rural environments, the organic nitrates are primarily derived from biogenic volatile organic compounds (BVOCs) such as isoprene and monoterpenes. Although there are numerous studies investigating the formation of SOA from monoterpenes, there are few studies investigating monoterpene gas-phase chemistry. Using a regional chemical transport model with an extended representation of organic nitrate chemistry, we investigate the processes controlling the production and fate of monoterpene nitrates (MTNs) over the boreal forest of Canada. MTNs account for 5–12 % of total oxidized nitrogen over the boreal forest, and production via NO₃ chemistry is more important than production via OH when the NO_x mixing ratio is greater than 75 pptv. The regional responses are investigated for two oxidation pathways of MTNs: one that returns NO_x to the atmosphere and one that converts MTNs into a nitrate that behaves like HNO₃. The likely situation is in between, and these two assumptions bracket the uncertainty about this chemistry. In the case where the MTNs return NO_x after oxidation, their formation represents a net chemical NO_x loss that exceeds the net loss to peroxy nitrate formation. When oxidation of MTNs produces a molecule that behaves like HNO₃, HNO₃ and MTNs are nearly equal chemical sinks for NO_x. This uncertainty in the oxidative fate of MTNs results in changes

in NO_x of 8–14 %, in O₃ of up to 3 %, and in OH of 3–6 % between the two model simulations.

1 Introduction

Measurements of concentrations and fluxes indicate that monoterpenes are emitted into the atmosphere at rates large enough to affect OH concentrations and to contribute a large fraction of the secondary organic aerosol (SOA) mass in such diverse environments as the Amazon (e.g., Karl et al., 2007), the Mediterranean (e.g., Owen et al., 1997; Davison et al., 2009; Seco et al., 2011), pine forests of western North America (e.g., Bouvier-Brown et al., 2009; Kim et al., 2010), the boreal forest (e.g., Spirig et al., 2004; Räisänen et al., 2009; Hakola et al., 2012), and in urban regions of California's Central Valley (Rollins et al., 2012). While there is a growing body of laboratory and field measurements related to monoterpene SOA (e.g., Tunved et al., 2006; Williams et al., 2007; Fry et al., 2009, 2011; Hallquist et al., 2009; Rollins et al., 2009; Slowik et al., 2010), the gas-phase chemistry of monoterpenes that must precede SOA formation has not been explored in detail with chemical transport models (CTMs). In part this situation is due to the uncertainties in isoprene chemistry that, until recently, were so large that they overwhelmed any uncertainties in modeling monoterpene chemistry. With substantial progress in understanding isoprene oxidation sequences (e.g., Paulot et al., 2009a, b; Peeters and

Müller, 2010), it is timely to explore the role of the gas-phase chemistry of monoterpenes in CTMs.

In the remote continental boundary layer, total RONO_2 (ΣANs) formation is the primary reaction determining the lifetime of NO_x (Browne and Cohen, 2012; Browne et al., 2013). Thus, in regions where monoterpene emissions are important to the total OH and NO_3 reactivity, the formation of monoterpene nitrates (MTNs) can be expected to affect the NO_x lifetime, which, in turn, will affect OH concentrations and the ozone production efficiency. In Browne et al. (2013) observations of volatile organic compounds (VOCs), OH, and NO_x were used to calculate that the instantaneous production of ΣANs is more rapid than production of HNO_3 over the Canadian boreal forest and that a significant fraction of the ΣANs production rate is due to the oxidative chemistry of α - and β -pinene. These are the two most abundant monoterpenes on the global scale, and thus insights from the Canadian forests are likely relevant to other locations. The analysis of observations described in Browne et al. (2013) also indicates that the lifetime of ΣANs is shorter than that of HNO_3 over the boreal forest, and that this short lifetime is due to a combination of oxidation of ΣANs resulting in the return of NO_x to the atmosphere (NO_x recycling), deposition, and the hydrolysis of particulate ΣANs (forming HNO_3). Each of these loss processes has different implications for the NO_x budget: the first one recycles NO_x , converting a reservoir species back to the active radical pool, while the latter two result in rapid removal of odd nitrogen from the atmosphere.

This paper explores the consequences of MTN chemistry for nitrogen oxides as well as the drivers of atmospheric oxidative chemistry (e.g., OH, O_3) using the Weather Research and Forecasting model with Chemistry (WRF-Chem) (Grell et al., 2005), a regional chemical transport model. The model is run using an extended representation of organic nitrate chemistry and the model calculations are compared to observations from the NASA Arctic Research of the Composition of the Troposphere from Aircraft and Satellites (ARCTAS) campaign (Jacob et al., 2010) over the Canadian boreal forest. We then explore the relative contributions of OH and NO_3 chemistry to the production of MTNs and investigate how the total production impacts NO_y partitioning. To understand the range of possible roles for MTNs, we examine their sinks, comparing model predictions for several atmospheric constituents in scenarios where oxidation of MTNs results in the release of NO_x to predictions where the $-\text{ONO}_2$ functional group is retained as an organic nitrate.

2 Model description

2.1 Domain and emissions

WRF-Chem v3.2.1 (Grell et al., 2005) at $36\text{ km} \times 36\text{ km}$ resolution over a 5364 km (east–west) by 3384 km (north–

south) domain centered over Canada was used for this study. Data from the outer 180 km of the domain are discarded to allow for relaxation of the boundary conditions taken from MOZART-4 model (Emmons et al., 2010) using meteorology from GEOS-5 (available at <http://www.acd.ucar.edu/wrf-chem/>). Meteorological data are from the North American Regional Reanalysis and the model was run for six days as a spin-up prior to simulating the time period corresponding to the ARCTAS measurements over the Canadian boreal forest from 29 June to 13 July 2008. The goal was not to directly simulate the ARCTAS conditions but rather to investigate the impacts of MTNs on NO_x and O_3 in the boreal forest. To that end, fire emissions of NO_x and volatile organic compounds were not included in the model. Modeled anthropogenic emissions were from Reanalysis of Tropospheric composition (RETRO) and Emissions Database for Global Atmospheric Research (EDGAR) using the global emissions preprocessor for WRF-Chem (Freitas et al., 2011) and modeled biogenic emissions were from the Model of Emissions of Gases and Aerosols from Nature (MEGAN) (Guenther et al., 2006) available at <http://www.acd.ucar.edu/wrf-chem/>. In order to achieve approximate agreement with the ARCTAS observations of NO_x and biogenic volatile organic compounds (BVOCs), isoprene emissions were uniformly reduced by 20% and soil NO_x , lumped α -pinene, and lumped limonene emissions were each increased by a factor of two.

Aerosols are treated using the Modal Aerosol Dynamics Model for Europe (MADE) with the Secondary Organic Aerosol Model (SORGAM) (Ackermann et al., 1998; Schell et al., 2001). This mechanism is a “two-product model” approach to aerosols and consequently does not treat the partitioning of individual chemical species such as organic nitrates. Therefore, particle-phase partitioning does not impact the distribution of organic nitrates.

Although more detailed aerosol chemical mechanisms that track the individual species as they transfer between the gas and particle phases do exist (e.g., Derwent et al., 2003; Bonn et al., 2005), our focus here is on investigating the impacts of the gas-phase representation of the chemistry; a full consideration of the aerosol is beyond the scope of this work.

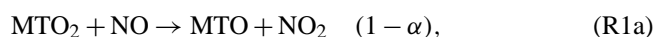
2.2 Chemical mechanism

The chemical mechanism is based on the RACM2 mechanism (Goliff et al., 2013), which in its original form includes three organic nitrate species: two isoprene-derived nitrates and one lumped nitrate (ONIT). This lumped nitrate is long-lived ($>100\text{ h}$ lifetime to oxidation by $1 \times 10^6\text{ molecules cm}^{-3}$ of OH at 298 K), assumed to release NO_2 with 100% efficiency upon oxidation, and has a long lifetime to deposition (Henry's law constant of $\sim 1\text{ M atm}^{-1}$). In contrast, Henry's law coefficients for hydroxy nitrates have been measured to be on the order of $10^3\text{--}10^5\text{ M atm}^{-1}$ (Shepson et al., 1996; Treves et al., 2000). Monoterpene nitrates are likely to be multifunctional nitrates

(containing a nitrate and most likely a hydroxy or peroxide group) and are thus likely to have deposition rates that are much faster than the rate assumed for ONIT. As a 10-carbon molecule, monoterpene nitrates will have a faster oxidation rate and return NO_2 to the atmosphere with less than 100 % efficiency. Furthermore, some monoterpene nitrates will be unsaturated molecules that in addition to having a faster OH oxidation rate will also undergo ozonolysis.

Due to these issues, investigating the low- NO_x , high-BVOC chemistry of organic nitrates required an expansion of the organic nitrate chemistry. The changes we make to the RACM2 mechanism include the reclassification of the lumped nitrates into the new species and the addition of oxidation and photolysis reactions for the new organic nitrate species. The RACM2 mechanism includes two lumped species to represent low-reactivity (lumped into the model species α -pinene) and high-reactivity (lumped as limonene) monoterpenes. Most of the monoterpene oxidation products (e.g., pinonaldehyde, organic nitrates) are lumped into generic products (e.g., aldehydes and ketones, ONIT).

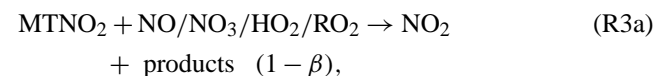
During the day, monoterpene nitrates are formed from the minor channel of the reaction of the monoterpene peroxy radical with NO:



where MTO_2 is the monoterpene-derived peroxy radical formed from the reaction of monoterpenes with OH, MTO is the monoterpene-derived alkoxy radical, and α is the yield of MTNs. At night, the reaction of NO_3 with monoterpenes results in the formation of a nitrooxy peroxy radical (MTNO_2):



This radical reacts with NO, NO_3 , HO_2 , or RO_2 with the following possible channels:



where β represents the yield of MTNs from this nocturnal chemistry. The exact reactions for both monoterpene species used in RACM2 and the identity of the products can be found in the supplemental material and are discussed briefly below.

For daytime chemistry, RACM2 has an 18 % yield of organic nitrate from the reaction of the lumped α -pinene peroxy radical with NO and a 0 % yield for the reaction of

the lumped limonene peroxy radical with NO. In our update, the yield from limonene was increased to 22 % as reported in Leungsakul et al. (2005) and as is assumed in the Master Chemical Mechanism v3.2 (MCM v3.2) available at <http://mcm.leeds.ac.uk/MCM> (Jenkin et al., 1997; Saunders et al., 2003); the yields of the other monoterpene oxidation products are reduced to account for the increase in organic nitrate yield. The exact yield of monoterpene nitrates carries some uncertainty since yields have only been directly measured for a few specific monoterpenes and these measurements are subject to biases due to loss of the nitrates to aerosol, chamber walls, and/or hydrolysis. The exact yield may be lower or higher than used here; however, any reasonable changes will only impact the exact numerical results and not the overall conclusion that MTNs are important in the NO_x and NO_y budgets.

RACM2 assumes that the oxidation of monoterpenes by NO_3 results in the formation of two nitrooxy peroxy radicals: one that primarily recycles NO_x , and one that primarily forms a nitrate. The split between these two radicals that is in RACM2 is used here, but they are renamed such that their products form MTNs (70 % saturated and 30 % unsaturated). The split of peroxy radicals for the lumped limonene is based on Spittler et al. (2006), who report an organic nitrate yield of 67 %. Fry et al. (2011) recently reported a smaller organic nitrate yield (30 %) from the reaction of NO_3 with limonene. The reason for the discrepancies between the two studies is unclear.

Two monoterpene-derived nitrates are introduced, one unsaturated (UTONIT) and one saturated (TONIT). The lumped limonene peroxy radicals react with NO to form unsaturated nitrates, while lumped α -pinene peroxy radicals react with NO to yield both saturated and unsaturated nitrates with yields of 12 and 6 %, respectively. We note that this branching is not constrained by laboratory measurements; however changes to this branching should only be important if the NO_x recycling from monoterpene nitrate oxidation is high. Oxidation rates of the MTN with OH are calculated using weighted averages of the MCM v3.2 rates of α -pinene and β -pinene (assuming a 50–50 mixture and ignoring the OH abstraction channels) for TONIT and from limonene for UTONIT. The ozonolysis rate of UTONIT is estimated using the EPA Estimation Program Interface (EPI) Suite v4.1 (available at <http://www.epa.gov/opptintr/exposure/pubs/episuite.htm>) (US EPA, 2011). In what we refer to as our BASE case, oxidation of both TONIT and UTONIT generates a second-generation monoterpene nitrate which is oxidized, photolyzed, and deposited identically to HNO_3 .

Assessing the impact of monoterpene chemistry on the NO_x budget also requires updating the isoprene chemistry scheme to be consistent with recent laboratory and theoretical studies. Our isoprene oxidation scheme follows that of Paulot et al. (2009a, b). The formation of hydro-peroxy aldehydes (HPALD) from the isomerization reaction of isoprene

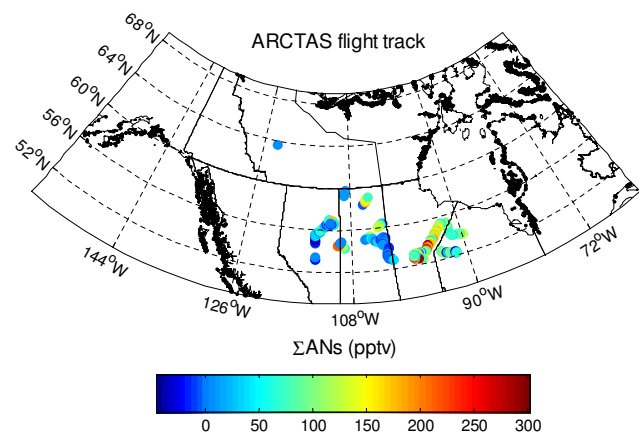


Fig. 1. Map of ARCTAS measurements of Σ ANs used in this analysis. These locations are removed from recent biomass burning influences and are at pressures greater than 600 mbar.

peroxy radicals is included using the rate measured by Crouse et al. (2011). The fate of HPALD follows the assumptions of Peeters and Müller (2010). The isomerization of the non-acyl methacrolein peroxy radical is included using the rate and products from Crouse et al. (2012). Peroxy radical cross reactions were determined following the protocol of Madronich and Calvert (1990) updated in some cases to Tyndall et al. (2001) and using updated reaction rates from IUPAC (Atkinson et al., 2006). Reactions of peroxy radicals with HO_2 were determined using the product yields from Hasson et al. (2004). Full details regarding the isoprene chemistry can be found in the Supplement.

Recently, Xie et al. (2013) implemented a revised isoprene chemistry scheme in SAPRC-07 based on assumptions similar to ours. Xie et al. (2013) show that this scheme, as implemented in the US EPA CMAQ (Community Multiscale Air Quality) model, results in significant improvement in the representation of chemistry over eastern US forests. They include a comparison of their results to the Σ ANs measured from the aircraft (Perring et al., 2009) and find good agreement.

Although of minor importance in the remote boreal forest, the treatment of the organic nitrates that are primarily of anthropogenic origin also required extension. The extended organic nitrate chemistry includes four nitrates primarily of anthropogenic origin (aromatic-derived, multifunctional unsaturated, multifunctional saturated, and monofunctional saturated nitrates) that were partitioned from the lumped precursors following the procedure of Middleton et al. (1990) and using branching ratios from Arey et al. (2001) and MCM v3.2. The yields of the nitrates are generally unchanged from RACM2, with the exception of the yield from the lumped species representing short-lived alkanes, alcohols, esters, and alkynes. This yield, originally derived using the branching ratio parameterization from Carter and Atkinson (1989), was reduced (and the non-nitrate products correspondingly in-

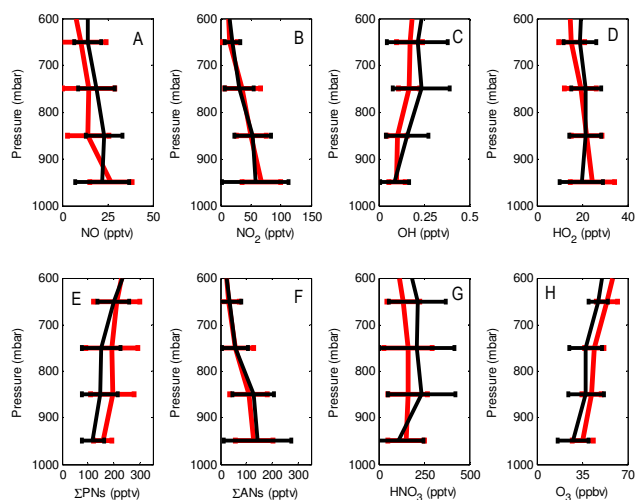


Fig. 2. Mean concentrations binned by altitude of (red) ARCTAS observations and (black) WRF-Chem sampled along the flight track for (a) NO, (b) NO_2 , (c) OH, (d) HO_2 , (e) Σ PNs, (f) Σ ANs, (g) HNO_3 , and (h) O_3 . ARCTAS observations are averaged to the resolution of WRF-Chem.

creased) to be consistent with the more recent parameterization from Arey et al. (2001).

The elements of our extended mechanism, including oxidation, photolysis, and dry deposition rates and reactions, are listed in the Supplement.

3 Evaluation of the model using ARCTAS observations

3.1 Description of ARCTAS observations

The model is compared to ARCTAS data from the 1 min merge version 13, which is publicly available at <http://www-air.larc.nasa.gov/missions/arctas/dataaccess.htm>. The data used include flight numbers 17–20 and 23–24. A full summary of the flights and the measurement suite can be found in Jacob et al. (2010). A map of the flight tracks, colored by observed Σ ANs concentration, is shown in Fig. 1. Comparisons of the vertical profiles from the surface to 600 mbar (~ 4.2 km pressure altitude) between the BASE model and the ARCTAS measurements for key NO_y and HO_x species are shown in Fig. 2. In making these comparisons, only ARCTAS data over land and removed from biomass burning influences (as defined from inspection of CO, HCN, and CH_3CN concentrations) are used.

Briefly, the measurements used to compare to the model output are from the NCAR chemiluminescence instrument for NO and O_3 (Weinheimer et al., 1994), the UC Berkeley thermal dissociation laser-induced fluorescence (TD-LIF) instrument for NO_2 , Σ PNs, and Σ ANs (Thornton et al., 2000; Day et al., 2002; Wooldridge et al., 2010), the Pennsylvania State University LIF for OH and HO_2 (Faloona et al.,

2004), and the California Institute of Technology chemical ionization mass spectrometer for HNO_3 (Crounse et al., 2006). Biogenic species include α - and β -pinene from the UC Irvine whole-air samples (Simpson et al., 2011) and isoprene, methyl vinyl ketone (MVK), and methacrolein (MACR) from the trace organic gas analyzer (Apel et al., 2003).

The ARCTAS measurements are averaged horizontally to the WRF-Chem resolution, use the closest WRF-Chem output time (output is hourly), and sample the WRF-Chem model along the flight track. However, during one flight leg (flight #20 at 21:51 to 22:28 UTC) the aircraft sampled a plume high in biogenics that WRF-Chem predicts to be southeast of the aircraft. We use the WRF-Chem predictions from this plume and not the flight location in our comparison.

3.2 Comparison of modeled and measured concentrations

The measurements and model results are averaged into 100 mbar bins to evaluate the ability of the model to capture the regional chemistry, as shown in Figs. 2 and 3. Overall the model compares favorably to the measurements of the different components of NO_y as well as OH, HO_2 , and O_3 , with the mean modeled value always within one standard deviation of the measured mean. NO , OH, and HNO_3 are, however, consistently higher in the model than in the measurements, with the mean in each bin higher than the measurement by an average of 3 pptv (27 %), 0.04 pptv (27 %), and 40 pptv (27 %), respectively. The mean values of the modeled total peroxy nitrates (ΣPNs) and O_3 are lower than the measurements by 35 pptv (19 %) and 6 ppbv (14 %), respectively. Some of the discrepancies are due to differences between modeled and observed clouds as reflected in comparison of measured and modeled photolysis rates of NO_2 that are 30 % higher on average in WRF (not shown). Overall, it can be concluded that within error, the model captures the regional features NO_y , HO_x , and O_3 despite some biases in the means of individual species.

Figure 3 shows the measurement–model comparison for the major biogenic species. As stated in Sect. 2.1, emissions over the entire domain have been reduced by 20 % for isoprene and have been doubled for monoterpenes to more closely match the ARCTAS observations. Due to errors in the WRF-Chem representation of the wind field, there are still discrepancies between the measurement and model. In the 950 mbar bin the mean value of the model and measurements agree to within 4 pptv (3 %); however, since only α - and β -pinene are measured during ARCTAS, this number is likely lower than the actual total monoterpene concentration. For instance the emissions of camphene and 3-carene were larger than those of α -pinene as measured by enclosure measurements of black spruce trees (Fulton et al., 1998). Black spruce trees are prevalent in the Canadian boreal forest. Summertime measurements in the Finnish boreal forest

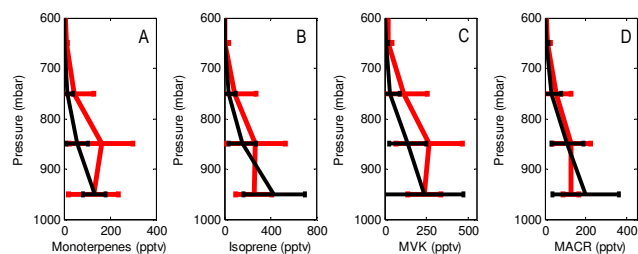


Fig. 3. Same as Fig. 2 but for (a) monoterpenes (only α - and β -pinene were measured during ARCTAS), (b) isoprene, (c) methyl vinyl ketone, and (d) methacrolein. The apparent maximum in the ARCTAS profiles (red) at 800–900 mbar is due to the plume high in biogenics sampled during flight #20 at 21:51 to 22:28 UTC. If this plume is removed, both the model and the measurements show a smoothly decreasing profile with increasing altitude, as expected for reactive species with surface emissions.

indicate that α - and β -pinene account for just over 60 % of the monoterpene concentration (Hakola et al., 2012).

There is more isoprene, 177 pptv (69 %), in the model than in the measurements at the lowest altitude, but at higher altitudes the model has less isoprene than was measured (by 113 pptv – 42 % at 850 mbar (Fig. 3b)). At 950 mbar the ratio of methacrolein (MACR) to isoprene is similar in the model (0.46) and the measurements (0.50), but the ratio of methyl vinyl ketone (MVK) to isoprene is much different (0.54 in the model compared to 0.93). This suggests the branching of MVK and MACR in either the OH oxidation or ozonolysis of isoprene in this low- NO_x environment is not described properly in the chemical mechanism (e.g., Liu et al., 2013), that there are some transport issues affecting the photochemical age of the air masses, or that depositional processes are poorly represented.

Figure 4a and b show comparisons of the WRF-Chem ΣANs production to the calculation of ΣAN production from the VOCs measured during ARCTAS (Browne et al., 2013). The two different calculations both show that biogenic precursors (isoprene, MVK, MACR, and monoterpenes) account for the vast majority of ΣAN production. In WRF-Chem, monoterpenes account for only 16 % of the total production, compared to 30 % during ARCTAS. This is consistent with the lower concentration of monoterpenes in the model (Fig. 3a).

The composition of ΣANs as calculated by WRF-Chem is shown in Fig. 5a along with the ARCTAS observations of the contribution of small ($\leq \text{C}_5$) alkyl nitrates measured in the whole-air samples (Simpson et al., 2011) to the total ΣANs measured by thermal dissociation laser-induced fluorescence (full details regarding this measurement during ARCTAS can be found in Browne et al., 2013). During ARCTAS the small alkyl nitrates measured in whole-air samples accounted for 26 % (median – Fig. 5b) of the ΣANs measurement, which is higher than the WRF-Chem prediction of 19 %. These small differences in the long-lived nitrates are

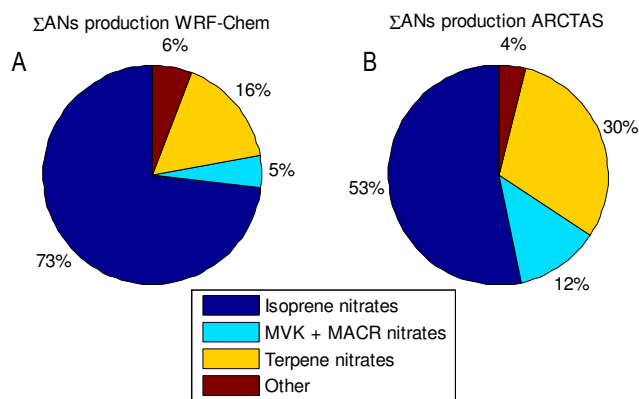


Fig. 4. (a) Instantaneous Σ ANs production rate as calculated by WRF-Chem along the ARCTAS flight track at altitudes less than 2 km. (b) The calculated instantaneous Σ ANs production based on the volatile organic compound precursors measured during ARCTAS for altitudes less than 2 km. Details regarding this calculation can be found in Browne et al. (2013).

likely associated with the boundary conditions. Due to their long lifetime, they do not affect any of the conclusions about the monoterpene chemistry.

In general, after adjustment of the emissions, the modeled and measured vertically averaged profiles of select BVOCs, NO_y constituents, HO_x , and O_3 agree to within one standard deviation over the domain (the boreal forest of Canada), and thus it can be concluded that the chemistry is represented well. There do exist some biases in the modeled mean values; however, the results presented below are fairly insensitive to these biases since two model runs are being compared to each other.

4 Monoterpene nitrate abundance, formation, and fate

The role of MTNs can be assessed using a 24 h boundary layer average from the 15 days corresponding to the ARCTAS measurements (28 June–13 July 2008) and using model output from areas located north of 49°N and defined as forest or wooded tundra in the USGS land use categories, an area of $5.59 \times 10^6 \text{ km}^2$. NO_x is defined as $\text{NO} + \text{NO}_2 + \text{NO}_3 + 2 \times \text{N}_2\text{O}_5$. In addition to assuming that the oxidation of MTNs forms a nitrate that behaves identically to HNO_3 as in the BASE case, it is instructive to compare a simulation in which monoterpene-derived nitrates release NO_2 upon oxidation (referred to as RECYCLE). These two situations represent extremes, and the likely situation is between them. Since there are no experimental constraints on the NO_x recycling from MTNs, the differences between the RECYCLE and BASE cases are useful in defining a range for the effects of MTNs.

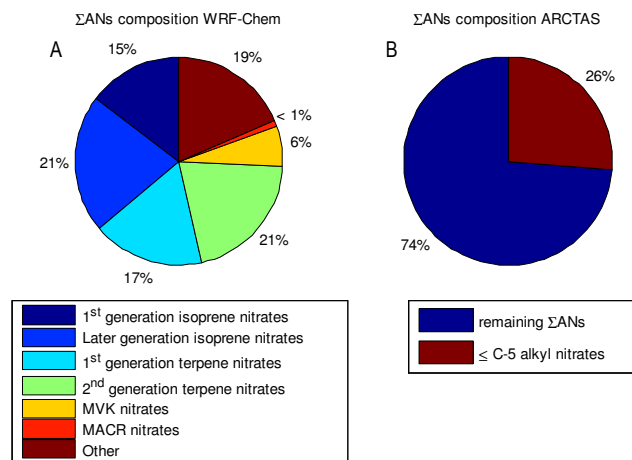


Fig. 5. (a) The Σ ANs composition predicted by WRF-Chem along the flight track at altitudes less than 2 km. (b) The Σ ANs composition during ARCTAS for the same altitudes. The $\leq \text{C}5$ nitrates were measured in the whole-air samples and the total was measured using TD-LIF. Details are in Browne et al. (2013).

4.1 Abundance

In the BASE case, over most of the boreal forest, first-generation MTNs account for $\sim 20\%$ of Σ ANs and second-generation MTNs account for $\sim 10\text{--}15\%$ (not shown). Together, the MTNs account for $30\text{--}40\%$ of Σ ANs over most of the domain and $60\text{--}80\%$ over British Columbia (not shown). However, although the fractional contributions over British Columbia are large, the absolute concentrations are very small in this region (Fig. 6a). The remaining Σ ANs are primarily of biogenic origin. In the northern part of the domain (north of approximately 56°N) $\sim 90\text{--}95\%$ of Σ AN are biogenic. This number decreases to $\sim 80\text{--}85\%$ in the southern portion (which has better overlap with the ARCTAS flight data), due to more anthropogenic influence (not shown).

Monoterpene nitrates are a significant contribution to NO_y , accounting for $\sim 8\text{--}12\%$ of NO_y over most of the domain (Fig. 6b); however in general they contribute less to NO_y ($\sim 6\text{--}8\%$) in areas where the absolute concentration of NO_y is highest (Fig. 6a). These high concentrations are in southern Canada, where the anthropogenic influence on total NO_y is larger. In the RECYCLE case the contribution of MTNs to NO_y has the same spatial distribution; however, the contribution to NO_y is reduced to $\sim 4\text{--}8.5\%$ over most of the domain.

4.2 Formation

Monoterpene nitrates may be formed as a result of either OH or NO_3 oxidation. Figure 7 shows the absolute production rates as a function of NO_x mixing ratio. Each point in the figure represents an equal number of model boxes (208).

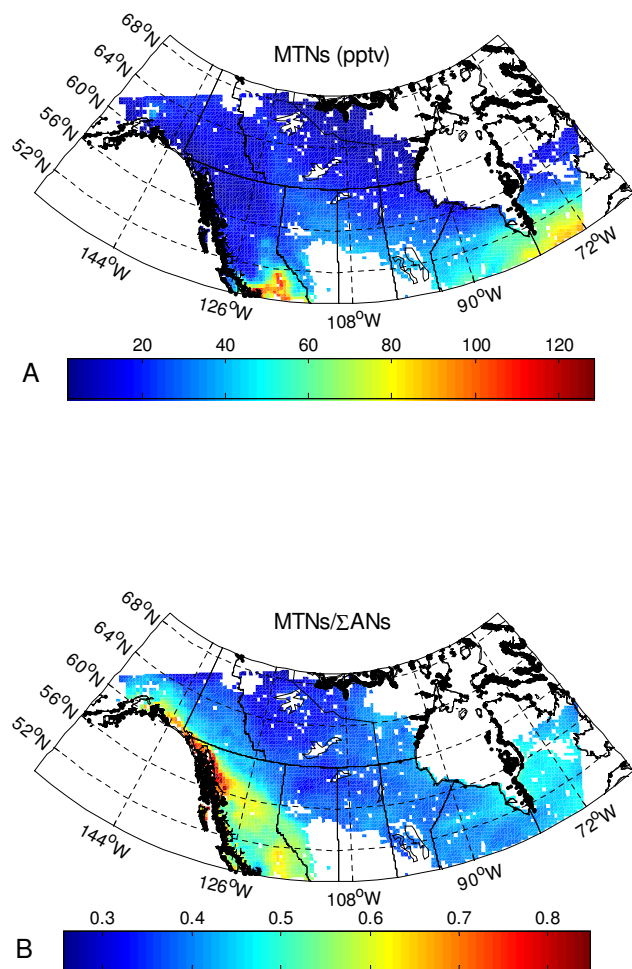


Fig. 6. (a) The 24 h, boundary-layer-averaged absolute concentration of MTNs in the BASE case. (b) Fractional contribution of MTNs to total oxidized nitrogen in the BASE case.

Production is dominated by OH chemistry for NO_x concentrations $< \sim 75$ pptv and is dominated by NO_3 chemistry for higher concentrations of NO_x . Since these averages are weighted by mass, this split between NO_3 and OH production is not an artifact due to differences in boundary layer heights between day and night. Rather the high production rates are due to a sharp increase in NO_3 and in the NO_3 -to-OH ratio above 50 pptv NO_x (not shown). There are no significant differences between the BASE and the RECYCLE (not shown) cases in the absolute or fractional production of MTNs.

4.3 Fate

Figure 8a shows the fractional loss of MTNs to OH, photolysis, and deposition for the BASE case. In the BASE case it is assumed that, upon oxidation, first-generation MTNs are converted into a more highly functionalized nitrate that behaves identically to HNO_3 . Since this oxidation step re-

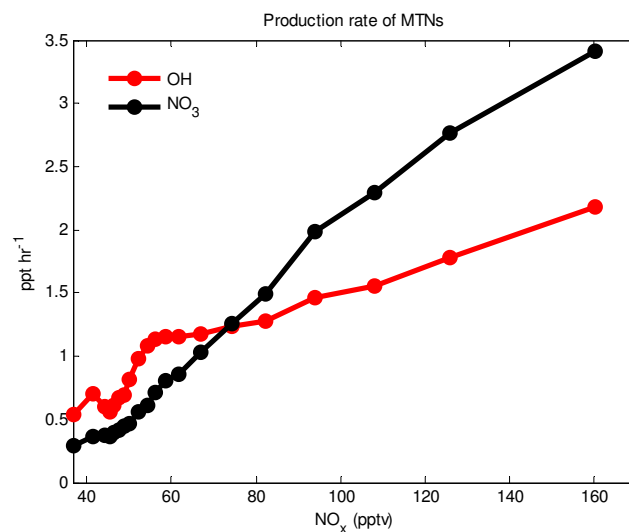


Fig. 7. The 24 h, boundary-layer-averaged production rates of MTNs by OH chemistry (red line) and by NO_3 chemistry (black line) as a function of NO_x concentration for the BASE case. Each point represents the mean NO_x value in each bin. Each bin contains the same number of model grid points (208). Note that the bins are not evenly spaced in terms of NO_x concentration.

tains the nitrate functionality, it is not a loss of MTNs. The loss of MTNs is dominated by deposition (due to the rapid depositional loss of the second-generation MTNs), with a small contribution from the photolysis of both first- and second-generation MTNs. In contrast, for the RECYCLE case (Fig. 8b), oxidation (and thus the return of NO_x to the atmosphere) is the primary contributor (48 %) to the loss of MTNs. Although oxidation by OH is more important, ozonolysis accounts for roughly one-third of the NO_x loss. Because most of the deposition loss in the BASE case is due to deposition of the second-generation nitrate, which is not formed in the RECYCLE case, deposition is a smaller loss process in the RECYCLE case (Fig. 8b) than in the BASE case (Fig. 8a); however it is still important, accounting for 16 % of the loss. The calculations show that the majority (93 %) of the MTN loss removes NO_x from the atmosphere by deposition in the BASE case, whereas this permanent removal drops to 16 % of the MTNs in the RECYCLE case.

The averaged MTNs loss rate is 8 % greater in the RECYCLE case (1.58 pptv h^{-1}) compared to the BASE case (1.47 pptv h^{-1}); however the averaged production rate is ~ 7 % greater in the RECYCLE case as well. These differences are due to the changes in OH, O_3 , and NO_x that are discussed in the next section. As a result of the slightly higher net MTNs loss in the RECYCLE case, the total concentration of MTNs is higher in the BASE case, with the second-generation MTNs accounting for most of this difference. In fact, the concentration of the first-generation MTNs is slightly larger (~ 5 %) in the RECYCLE case. This larger value comes from the difference between the production of

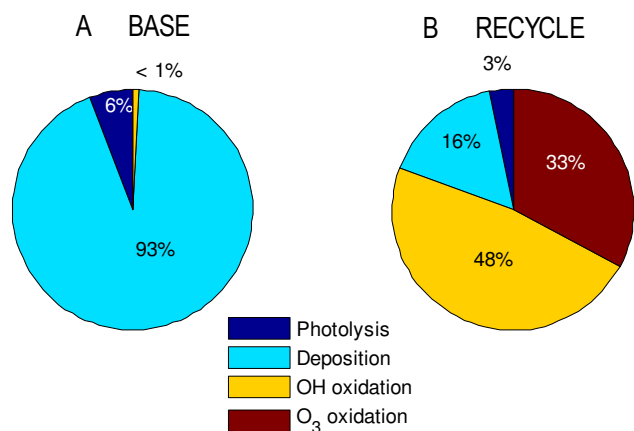


Fig. 8. The partitioning of the 24 h, boundary-layer-averaged loss processes of MTNs in (a) the BASE case and (b) the RECYCLE case. The averaged total loss is 8 % larger in the RECYCLE case compared to the BASE case. Loss of MTNs through oxidation by OH or O₃ and by photolysis results in the return of NO_x to the atmosphere. Loss of MTNs through deposition removes NO_x from the atmosphere and introduces it into the biosphere.

first-generation MTNs and their loss through reaction with OH and that O₃ is larger in the RECYCLE case.

5 MTNs and NO_x, NO_y, OH, and O₃

5.1 NO_x and NO_y

The lifetime of NO_x and the mechanism of NO_x removal are affected by MTN chemistry, as shown in Fig. 9. The net chemical loss rates (loss of NO_x – production from photolysis and oxidation) are shown as a function of NO_x to illustrate how, in low-NO_x environments, the formation of ΣANs represents the dominate NO_x loss as discussed in Browne and Cohen (2012). Figure 9 also shows that the net NO_x loss to MTNs (red lines) is always larger than the NO_x loss to ΣPNs and in the BASE case is similar to the NO_x loss to HNO₃. Monoterpene nitrate formation thus represents a significant NO_x sink.

The decrease in NO_x loss to MTNs in the RECYCLE case compared to the BASE case is evident when the NO_x concentrations of the BASE and RECYCLE cases are compared. The oxidation of MTNs in the RECYCLE case results in a ~8–14 % increase in NO_x (mean of ~5 pptv and max of 25 pptv) (Fig. 9a). This increase in NO_x results in an increase in ΣPNs by almost the same amount (mean 8.5 pptv and max of 30 pptv) with the same spatial distribution (not shown) in the RECYCLE versus the BASE case.

5.2 OH and O₃

The NO_x differences between the BASE and RECYCLE cases in turn affect the concentrations of O₃ and OH.

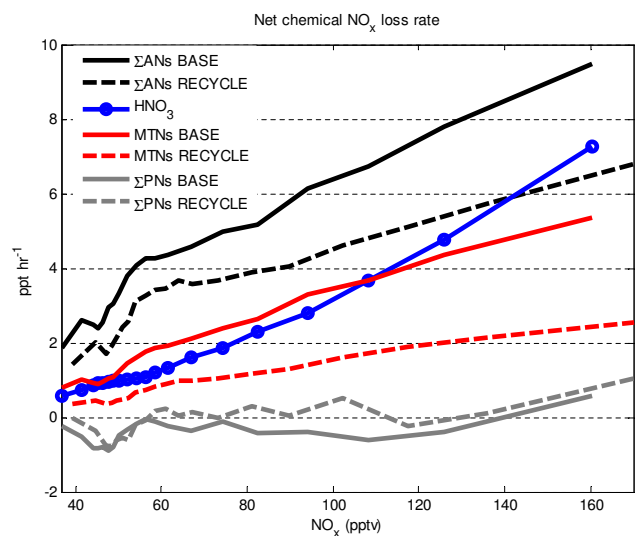


Fig. 9. The 24 h, boundary-layer-averaged, net chemical NO_x loss partitioned by class of reaction as a function of NO_x. The losses to HNO₃ for the BASE and RECYCLE cases are nearly identical and we show only the BASE case for clarity. The symbols on the HNO₃ curve represent the mean NO_x concentration of each bin. The NO_x bins contain equal numbers of model points.

Changes in OH follow the same spatial pattern as NO_x (Fig. 10a) and are about half as large – increases of ~3–6 % (mean of 5.2×10^4 molecules cm⁻³ and max of 2.3×10^5 molecules cm⁻³) in the RECYCLE case over the BASE case. Ozone also increases by up to 3 % (Fig. 10b). In absolute values, ozone increases by a mean of 0.4 ppbv and a maximum of 1 ppbv. The spatial pattern of the ozone change is shifted slightly downwind from the NO_x and OH changes, reflecting the slower kinetics of ozone production compared to the timescale of the kinetics affecting OH.

5.3 Mid-tropospheric effects

In addition to the boundary layer averages discussed above, we see changes between the RECYCLE and BASE at 600 mbar are ~4 % for ΣPNs and 1–2 % for O₃ over the eastern part of the domain. NO_x changes by ~2.5–5 % over most of the domain, with the hot spots occurring in the northwest and the east. By altering the mid-tropospheric burden, as well as the boundary layer burden of peroxy nitrates, monoterpene nitrates act to change the export of nitrogen from the continent, thus affecting ozone and OH concentrations downwind. These changes, while different in magnitude and location, should be qualitatively similar to the effects of isoprene nitrate chemistry, which have been discussed in detail in previous global modeling studies (e.g., von Kuhlmann et al., 2004; Fiore et al., 2005, 2011; Ito et al., 2007, 2009; Paulot et al., 2012).

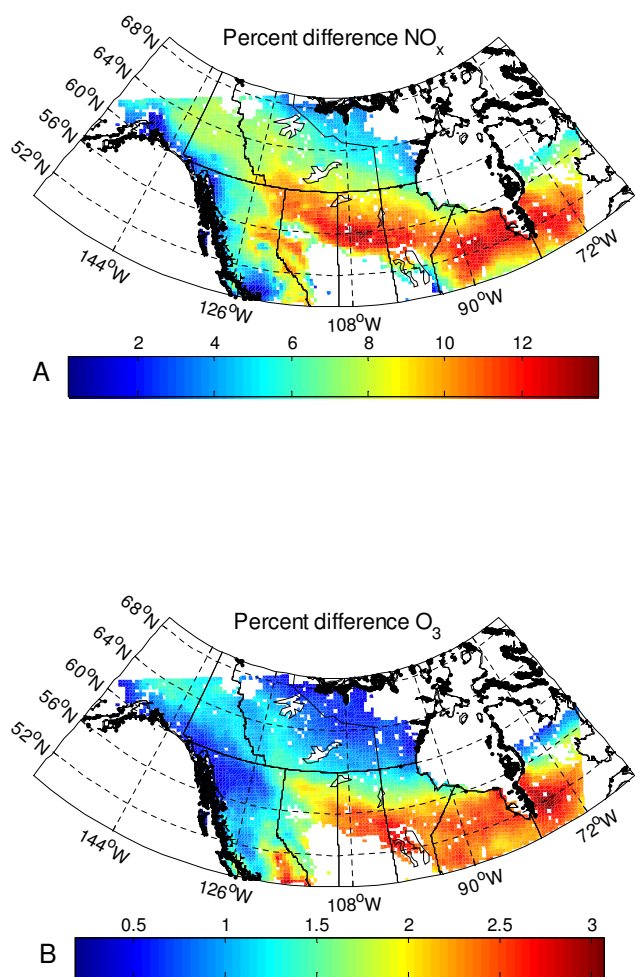


Fig. 10. Percent differences $((\text{RECYCLE} - \text{BASE})/\text{BASE} \times 100)$ between the RECYCLE and BASE cases for the 24 h, boundary-layer-averaged (a) NO_x and (b) O_3 concentrations.

6 Hydrolysis of tertiary MTNs

Recent studies have shown that tertiary nitrates undergo rapid hydrolysis in aqueous solutions (Darer et al., 2011; Hu et al., 2011) and laboratory-generated SOA (Liu et al., 2012), with the assumed product being HNO_3 and thus a “permanent” loss of nitrogen from the atmosphere. Browne et al. (2013) provide evidence in the ARCTAS data that particle-phase hydrolysis of MTNs is likely a significant loss process and an important source of HNO_3 . Due to the limitations of the model representation of organic aerosol (and its water content), the calculation of this chemistry is not attempted in WRF-Chem, but rather its effect is estimated using the organic aerosol loadings observed during ARCTAS. Two distinct regions of organic aerosol loading were encountered in the boundary layer during ARCTAS (excluding air masses with recent biomass burning or anthropogenic influences): a region with low loading (average of $1 \mu\text{g m}^{-3}$) and a high

loading (average of $6.6 \mu\text{g m}^{-3}$). The area of high loading was correlated with higher concentrations of acetone, an oxidation product of some monoterpenes, consistent with previous observations of high SOA yields from monoterpene oxidation (e.g., Tunved et al., 2006; Fry et al., 2009; Hallquist et al., 2009; Slowik et al., 2010; Fry et al., 2011).

WRF-Chem predicts significantly less acetone (24 h average boundary layer maximum of ~ 500 pptv) than was measured during ARCTAS (boundary layer median ~ 2 ppbv) by proton transfer reaction mass spectrometry (Wisthaler et al., 2002), possibly indicating that monoterpene emissions and oxidation rates are underestimated or that the boundary conditions for acetone are too low. WRF-Chem does, however, predict areas of higher acetone concentration that are correlated with higher monoterpene concentrations. In these areas of high acetone (≥ 250 pptv) the organic aerosol loading is assumed to be $6.6 \mu\text{g m}^{-3}$. Elsewhere we assume $1 \mu\text{g m}^{-3}$ of aerosol. A hydrolysis loss rate is calculated only for the first-generation MTNs since presumably the formation of second-generation MTNs would be greatly diminished if hydrolysis of MTNs results in HNO_3 . The calculation includes the assumption that there is sufficient liquid water content in the aerosol and uses the same two hydrolysis rates as in Browne et al. (2013) to represent the possible range of hydrolysis rates. As discussed in Browne et al. (2013), there is substantial variation in the hydrolysis rates that have been reported in the literature. This range is likely due to variation of the rate depending upon the molecular structure of the nitrate, although comparing bulk solution experiments (Darer et al., 2011; Hu et al., 2011) to aerosol experiments (Liu et al., 2012) may also explain part of the variation. Additionally it is assumed that 75 % of the MTNs formed from the reaction of OH with monoterpenes are tertiary, with a vapor pressure of 4×10^{-6} torr, and that NO_3 initiated oxidation results primarily in secondary organic nitrates whose lifetime to hydrolysis is long and can be ignored. With these assumptions and conditions, the calculated loss rate of MTNs and a corresponding production rate of HNO_3 averaged over the entire domain of our calculations ranges from 0.11 pptv h^{-1} (hydrolysis rate of $4.63 \times 10^{-5} \text{ s}^{-1}$) to 1.01 pptv h^{-1} (hydrolysis rate of $4.15 \times 10^{-4} \text{ s}^{-1}$). For comparison, the production rate of HNO_3 via reaction of NO_2 with OH in the domain is 3.14 pptv h^{-1} , and thus this HNO_3 source is ~ 3.5 to 32 % as large as the known daytime HNO_3 source.

This extra source of HNO_3 initially seems incompatible with the HNO_3 budget since WRF-Chem generally predicts larger concentrations of gas-phase HNO_3 (Fig. 2g) than indicated by the ARCTAS measurements. This measurement–model discrepancy of HNO_3 is in part due to the higher OH concentrations predicted by WRF-Chem and the lower particle-phase NO_3^- predicted by WRF-Chem compared to the observations. This extra loss would also necessitate an increase in the source of ΣANs . It is reasonable to believe that the source of ΣANs may be larger; in particular, monoterpenes may be increased (or sesquiterpene emissions added),

while still maintaining agreement between the measurements and the model. Thus, this back-of-the-envelope calculation for this loss process is compatible with the measurement–model comparison.

7 Discussion

The 3-D CTM calculations presented here indicate that oxidation of monoterpenes is a major sink of NO_x , a source of low-vapor-pressure MTNs, and a likely source of HNO_3 . Furthermore, given the differences in O_3 and OH observed between the BASE and RECYCLE cases here, even larger differences are likely when comparing chemical mechanisms with MTN representation to those without.

The chemistry as parameterized here represents a range that brackets some of the key uncertainties of MTNs, while remaining consistent with the measurements from ARCTAS. Although there remain important issues to resolve concerning the gas-phase and multiphase chemistry of monoterpenes and MTNs, the results of these calculations indicate that this chemistry will be locally important wherever monoterpene emissions are a large fraction of VOC reactivity. In addition to these local changes in the chemistry of the atmosphere, the depositional loss of monoterpene nitrates will have important impacts on soil nitrogen and, consequently, the carbon cycle.

To our knowledge, there has been no prior work specifically looking at how the chemistry of MTNs impacts the composition and oxidizing capacity of the troposphere. Past global modeling studies, however, have included the oxidation of monoterpenes and the formation of MTNs (Horowitz et al., 2007; Ito et al., 2007, 2009), but have investigated the impact of MTNs in conjunction with isoprene-derived nitrates. Nevertheless, the results of these studies imply that modeled concentrations of NO_x , OH, O_3 , and ΣPNs are sensitive to the assumptions regarding the formation and fate of biogenic organic nitrates. Our finding that the production of MTNs from NO_3 chemistry accounts for the majority of MTNs production at higher NO_x concentrations is consistent with the results of Horowitz et al. (2007) for isoprene nitrates over the eastern United States and with the results of Pye et al. (2010), who found that the aerosol produced from monoterpenes and sesquiterpenes doubled over the southeastern United States when NO_3 oxidation of these species was included in the model. Furthermore, a recent 1-D model study simulating a northern Michigan forest calculated a nighttime production rate larger than the daytime production rate for the monoterpene-derived nitrates (Pratt et al., 2012). Together, these studies in conjunction with the work presented here indicate that the chemistry of MTNs is necessary to accurately simulate SOA and tropospheric chemistry.

Although the focus here was on the boreal forest of Canada, where there were observations to test the calculations, similar results are likely wherever monoterpene emissions are abundant, including the Mediterranean (e.g., Owen

et al., 1997; Davison et al., 2009; Seco et al., 2011), the Pearl River delta (e.g., Wang et al., 2011), and ponderosa pine forests (e.g., Bouvier-Brown et al., 2009; Kim et al., 2010). It is worth noting that the speciation of the monoterpenes in these environments is likely different and that a parameterization using two representative monoterpenes may not be sufficient to capture the resulting differences in chemistry. We believe that limitations in our knowledge of monoterpene emissions and their gas-phase chemistry likely overshadow any uncertainties introduced with the use of two representative species in a chemical transport model. Nonetheless, our work has demonstrated that gas-phase monoterpene chemistry is important and further improvement in emissions and representations of their chemistry appropriate for reduced chemical mechanisms is warranted.

It is also likely that emissions of sesquiterpenes ($\text{C}_{15}\text{H}_{24}$), whose emissions are currently lumped into the monoterpenes, are important sinks of NO_x and sources of SOA. The oxidative chemistry of sesquiterpenes will likely have a different impact on the oxidative capacity of the atmosphere due to their higher reactivity and lower vapor pressures. For example, a recent study using 2-methyl-1-alkenes as surrogates for terpenes found > 22 % yields of particle-phase β -hydroxy organic nitrates with a 15-carbon alkene (Matsunaga and Ziemann, 2010). This large yield suggests that sesquiterpenes (and their nitrates) should have significant local impacts on both NO_y and SOA.

While the global impacts of this chemistry were not investigated here, Paulot et al. (2012), however, show that over the tropics the formation of isoprene nitrates results in a net chemical NO_x sink, while over the oceans isoprene nitrates act as a net NO_x source. It can be expected that MTNs have similar effects on global chemistry. MTNs will act to increase the ozone burden if the NO_x is released in areas with a higher ozone production efficiency than that in which it was initially sequestered. This effect will depend on the details of the correct MTN chemistry, both directly through the reactions of MTNs and indirectly through their effect on NO_y partitioning, OH, and O_3 . For example, the concentration of ΣPNs is higher in the RECYCLE case than in the BASE case. As a result, the transport of NO_x reservoirs from the continent to the oceans is larger in the RECYCLE than in the BASE case – a fact that amplifies differences in downwind O_3 .

8 Conclusions

Using the WRF-Chem model with an expanded organic nitrate representation, we are able to reproduce observations of a wide suite of chemicals, including ΣANs , observed during ARCTAS. Monoterpene nitrates were ~ 5 –12 % of NO_y over the boreal forest of Canada, and NO_3 chemistry is the most important production pathway for MTNs when NO_x is greater than ~ 75 pptv.

The fate of MTNs depends on the assumed oxidation products. In the BASE case, where oxidation results in a more functionalized nitrate that behaves like HNO_3 , deposition dominates the loss of MTNs. In this calculation MTN and HNO_3 formation are approximately equal sinks of NO_x . In the RECYCLE case, where oxidation returns NO_x to the atmosphere, MTNs are still $\sim 17\%$ of the net NO_x removal and this sink is similar to or greater than the net chemical sink from peroxy nitrates. These calculations are likely lower bounds on the net NO_x sink represented by MTNs as particle-phase hydrolysis of tertiary MTNs is likely an important loss process for MTNs, as is hinted at by the ARCTAS observations (Browne et al., 2013) and as suggested by laboratory measurements (Darer et al., 2011; Hu et al., 2011; Liu et al., 2012). The particle-phase hydrolysis could be between ~ 7 and $\sim 70\%$ of the MTNs loss rate calculated using the WRF-Chem results as well as an additional source of HNO_3 that ranges from a few percent to one-third as large as the source from the reaction of NO_2 with OH.

A complete representation of monoterpene chemistry will strain the capabilities of modern CTMs. However, until there is a more thorough understanding of monoterpene oxidation and the appropriate means of representing their chemistry in a condensed chemical mechanism, we recommend that models implement a basic gas-phase chemistry of monoterpenes in addition to their SOA chemistry. In parallel, evaluation of key parameters in the lab and consequences for ambient O_3 , NO_x and OH should be explored both on local and global scales.

Supplementary material related to this article is available online at <http://www.atmos-chem-phys.net/14/1225/2014/acp-14-1225-2014-supplement.pdf>.

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