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Zare, Azimeh
Fahey, Kathleen M
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Vapor-pressure pathways initiate but hydrolysis products dominate the aerosol estimated from organic nitrates

Azimeh Zare[†,‡], **Kathleen M. Fahey**[†], **Golam Sarwar**[†], **Ronald C. Cohen**[‡,§,*], **Havala O. T. Pye**[†,*]

[†]National Exposure Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711, United States

[‡]Department of Chemistry, University of California Berkeley, Berkeley, California 94720, United States

[§]Department of Earth and Planetary Sciences, University of California Berkeley, Berkeley, California 94720, United States

Abstract

Organic nitrates contribute significantly to the total organic aerosol burden. However, the formation and loss mechanisms of particulate organic nitrates (PONs) remain poorly understood. In this study, with the CMAQ modeling system, we implement a detailed biogenic volatile organic carbon gas phase oxidation mechanism and an explicit representation of multiphase organic nitrate formation and loss, including both aqueous-phase uptake and vapor-pressure driven partitioning into organic aerosol as well as condensed-phase reactions. We find vapor-pressure dependent partitioning is the leading mechanism for formation of PONs and hydrolysis is a major loss mechanism for PON resulting in substantial amounts of organic aerosol that originate as an organic nitrate. Partitioning and hydrolysis together can produce high concentrations (up to 5 μg/m^3) of PON-derived aerosols over the southeast United States. The main source of PON-derived aerosols is monoterpene nitrates that have been chemically processed to lose their nitrate functionality through aqueous chemistry. In contrast, the major portion of aqueous aerosol and in-cloud PON, which retains its nitrate moiety, are soluble isoprene nitrates. We evaluate the model using the observations from the Southern Oxidant and Aerosol Study (SOAS) campaign in the Southeast US in summer 2013 and show implementing aerosol-phase pathways for organic nitrates dramatically improves the magnitude of total alkyl nitrates (ANs) in CMAQ. The contribution of PONs to the total ANs at the SOAS site is estimated to be ~20%, a value in the range of the measurements. The predicted AN composition is shifted from monoterpene to isoprene and anthropogenic organic nitrates.
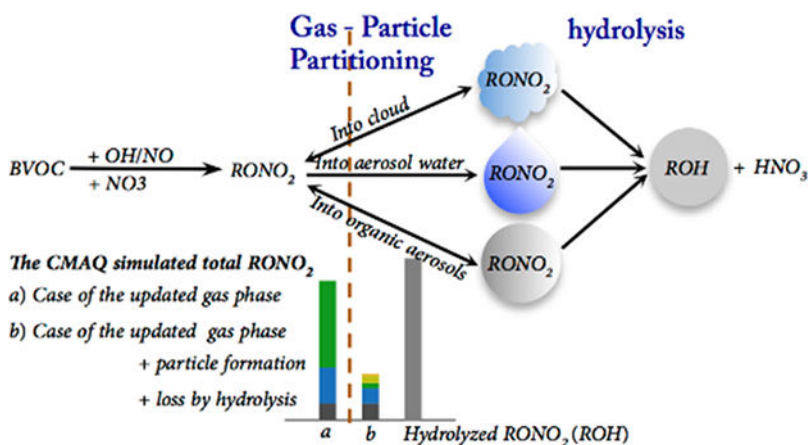
Graphical Abstract

*Corresponding Author: Phone: +1 (919)541-3557: pye.havala@epa.gov; Phone: +1 (510)642-2735; rccohen@berkeley.edu.

Introduction

Organic aerosol (OA) is a major component of particulate matter[1,2] and has significant impacts on human health, Earth's radiation budget, and climate.[3] The impacts vary depending on the size distribution and the chemical composition of the particles.[4] Properties of OA remain incompletely characterized, and OA is a poorly understood constituent of aerosol. Radiocarbon measurements indicate that ambient OA is largely modern which is characteristic of biogenic emissions[5,6] while OA plumes from remote areas as well as urban locations have been observed to be correlated with anthropogenic tracers.[7]

One possible way to reconcile this apparent paradox is formation of particulate organic nitrates from biogenic precursors. The anthropogenic influence would be nitric oxide (NO) and nitrate radical (NO_3) while the volatile organic compounds (VOCs) from biogenic sources would be "modern" and provide the carbon backbone of the molecules in the aerosol. Several field[8–10] and modeling[11,12] studies have provided evidence suggesting a significant portion of atmospheric OA is PONs. Despite the potential importance of PONs in the aerosol budget and updates to our understanding of the yield of PONs,[13–17] the chemical formation mechanism and spatial and temporal distribution of PON need to be better assessed.

Following the initial production in the gas phase, organic nitrates ($RONO_2$) can be transported by winds, undergo chemical transformations and deposit to the surface. Critical determinants of whether an organic nitrate is found in the aerosol phase (as opposed to the gas phase) are vapor pressure,[18] solubility in aqueous media, and chemical reactions in the condensed phase.[19]

The fraction of a semivolatile organic nitrate in the particle phase is generally parameterized based on partitioning theory[18] assuming partitioning into an organic medium based on vapor

pressure. This type of partitioning can be represented using an Odum 2-product,[20] volatility basis set,[21] or chemical surrogate-based approach.[22] Recently, Pye et al.[12] developed an aerosol system in the Community Multiscale Air Quality (CMAQ) model to explicitly describe the PONs produced from oxidation of biogenic VOCs based on the vapor pressure-driven partitioning. As a result, they improved the simulated concentrations of both organic aerosol and gas-phase organic nitrates in comparison to observations in the Southeast United States. In addition to the organic constituents in particles, aerosol water can serve as partitioning media.[23] Under humid conditions, where condensed water is an abundant medium, aqueous-phase chemistry is an important mechanism for the formation of organic aerosols,[24,25] and Carlton and Turpin[26] predicted that uptake of water-soluble organic carbon into particle water could comprise a substantial fraction of the total secondary organic aerosol (SOA) mass in the Eastern US. Marais et al.[27] developed an aqueous-phase mechanism based on heterogeneous uptake for formation of isoprene aerosols, including select particulate isoprene nitrates, in the GEOS-Chem model and found a mean isoprene aerosol mass yield (including high and low NOx conditions) consistent with surface and aircraft observations in the Southeast US. While Marais et al.[27] included the gas-particle partitioning to aerosol water, aqueous-phase in-cloud processing was neglected. Both cloud droplets and aerosol water are proposed to be media for water-soluble organic partitioning. [19,28,29]

Estimating PON from all pathways requires taking into account formation processes and loss terms simultaneously. One proposed removal mechanism for PON in the atmosphere is hydrolysis as described in recent analyses of field observations.[30,31] Hydrolysis of PON leads to the formation of HNO_3,[32] which is a more permanent sink of NO_x than organic nitrates which for some oxidation pathways release NO_x downwind of formation. Therefore, representation of PON hydrolysis together with depositional loss in the models has significant implications not only for aerosol mass and properties but also for NO_x, ozone, and spatial patterns of N deposition. Implementing the organic nitrate removal by hydrolysis in 3D chemical transport models has been a recent modeling effort for improving ozone and NO_y predictions.[33–35] However, due to large uncertainties in the estimated rate of reaction, these studies applied different $RONO_2$ lifetimes against hydrolysis (6h, 1h and 3h, respectively).

To fully represent PON formation and lifetime, and OA mass a comprehensive system coupling gas and aerosol chemistry is needed. Here, we create such a system incorporating a gas phase chemical mechanism with a detailed representation of the most important individual organic nitrates into the CMAQ model. Then, we develop a coupled gas and aerosol system to explicitly represent 1) vapor-pressure driven gas-particle partitioning to organic particulate matter for individual organic nitrates introduced in our gas-phase chemical mechanism, 2) heterogeneous uptake to aqueous particles and 3) uptake to cloud droplets. Applying this gas- and aerosol-phase mechanism, we are able to describe the relative role of water-mediated and vapor pressure processes in determining the composition of aerosol derived from organic nitrates. Our approach also allows us to compare cloud and aerosol water mediated aqueous PONs, two competing pathways for formation of water-soluble organic aerosols.[36,19,37] After incorporating the hydrolysis of PONs in CMAQ, we also assess model performance for simulation of total organic nitrates (gas+aerosol) against

ground-based observations from the Southern Oxidant and Aerosol Study (SOAS) campaign over the southeastern United States during June 2013.

Experimental Section

The Model Framework

For this analysis we used a developmental version of CMAQ based on v5.2β (see code availability). Version 5.2 includes several science updates and fast and efficient computational techniques (https://www.epa.gov/cmaq). Meteorological fields were generated by the WRF v3.7 model and processed for use in CMAQ by MCIP (the Meteorological Chemistry Interface; Otte and Pleim[38]). Our simulation was performed over the contiguous United States with a horizontal resolution of 12 km and used 35 vertical layers extending to 50 mb.

The model simulation period is for June 2013 with a 10-day spin-up period to minimize the impact of initial conditions. Boundary conditions for the 12 km domain are prepared from a 36 km CMAQ simulation with boundary conditions from global concentration fields simulated by GEOS-Chem. Anthropogenic emissions for 2013 are based on the 2011 EPA National Emission Inventory (NEI) versions 6.2 and 6.3 model emission platforms (https://www.epa.gov/air-emissions-modeling/2011-version-6-air-emissions-modeling-platforms) and processed with the Sparse Matrix Operator Kernel Emissions (SMOKE[39]) system to generate time varying CMAQ ready emission fields. Biogenic emissions are calculated online with the Biogenic Emissions Inventory System (BEIS 3.6, Bash et al.[40]).

Gas Chemistry Mechanism

The gas phase chemistry used in this study is based on the original RACM2 (Regional Atmospheric Chemistry Mechanism) mechanism,[41] and its upgraded versions, which are named RACM2_Berkeley[42] and RACM2_Berkeley2.[35] The original RACM2 is available in CMAQ v5.0.2 and later versions[43] and has been used to examine the impacts of this chemical mechanism on model predictions for the formation of ozone and secondary organic aerosols over the United States. In RACM2_Berkeley, Browne et al.[42] modified RACM2 to be consistent with the recent parameterization for hydroxyl radical (OH) oxidation of isoprene. They also reclassified the lumped organic nitrates from monoterpenes and anthropogenic VOC precursors into new species and added oxidation reactions for the new organic nitrate species. The RACM2_Berkeley2 mechanism described in Zare et al.[35] is an updated version of RACM2_Berkeley that reflects more recent advances in the understanding of atmospheric organic chemistry in both low- and high-NO_x conditions, with a focus on detailed representation of isoprene nitrates from NO_3 oxidation and production and fate of the most important individual organic nitrates. The RACM2_Berkeley2 mechanism was used within the WRF-Chem model to study the fate and lifetime of organic nitrates and their effects on nitrogen oxide chemistry.[35] Compared to observations from the SOAS campaign over Southeastern United States, the RACM2_Berkeley2 mechanism

provides a reasonable lifetime for organic nitrates (2-3.2 h)[31] with the addition of an adhoc parameter to describe hydrolysis of nitrates (following Boyd et al.[44]).

RACM2_Berkeley2.1, which is implemented into CMAQ for this study, is a revised version of RACM2_Berkeley2. In this new version, the explicit representation of multifunctional isoprene nitrates from NO_3 chemistry that are subject to reactive uptake to the aerosol phase are further updated (based on Schwantes et al.[45]). We retain the treatment of monoterpene nitrates and isoprene nitrates from OH oxidation from RACM2_Berkeley2 in RACM2_Berkeley2.1. Our treatment of isoprene nitrates from OH oxidation is consistent with the recently developed mechanism by Wennberg et al.,[46] and Bates and Jacob[47] with regards to isomer distributions (~90% β) and tertiary fraction (~60%).

The newly introduced species into the mechanism include C5 hydroxy nitrooxy dihydroperoxide (IHDPN), C5 dihydroxy nitrooxy hydroperoxide (IDHPN), C5 hydroxy nitrooxyperoxy radical (IHNO2), C5 hydroxy nitrooxyalkoxy radical (IHNO), C5 hydroxy hydroperoxide nitrate (IHPN) and INO2IN. INO2IN is a ROOR from INO2+INO2 reaction, where INO2 is produced from NO_3 addition to isoprene and subsequent O_2 addition. This part of our work was completed prior to the review of Wennberg et al..[46]

IHDPN and IDHPN are 2nd generation nitrates produced from oxidation of δ and β isomers of C5 nitrooxy hydroperoxide (INPD and INPB) and C5 hydroxy nitrate (IHND and IHNB), respectively.[45] OH oxidation of the 1st generation isoprene nitrates (INPD, INPB and IHND, IHNB) produces RO_2 radicals (INPHO2s and IDHNO2s), which react with HO_2 to form IDHPN and IHDPN. Pye et al.[12] showed the dominant peroxy radical (RO_2) fate is reaction with HO_2 and to a small extent reaction with other RO_2. The RO_2+NO_3 reaction is negligible. Therefore, in this study where we add the RO_2+HO_2 reactions to form IDHPN and IHDPN, we omit RO_2+NO_3 reactions to save computational time.

Schwantes et al.[45] showed that INO2 can react with itself or with another RO_2 radical to form C5 hydroxy nitrates, C5 carbonyl nitrates, INO2IN and alkoxy radicals (INO). INO can either react with O_2 or rapidly undergo a [1,5]-H-shift to form a C5 dihydroxy nitrate, a C5 hydroxy carbonyl nitrate or a C5 hydroxy hydroperoxide nitrate.[45,48] We implement these reactions into the scheme and use the lumped IHPN indicator as a surrogate for these 3 products.

The treatment of monoterpenes nitrates in the current version of RACM2_Berkeley2.1 is retained as described at RACM2_Berkeley2.[35] In total the updated reaction set in RACM2_Berkeley2.1 includes 28 lumped organic nitrate surrogate species (Table S1 in the Supplement), in contrast to only three organic nitrate species (two isoprene-derived nitrates and one lumped terpene nitrate) were included in the original RACM2 mechanism. All new introduced species and modifications implemented into the RACM2_Berkeley2.1 mechanism are listed in Table S2 and S3.

Aerosol Formation Mechanism

The gas-phase organic nitrate surrogates are potential aerosol precursors. Here, we assume that the organic nitrates in the gas-phase partition in parallel to a liquid-like organic phase,

particulate water, and cloud water based on their species-specific vapor pressure and solubility to form organic nitrates in the particle phase. In each phase, the particulate organic nitrates can undergo irreversible hydrolysis to form nonvolatile organic aerosols and release nitric acid. These treatments for PONs in CMAQ are described in the next subsections.

Gas-particle partitioning to organic aerosol phase

The general approach for SOA formation of hydrophobic surrogates is vapor-pressure based gas-particle partitioning following Raoult's Law.[18,21] The fraction of each semivolatile compound i in the particle phase (F_i) in terms of C_i^* (saturation concentration, µg m^{-3}) is given by

$$F_i = \frac{P_i}{P_i + C_i} = \left(1 + \frac{C_i^*}{M_0}\right)^{-1}$$

where C_i and P_i are gas and particle concentration of non-zero vapor pressure species i. M_0 is the total concentration of all condensed-phase organics available for partitioning. In CMAQ v5.2, an empirical framework[20] represents semivolatile SOA formation from VOCs, wherein gas-phase oxidation of VOCs produces one or two semivolatile organic compounds.

For explicit representation of the individual organic nitrate species, we track their phase as they equilibrate between the gas and particle phases based on their individual vapor pressures. Measured vapor pressures for many multifunctional and low volatility organic species such as most semi-volatile organic nitrates are not available. Vapor pressures of compounds with known structures can be estimated based on group contribution methods: EVAPORATION[49] and SIMPOL[50] or based on molecular structures and boiling point temperatures.[51,52]

In this study, the structures of lumped organic nitrate species are determined based on the Master Chemical Mechanism (MCM V3.3.1)[53] and the study by Schwantes et al..[45] Most of the lumped species in RACM2_Berkeley2.1 include a number of different organic nitrates, each with a unique structure. For instance, the monoterpene nitrate surrogates include products from different precursors (α-pinene, β-pinene and Limonene). In addition, some organic nitrates such as IMONIT (Multifunctional isoprene nitrate) are produced from multiple chemical pathways resulting in different structures with different features. We collect all possible structural representations (as SMILES strings) for the surrogates in our scheme. For surrogates in which multiple structures are possible, we estimate the yield-weighted C_{ref}^* (C* at 298 K) for each surrogate nitrate using SIMPOL vapor pressures (Table S4).

The calculated saturation vapor pressures for monoterpene organic nitrates are at least two orders of magnitude higher than the values inferred from the observations (Fry et al.[16] and[54] for nitrates from Limonene+NO$_3$ and β-pinene+NO$_3$ pathways). However, consistent with findings by D'Ambro et al.,[55] SIMPOL calculations are closer to the experimental results. Therefore, in this study we use the predicted vapor pressures for organic nitrate species from the group contribution SIMPOL method and adjust the calculated values toward

observations. Specifically, we specify C_{ref}*for the unsaturated monoterpenes nitrates from NO_3 chemistry (UTONIN) as the experimental available value of Fry et al.[54] and for the saturated monoterpenes nitrates from NO_3 chemistry (TONIN) the value of Fry et al..[16] For the rest of the organic nitrates from isoprene and monoterpenes precursors, we scale the calculated C_{ref}* from SIMPOL by a constant factor (8.5×10^{-3}). The factor is calculated based on average difference between the predicted C_{ref}* for UTONIN and TONIN by SIMPOL and the observed values given by Fry et al[16] and Fry et al.[54]. This imposed reduction in vapor pressure may take in to account missing structures in current mechanisms such as the highly functionalized nitrate products[10] from autoxidation.[56]

The enthalpies of vaporizations to adjust the saturation concentrations for different temperatures are also provided by the SIMPOL method. The parameters of our mechanism including C_{ref}* and H_{vap} for individual nitrates are listed in Table S5 in the Supplement.

Gas-particle partitioning to aerosol water

In parallel to vapor-pressure driven condensation, heterogeneous uptake of hydrophilic oxidation products into aerosol water also results in secondary OA. This mechanism is already used for aqueous processing of glyoxal, methylglyoxal, isoprene epoxydiols (IEPOX), and methacryloylperoxynitrate (MPAN) and MPAN oxidation products in CMAQ v5.2.[12,57]

A heterogeneous uptake includes several physicochemical processes in one step with a rate constant parameterized as:

$$k_{het} = \frac{A}{(\frac{r_p}{D_g} + \frac{4}{\gamma v})}$$

where A ($m^2 m^{-3}$) is the aerosol surface area per unit volume, r_p is the effective particle radius and D_g is the molecular diffusivity coefficient in the gas phase and v is the mean gas phase thermal molecular speed of species i with molecular weight MW_i. γ is the unitless reactive uptake coefficient that represents the probability and efficiency of a heterogeneous uptake from a gas-surface collision and subsequent reactivity in the liquid phase resulting in SOA. γ in this study calculated from parameterization originally given by Hanson et al.[58] and Jacob[59]. It is a function of the Henry's Law constant (H*) and first order reaction rate constant, k_p (s^{-1}) (see Pye et al.).[57]

Henry's Law constants are estimated using HenryWin 3.2 based on a bond contribution method.[60] We estimate H* for 1st generation isoprene and monoterpenes nitrates to be 10^3-10^4 (M atm^{-1}) which are in the range values given by with Nguyen et al. (2015) from observations at the SOAS campaign and the calculated values by Rollins et al. (2009)[15] and Marais et al. (2016)[27] using SPARC online calculator (Hilal et al., 2003)[61]. We estimate H* for the multifunctional isoprene and monoterpene nitrates (Table S5) to be large and within the range of the Henry's law constants for IEPOX and glyoxal, well-known highly water-soluble carbonyl compounds. The second parameter used in calculation of γ for organic nitrates is the particle-phase reaction rate constant (k_p). Laboratory studies of condensed

phase chemistry have shown that organic nitrates hydrolyze in aqueous solution.[62–65] Therefore, k_p for organic nitrates is the hydrolysis rate constant in the condensed phase.

Gas-cloud partitioning

In addition to aerosol water, cloud and fog droplets are candidates for hydrophilic organic nitrate partitioning. However, the liquid water content and lifetime of solutions as well as rates of reactions taking place in cloud droplets vs. aerosol water, particularly for acid-catalyzed aerosol formation, can be different.[66] This can result in a different dominant aqueous-phase process in dilute and concentrated conditions (cloud- and aerosol water, respectively). Even if the same parameters are used for organics such as IEPOX, because the clouds are more dilute, the pseudo first order rate can be lower if it depends on the concentration of any ions.[66,67]

In CMAQ, aqueous aerosol formed via heterogeneous uptake is irreversible while reversible partitioning of unreacted and dissolved VOCs is allowed in clouds.[67] For species with relatively fast reaction rates in the aqueous phase, the irreversible assumption for aerosol water uptake pathway has been shown to perform the same as the reversible VOC assumption within the range of other model simulation uncertainties.[68] Reversible partitioning is likely to be more important for aqueous pathways in cloud droplets compared to aerosol particles due to higher volumes of liquid water and more rapid cycling of water abundance.[19]

In-cloud aqueous-phase chemistry is integrated into the CMAQ's cloud chemistry module that is detailed in the works of Carlton et al.[69] and Fahey et al.[67]. In this work, the cloud chemistry mechanism with kinetic mass transfer considerations (AQCHEM-KMT) was applied.[67] At the end of cloud processing the concentration of a species in the cloud water is returned to the aerosol species, while species that are in the gas phase at the end of cloud processing are returned to the gas phase species, until the next cloud cycle when the species are allowed to transfer between the gas and aqueous phases again.

Organic nitrate fate in the condensed phase

In addition to deposition to the surface, recent ambient measurements[30,31] and chamber experiments (e.g. Liu et al.; [67] Boyd et al.[44]) have proposed heterogeneous hydrolysis as an efficient loss process for some particulate organic nitrates. In the hydrolysis process, particle organic nitrates likely convert to alcohols.[71] Some alcohols have been observed to be relatively volatile and may partition back to the gas phase[65] while others are likely to remain in the aerosol phase. In this study we assume the hydrolysis products of organic nitrates are nonvolatile organic compounds and nitric acid.

Organic nitrate hydrolysis rate constants span a substantial range from 6.8×10^{-3} (s^{-1}) (~lifetime of 2.4 minutes, Jacobs et al.[72]) to 1.1×10^{-7} (s^{-1}) (~lifetime of 2500 hr., Darer et al.[32]). Chemical structures of the nitrates (primary, secondary and tertiary) determine the hydrolysis lifetime. Boyd et al.[44] found that the primary organic nitrates do not appear to hydrolyze while the tertiary organic nitrates undergo hydrolysis with an expected lifetime of 3-4.5 h. Some experiments have been done with injection of reactants and humid air into the chamber,[70] in contrast to experiments with bulk aqueous solutions.[32,71,72] Chamber

experiments have been conducted in the presence of aerosol seed[44,73] and in the absence of aerosol seed.[63,70] The wide range of approaches may explain some of the variability interferences of hydrolysis lifetime.

One potential regulator of hydrolysis rates is acidity. Jacobs et al.[72] found that the rate for hydrolysis of the tertiary and non-tertiary hydroxynitrate isomers remained constant in a variety of acid concentrations. While Boyd et al.[44] agree that hydrolysis of tertiary nitrates is accelerated under more acidic conditions, but primary organic nitrates are stable against hydrolysis for pH> 0. However, other studies observed a positive trend in hydrolysis rate constants for all organic nitrates with increasing solution acidity and proposed acid-catalyzed particle-phase reactions for organic nitrates.[62,64,74,65] Table S6 summarizes recent estimates of organic nitrate hydrolysis rates and the conditions they were obtained under.

To determine what effective hydrolysis timescale to apply to each organic nitrate surrogate in our model we categorize the organic nitrates as hydroxyl or carbonyl nitrates and saturated or unsaturated nitrates as well as tertiary or non-tertiary nitrates. We apply the hydrolysis lifetimes of 0.03h for the tertiary saturated with one adjacent OH group,[71] 0.67h for the tertiary saturated with more than one adjacent OH group,[32] and the hydrolysis lifetimes of 0.04h for tertiary unsaturated nitrates.[72] The applied hydrolysis rates for all other saturated and unsaturated surrogates are 2500 h and 17.5 h respectively.[32,72]

The condensed-phase reaction rate constant could be a constant, or specified as a function of particle composition (including pH) as is done for isoprene epoxydiol uptake in CMAQ v5.1 and later.[57] Here, we follow the finding that aerosol pH has little impact on the hydrolysis of organic nitrates and hold the rates of hydrolysis of organic nitrates constant to be consistent with our choices of hydrolysis rates from the experimental studies by Darer et al.,[32] Hu et al.,[71] and Jacobs et al..[72] However, we assume that β and δ isomers of isoprene nitrooxy hydroxy epoxides (INHEB and INHED) undergo similar heterogeneous chemistry as IEPOX[45] and their uptake is mediated as an acid-catalyzed process. Pye et al.[53] provided details and formulation for calculation of particle-phase rate constant for IEPOX that is an acid-catalyzed ring opening and nucleophilic addition in the aqueous phase.[75] The required concentrations of acids (includes specific acid ($[H^+]$) and general acid ($[HSO4-]$)) and nucleophiles (includes aerosol water, sulfate, and nitrate) for calculation of the hydrolysis rates in CMAQ are predicted using ISORROPIA II.[76]

We assume that regardless of how the organic nitrate entered the particle (via vapor-pressure driven condensation or dissolution in an aqueous phase), it can undergo hydrolysis with the same rate constant thus implicitly assuming that the abundance of water is not rate limiting. For reversible vapor-pressure-driven PON and in-cloud organic nitrates, hydrolysis is implemented as an explicit reaction after partitioning. For aqueous aerosols, hydrolysis is embedded in the heterogeneous uptake process. For diagnostic purposes only (tracking of the parent ON vs. hydrolysis product) a separate hydrolysis reaction is implemented for aqueous aerosol (Table S7).

In addition to hydrolysis, dry deposition and scavenging by cloud droplets are known loss processes of organic nitrates. For soluble species, wet deposition in the gas-phase can be an

effective form of deposition[77,78] and PONs can be lost by returning to the gas phase. Table S1 lists the dry deposition surrogates that are applied in the model for the gas-phase organic nitrates. Deposition properties of the species have been discussed in the studies by Browne et al.[42] and Zare et al.[35] and observed by Nguyen et al.. [79]

Figure 1 shows all of the aerosol pathways implemented in CMAQ. We reconfigure the standard Odum two-product semivolatile SOA such that only RO_2+HO_2 reactions lead to traditional aerosol, thus excluding organic nitrate-derived SOA and avoiding double counting with the new explicit organic nitrates.

Results

Comparison of PON formation pathways; derived aerosol mass predictions

To understand the importance of the different pathways to aerosol formation for organic nitrates we compare the predicted concentrations of PONs associated with vapor-pressure and aqueous (aerosol water and in-cloud) driven condensation, together with their organic hydrolysis products (vpPON-derived, aqPON-derived, and cldPON-derived OA respectively) (Figures 2a, 2b and 2c). Although heterogeneous uptake has been a significant source of OA in previous work[80,57,27] our simulation suggests that, for the case of organic nitrates, traditional semivolatile aerosol formation involving an organic-rich condensed phase is the main mechanism that initiates PON formation. This is consistent with the chamber experiments[73] and field measurements[81] that provided evidence that absorptive partitioning into OA has some control over the $RONO_2$ phase partitioning and could describe the PON represented in a volatility basis set. However, our simulations also show that hydrolysis reactions drive the total amount of PON-derived aerosols (PON+hydrolysis products), representing a mechanism by which water also influences OA. Therefore, volatility in combination with aqueous-phase reactions together dictate OA abundance at the surface.

Figure 3 also shows the mean predicted vpPON, aqPON and cldPON vertical profile at the CTR site. We find the vapor-pressure dependent partitioning pathway is the dominant mechanism not only in the layers closest to the surface but in the boundary layer. However, concentrations sharply decrease with altitude due to less precursor. Similarly, aerosol water mass also decreases with increasing altitude due to the decrease in water vapor mixing ratio. Aqueous aerosol formation through in-cloud process could be more significant at higher altitudes, potentially in the transition layer and on top of mixing layer with implications for long-range transport of the aerosols. [37]

The spatial distribution of vpPON-derived, aqPON-derived and cldPON-derived SOA reflects the spatial distribution in total organic aerosol, relative humidity (which drives aerosol water), cloud liquid water content and biogenic VOC emissions. In figure 2a, we estimate a local maximum (2 μg/m^3) of vpPON-derived OA over California and 1-1.5 μg/m^3 over the remainder of the West and Midwest, where due to low relative humidity (Figure S1a), aqPON-derived OA is negligible (Figure 2b). The highest averaged concentrations of aqPON-derived OA coincide with high RH (>70%) over the East and southeast portion of the domain (Figure S1a).

Estimated vpPON-derived OA is one order of magnitude larger than aqPON-derived OA, and spatial distributions for aqPON-derived and vpPON-derived OA, while both reflecting enhancements in the eastern US, exhibit spatial differences within the southeast. VpPON-derived OA is predicted to be highest in the vicinity of highest total organic aerosol (Figure S1b). Availability of organic aerosol is also vital for formation of aqPON, and figures S2a and S2b show PONs-derived from both pathways increase with organic aerosol which may be due to uptake being facilitated by surface area for aqPON-derived OA and the fact that once taken up, the PON-derived OA contributes to the total. However, aqPON is more dependent on particle radius than the aerosol mass; thus maximum aqPON do not necessarily correspond to the highest total OA concentrations.

Figures 2b and 2c compare the importance of in-cloud processes vs. aqueous aerosol in the formation of aqueous PONs. We find that PON concentrations in clouds and in aerosol water are roughly comparable (figures S3b and S3c), but cldPON-derived OA (cldPON+hydrolysis product aerosols) is ~4 times more abundant than aqPON-derived OA. That implies cloud processing is associated with a greater tendency to remove the nitrate group through hydrolysis than aqueous aerosol processing (figures S3e and S3f). The reason is that the June 2013 average maxima in clouds (Figure S4), which provide the liquid water content for dissolution, over southeastern part of the domain coincides with more abundant monoterpenes nitrates (MTNs, Figure 2) that have a shorter lifetime against hydrolysis than most isoprene nitrates and thus more quickly release their nitrate functionality. Maxima in aqPON-derived concentrations tend to be in the vicinity of the Ohio river and part of the Mississippi river where inorganic aerosol promotes water uptake and formation of larger size particles. The area geographically coincides with regions of higher water-solubility of isoprene nitrates (ISNs). Particulate ISNs efficiently form in an aqueous phase mostly due to physical solvation and diffusion into the aerosol bulk phase. Therefore, dominant components of aqPON-derived OA are isoprene nitrates that undergo a slower hydrolysis than monoterpene nitrates and keep their nitrate functionality.

Isoprene and monoterpene organic nitrates aerosols

Particulate monoterpene nitrates are a significant contribution to vpPONs and account for the dominant PONs in the southeast consistent with the dominance of monoterpene emissions. Figures 4a and 4b show that the spatial pattern of the particulate ISNs is shifted to the north of particulate MTNs in the eastern part of the domain, reflecting the isoprene dominant regions compared to the monoterpene dominant regions (Figure 4e and 4f). In terms of magnitude, particulate ISNs are also predicted to be abundant and on the same order of magnitude as particulate MTN concentrations. This contrasts with the modeling study by Pye et al.[12] over the southeastern United States that suggested much lower isoprene nitrates in the condensed phase compared to monoterpene nitrates. The RACM2_Berkeley2.1 mechanism considers many more multifunctional isoprene nitrates and we estimate their scaled saturation concentrations are much lower than the assigned saturation concentration for the single semivolatile isoprene multifunctional dinitrate in Pye et al..[12] Here, we also apply shorter hydrolysis lifetimes for MTNs (2.2-40 minutes) than the 3 h hydrolysis lifetime in Pye et al..[12] This results in a larger loss of nitrate functionality by

particulate MTNs due to hydrolysis and lower MTN concentration in the condensed phase in this study compared to the simulations by Pye et al..[12]

Figures 4c and 4d compare the spatial distribution of aqueous MTN aerosols and ISN aerosols. High concentrations result from heterogeneous uptake of ISNs to aqueous aerosols downwind of the regions with higher isoprene emissions and also in West Virginia, Kentucky and Tennessee suggesting the efficient transport of the cloud-produced particle isoprene nitrates to those regions. Similarly for MTN in figure 4c, the high aqPON concentrations in the easternmost states including Virginia, North and South Carolina and Georgia are formed through cloud processing. However, aqueous MTN aerosols are calculated to be much lower than aqueous ISN aerosols over the whole domain.

PONs at the SOAS CTR site

Simulated vpPON-derived aerosols at CTR are dominated by the hydrolysis products without nitrate functionality (Figure 5a). We predict the hydrolysis products as well as MTN aerosols to be more abundant during the nighttime, as a result of higher monoterpene emissions relative to isoprene from sunset to sunrise and large aerosol mass yields from NO_3 oxidation of monoterpenes (e.g. Fry et al.[16,54]; Ng et al.[82]). The particulate ISNs are predicted to be more abundant during daytime in agreement with observations by Lee et al.. [10] Although we predict the hydrolysis products, which are dominantly from MTNs, are much higher during nighttime than during daytime, monoterpene nitrates from OH oxidation are calculated to have a higher fraction of tertiary nitrates than those from NO_3 oxidation (Table S1). That means they have shorter lifetime against hydrolysis, consistent with the difference in the estimated hydrolysis lifetimes of particulate MTNs in experiments by Rindelaub et al.[65] (OH-dominated) versus Boyd et al.[44] (NO_3-dominated).

At CTR we also find that isoprene-derived nitrates account for a dominant portion of aqPON (Figure 5b) and most monoterpene aqPON, similar to monoterpenes vpPON, probably eliminate the nitrate functionality due to rapid hydrolysis.

Figure 5c compares the composition of the simulated total ANs using the updated gas-phase RACM2_Berkeley2.1 mechanism with and without explicit representation of PON formation. As a result of adding particle pathways for organic nitrates, the composition of the total ANs shifts from ~62 % gas-phase MTNs to ~11% gas-phase MTNs. Due to short hydrolysis lifetimes of MTN (Figure 5a) we conclude monoterpenes are the most important precursor for formation of PON-derived OA without nitrate functionality (hydrolysis product aerosols) and can be a significant contribution to total OA in the Southeast United States, consistent with findings by Zhang et al..[83]

Figure 5c also shows that implementing aerosol-phase pathways for organic nitrates dramatically reduces the magnitude of total alkyl nitrates (ANs). Figure 6 shows that the magnitude of total alkyl nitrates is reduced at all times of day and particularly during the night leading to an improved magnitude of and diurnal trend in organic nitrates compared to observed total ANs. The model prediction without the explicit PON aerosol simulation overestimates total ANs at CTR and predicts a maximum that is earlier than the observations by 3 hours. With the updated PON mechanism developed in this work, the model prediction

is significantly improved and temporal variability in the total organic nitrates for the entire time series is reproduced with little bias. Particulate organic nitrates contribute an estimated ~20% of total alkyl nitrates at CTR (Figure 5c), in the range of measurements during the campaign in summer 2013.[10,84] Although the model gives a reasonable relative contribution of organic nitrates in the condensed phase to total ANs, both PONs and total ANs are underestimated in our simulation compared to the TD-LIF (thermal dissociation laser-induced fluorescence) measurements.[85]

Discussion

Chemical transport models have traditionally used SOA formation mechanisms that are based on vapor pressure dependent partitioning of semivolatiles into other organic compounds. However, some recent studies highlight that heterogeneous uptake into aqueous media is important to the chemistry for SOA. In this study, we implemented an extensive mechanism including chemistry for gas-particle partitioning to organic aerosol, aerosol water, and cloud droplets to explicitly simulate PONs. Our calculations indicate that formation of organic nitrate aerosols through reversible vapor-pressure based partitioning to organic aerosol phase is still the most efficient mechanism facilitating partitioning toward the condensed phase over the United States and dominates over aqueous pathways near the surface. However, we assume that, in the presence of water, PONs from all pathways undergo hydrolysis reactions and we find that these aqueous reactions significantly affect the molecular composition of organic aerosols. Our simulations suggest volatility initiates the uptake, but hydrolysis is a dominant process affecting aerosol mass. A key remaining uncertainty is the rate of hydrolysis as literature indicates a large range in the tertiary nitrate hydrolysis lifetimes (0.019-8.8 h). Our work uses the shorter lifetimes, provided by bulk solution experiments. These rates are thus likely upper bounds on the particle organic nitrate sink through hydrolysis. However, implications of uncertainties in the lab-determined hydrolysis lifetime on ambient NOx and O3 should be explored both on local and global scales. Moreover, hydrolysis in our study is not rate-limited by the availability of water nor acidity, and additional work is needed to determine atmospherically relevant hydrolysis rates. By treating the aqueous reaction products as nonvolatile in this study, a large portion of PON-derived aerosols is simulated to be nitrate-mediated aerosols. However, if hydrolysis products were relatively volatile and partitioned back to the gas phase this would lead to a reduction in total aerosol mass compared to our simulation. Although the predicted total alkyl nitrates are significantly improved by implementing explicit chemistry for PON formation, total ANs are still slightly underestimated compared to the observations at CTR. Future comparison to aerosol mass and composition should be explored.

Distinct and parallel simulation of PON formed in dilute and concentrated conditions allows a detailed comparison of the importance of aerosol water and cloud aqueous-phase SOA formation. We find aqueous-phase chemistry in dilute in-cloud conditions forms PON-derived aerosols ~5 times more efficiently than in concentrated aqueous aerosol conditions throughout the boundary layer. Aqueous aerosol formation through in-cloud processes at higher altitude, potentially in the transition layer and on top of the mixing layer, should be further explored.

Our model simulates that isoprene nitrates are the most important contributor to PON from aqueous pathways while both isoprene and monoterpene nitrates contribute significantly to vapor-pressure induced PONs. However, due to faster hydrolysis, monoterpene nitrates are more important for overall PON-derived SOA. In anthropogenically influenced areas we predict considerable contributions from anthropogenic hydrocarbons to total alky nitrates (gas+particle). Although biogenic VOCs are dominant sources for SOA production globally, depending on time and location, organic nitrate SOA can also be produced from anthropogenic VOC precursors (e.g. aromatics) and their explicit treatment should be considered in future work.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

ACKNOWLEDGMENT

REFERENCES

(1). Fuzzi S; Andreae MO; Huebert BJ; Kulmala M; Bond TC; Boy M; Doherty SJ; Guenther A; Kanakidou M; Kawamura K; et al. Critical Assessment of the Current State of Scientific Knowledge, Terminology, and Research Needs Concerning the Role of Organic Aerosols in the Atmosphere, Climate, and Global Change. Atmospheric Chemistry and Physics 2006, 6 (7), 2017–2038. 10.5194/acp-6-2017-2006.

(2). Attwood AR; Washenfelder RA; Brock CA; Hu W; Baumann K; Campuzano-Jost P; Day DA; Edgerton ES; Murphy DM; Palm BB; et al. Trends in Sulfate and Organic Aerosol Mass in the Southeast U.S.: Impact on Aerosol Optical Depth and Radiative Forcing: Aerosol Mass and Optical Depth in SE US. Geophysical Research Letters 2014, 41 (21), 7701–7709. 10.1002/2014GL061669.

(3). Forster P; Ramaswamy V; Artaxo P; Berntsen T; Betts R; Fahey DW; Haywood J; Lean J; Lowe DC; Raga G; et al. Climate Change 2007: The Physical Science Basis: Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change; Cambridge University Press: Cambridge; New York, 2007.

(4). Myhre G; Myhre CEL; Samset HB; Storelvmo T Aerosols and Their Relation to Global Climate and Climate Sensitivity. Nature Education Knowledge 2013, 4(5):7.

(5). Schichtel BA; Malm WC; Bench G; Fallon S; McDade CE; Chow JC; Watson JG Fossil and Contemporary Fine Particulate Carbon Fractions at 12 Rural and Urban Sites in the United States. Journal of Geophysical Research 2008, 113 (D2). 10.1029/2007JD008605.

(6). Marley NA; Gaffney JS; Tackett M; Sturchio NC; Heraty L; Martinez N; Hardy KD; Marchany-Rivera A; Guilderson T; MacMillan A; et al. The Impact of Biogenic Carbon Sources on Aerosol Absorption in Mexico City. Atmospheric Chemistry and Physics 2009, 9 (5), 1537–1549. 10.5194/acp-9-1537-2009.

(7). Weber RJ; Sullivan AP; Peltier RE; Russell A; Yan B; Zheng M; de Gouw J; Warneke C; Brock C; Holloway JS; et al. A Study of Secondary Organic Aerosol Formation in the Anthropogenic-Influenced Southeastern United States: SOA FORMATION IN THE POLLUTED SOUTHEAST. Journal of Geophysical Research: Atmospheres 2007, 112 (D13), n/a-n/a 10.1029/2007JD008408.

(8). Rollins AW; Browne EC; Min K-E; Pusede SE; Wooldridge PJ; Gentner DR; Goldstein AH; Liu S; Day DA; Russell LM; et al. Evidence for NOx Control over Nighttime SOA Formation. Science 2012, 337 (6099), 1210–1212. 10.1126/science.1221520. [PubMed: 22955831]

(9). Xu L; Guo H; Boyd CM; Klein M; Bougiatioti A; Cerully KM; Hite JR; Isaacman-VanWertz G; Kreisberg NM; Knote C; et al. Effects of Anthropogenic Emissions on Aerosol Formation from Isoprene and Monoterpenes in the Southeastern United States. PNAS 2015, 112 (1), 37–42. 10.1073/pnas.1417609112. [PubMed: 25535345]

(10). Lee BH; Mohr C; Lopez-Hilfiker FD; Lutz A; Hallquist M; Lee L; Romer P; Cohen RC; Iyer S; Kurtén T; et al. Highly Functionalized Organic Nitrates in the Southeast United States: Contribution to Secondary Organic Aerosol and Reactive Nitrogen Budgets. PNAS 2016, 113 (6), 1516–1521. 10.1073/pnas.1508108113. [PubMed: 26811465]

(11). Russell M; Allen DT Predicting Secondary Organic Aerosol Formation Rates in Southeast Texas. J. Geophys. Res. 2005, 110 (D7), D07S17 10.1029/2004JD004722.

(12). Pye HOT; Luecken DJ; Xu L; Boyd CM; Ng NL; Baker KR; Ayres BR; Bash JO; Baumann K; Carter WPL; et al. Modeling the Current and Future Roles of Particulate Organic Nitrates in the Southeastern United States. Environ. Sci. Technol. 2015, 49 (24), 14195–14203. 10.1021/acs.est.5b03738. [PubMed: 26544021]

(13). Ng NL; Kwan AJ; Surratt JD; Chan AWH; Chhabra PS; Sorooshian A; Pye HOT; Crounse JD; Wennberg PO; Flagan RC; et al. Secondary Organic Aerosol (SOA) Formation from Reaction of Isoprene with Nitrate Radicals (NO3). Atmos. Chem. Phys. 2008, 8 (14), 4117–4140. 10.5194/acp-8-4117-2008.

(14). Brown SS; Degouw JA; Warneke C; Ryerson TB; Dubé WP; Atlas EL; Weber RJ; Peltier RE; Neuman JA; Roberts JM; et al. Nocturnal Isoprene Oxidation over the Northeast United States in Summer and Its Impact on Reactive Nitrogen Partitioning and Secondary Organic Aerosol. Atmospheric Chemistry and Physics 2009, 9 (9), 3027–3042. 10.5194/acp-9-3027-2009.

(15). Rollins AW; Kiendler-Scharr A; Fry JL; Brauers T; Brown SS; Dorn H-P; Dubé WP; Fuchs H; Mensah A; Mentel TF; et al. Isoprene Oxidation by Nitrate Radical: Alkyl Nitrate and Secondary Organic Aerosol Yields. Atmospheric Chemistry and Physics 2009, 9 (18), 6685–6703. 10.5194/acp-9-6685-2009.

(16). Fry JL; Kiendler-Scharr A; Rollins AW; Wooldridge PJ; Brown SS; Fuchs H; Dubé W; Mensah A; dal Maso M; Tillmann R; et al. Organic Nitrate and Secondary Organic Aerosol Yield from NO3 Oxidation of β-Pinene Evaluated Using a Gas-Phase Kinetics/Aerosol Partitioning Model. Atmos. Chem. Phys. 2009, 9 (4), 1431–1449. 10.5194/acp-9-1431-2009.

(17). Fry JL; Draper DC; Barsanti KC; Smith JN; Ortega J; Winkler PM; Lawler MJ; Brown SS; Edwards PM; Cohen RC; et al. Secondary Organic Aerosol Formation and Organic Nitrate Yield from NO3 Oxidation of Biogenic Hydrocarbons. Environ. Sci. Technol. 2014, 48 (20), 11944–11953. 10.1021/es502204x. [PubMed: 25229208]

(18). Pankow JF An Absorption Model of Gas/Particle Partitioning of Organic Compounds in the Atmosphere. Atmospheric Environment 1994, 28 (2), 185–188. 10.1016/1352-2310(94)90093-0.

(19). Ervens B; Turpin BJ; Weber RJ Secondary Organic Aerosol Formation in Cloud Droplets and Aqueous Particles (AqSOA): A Review of Laboratory, Field and Model Studies. Atmospheric Chemistry and Physics 2011, 11 (21), 11069–11102. 10.5194/acp-11-11069-2011.

(20). Odum JR; Hoffmann T; Bowman F; Collins D; Flagan RC; Seinfeld JH Gas/Particle Partitioning and Secondary Organic Aerosol Yields. Environ. Sci. Technol. 1996, 30 (8), 2580–2585. 10.1021/es950943+.

(21). Donahue NM; Robinson AL; Stanier CO; Pandis SN Coupled Partitioning, Dilution, and Chemical Aging of Semivolatile Organics. Environ. Sci. Technol. 2006, 40 (8), 2635–2643. 10.1021/es052297c. [PubMed: 16683603]

(22). Seinfeld JH; Pankow JF Organic Atmospheric Particulate Material. Annual review of physical chemistry 2003, 54, 121–140. 10.1146/annurev.physchem.54.011002.103756.

(23). Zhang X; Liu J; Parker ET; Hayes PL; Jimenez JL; Gouw J. A. de; Flynn JH; Grossberg N; Lefer BL; Weber RJ On the Gas-Particle Partitioning of Soluble Organic Aerosol in Two Urban Atmospheres with Contrasting Emissions: 1. Bulk Water-Soluble Organic Carbon. Journal of Geophysical Research: Atmospheres 2012, 117 (D21). 10.1029/2012JD017908.

(24). Ding X; Zheng M; Yu L; Zhang X; Weber RJ; Yan B; Russell AG; Edgerton ES; Wang X Spatial and Seasonal Trends in Biogenic Secondary Organic Aerosol Tracers and Water-Soluble Organic Carbon in the Southeastern United States. Environ. Sci. Technol. 2008, 42 (14), 5171–5176. [PubMed: 18754365]

(25). Wozniak AS; Bauer JE; Dickhut RM Characteristics of Water-Soluble Organic Carbon Associated with Aerosol Particles in the Eastern United States. Atmospheric Environment 2012, 46, 181–188. 10.1016/j.atmosenv.2011.10.001.

(26). Carlton AG; Turpin BJ Particle Partitioning Potential of Organic Compounds Is Highest in the Eastern US and Driven by Anthropogenic Water. Atmospheric Chemistry and Physics 2013, 13 (20), 10203–10214. 10.5194/acp-13-10203-2013.

(27). Marais EA; Jacob DJ; Jimenez JL; Campuzano-Jost P; Day DA; Hu W; Krechmer J; Zhu L; Kim PS; Miller CC; et al. Aqueous-Phase Mechanism for Secondary Organic Aerosol Formation from Isoprene: Application to the Southeast United States and Co-Benefit of SO2 Emission Controls. Atmos. Chem. Phys. 2016, 16 (3), 1603–1618. 10.5194/acp-16-1603-2016.

(28). Ervens B Modeling the Processing of Aerosol and Trace Gases in Clouds and Fogs. Chem. Rev. 2015, 115 (10), 4157–4198. 10.1021/cr5005887. [PubMed: 25898144]

(29). McNeill VF Aqueous Organic Chemistry in the Atmosphere: Sources and Chemical Processing of Organic Aerosols. Environ. Sci. Technol. 2015, 49 (3), 1237–1244. 10.1021/es5043707. [PubMed: 25609552]

(30). Browne EC; Min K-E; Wooldridge PJ; Apel E; Blake DR; Brune WH; Cantrell CA; Cubison MJ; Diskin GS; Jimenez JL; et al. Observations of Total RONO2 over the Boreal Forest: NOx Sinks and HNO3 Sources. Atmos. Chem. Phys. 2013, 13 (9), 4543–4562. 10.5194/acp-13-4543-2013.

(31). Romer PS; Duffey KC; Wooldridge PJ; Allen HM; Ayres BR; Brown SS; Brune WH; Crounse JD; de Gouw J; Draper DC; et al. The Lifetime of Nitrogen Oxides in an Isoprene-Dominated Forest. Atmos. Chem. Phys. 2016, 16 (12), 7623–7637. 10.5194/acp-16-7623-2016.

(32). Darer AI; Cole-Filipiak NC; O'Connor AE; Elrod MJ Formation and Stability of Atmospherically Relevant Isoprene-Derived Organosulfates and Organonitrates. Environ. Sci. Technol. 2011, 45 (5), 1895–1902. 10.1021/es103797z. [PubMed: 21291229]

(33). Appel KW; Napelenok SL; Foley KM; Pye HOT; Hogrefe C; Luecken DJ; Bash JO; Roselle SJ; Pleim JE; Foroutan H; et al. Description and Evaluation of the Community Multiscale Air Quality (CMAQ) Modeling System Version 5.1. Geoscientific Model Development 2017, 10 (4), 1703–1732. 10.5194/gmd-10-1703-2017. [PubMed: 30147852]

(34). Fisher JA; Jacob DJ; Travis KR; Kim PS; Marais EA; Chan Miller C; Yu K; Zhu L; Yantosca RM; Sulprizio MP; et al. Organic Nitrate Chemistry and Its Implications for Nitrogen Budgets in an Isoprene- and Monoterpene-Rich Atmosphere: Constraints from Aircraft (SEAC4RS) and Ground-Based (SOAS) Observations in the Southeast US. Atmos. Chem. Phys. 2016, 16 (9), 5969–5991. 10.5194/acp-16-5969-2016. [PubMed: 29681921]

(35). Zare A; Romer PS; Nguyen T; Keutsch FN; Skog K; Cohen RC A Comprehensive Organic Nitrate Chemistry: Insights into the Lifetime of Atmospheric Organic Nitrates. Atmospheric Chemistry and Physics 2018, 18 (20), 15419–15436. 10.5194/acp-18-15419-2018.

(36). Lim YB; Tan Y; Perri MJ; Seitzinger SP; Turpin BJ Aqueous Chemistry and Its Role in Secondary Organic Aerosol (SOA) Formation. Atmospheric Chemistry and Physics 2010, 10 (21), 10521–10539. 10.5194/acp-10-10521-2010.

(37). Wagner NL; Brock CA; Angevine WM; Beyersdorf A; Campuzano-Jost P; Day D; de Gouw JA; Diskin GS; Gordon TD; Graus MG; et al. In Situ Vertical Profiles of Aerosol Extinction, Mass, and Composition over the Southeast United States during SENEX and SEAC4RS: Observations of a Modest Aerosol Enhancement Aloft. Atmospheric Chemistry and Physics 2015, 15 (12), 7085–7102. 10.5194/acp-15-7085-2015.

(38). Otte TL; Pleim JE The Meteorology-Chemistry Interface Processor (MCIP) for the CMAQ Modeling System: Updates through MCIPv3.4.1. Geosci. Model Dev. 2010, 3 (1), 243–256. 10.5194/gmd-3-243-2010.

(39). Houyoux MR; Vukovich JM; Coats CJ; Wheeler NJM; Kasibhatla PS Emission Inventory Development and Processing for the Seasonal Model for Regional Air Quality (SMRAQ) Project. Journal of Geophysical Research: Atmospheres 2000, 105 (D7), 9079–9090. 10.1029/1999JD900975.

(40). Bash JO; Baker KR; Beaver MR Evaluation of Improved Land Use and Canopy Representation in BEIS v3.61 with Biogenic VOC Measurements in California. Geoscientific Model Development 2016, 9 (6), 2191–2207. 10.5194/gmd-9-2191-2016.

(41). Goliff WS; Stockwell WR; Lawson CV The Regional Atmospheric Chemistry Mechanism, Version 2. Atmospheric Environment 2013, 68, 174–185. 10.1016/j.atmosenv.2012.11.038.

(42). Browne EC; Wooldridge PJ; Min K-E; Cohen RC On the Role of Monoterpene Chemistry in the Remote Continental Boundary Layer. Atmos. Chem. Phys. 2014, 14 (3), 1225–1238. 10.5194/acp-14-1225-2014.

(43). Sarwar G; Godowitch J; Henderson BH; Fahey K; Pouliot G; Hutzell WT; Mathur R; Kang D; Goliff WS; Stockwell WR A Comparison of Atmospheric Composition Using the Carbon Bond and Regional Atmospheric Chemistry Mechanisms. Atmospheric Chemistry and Physics 2013, 13 (19), 9695–9712. 10.5194/acp-13-9695-2013.

(44). Boyd CM; Sanchez J; Xu L; Eugene AJ; Nah T; Tuet WY; Guzman MI; Ng NL Secondary Organic Aerosol Formation from the β-Pinene+NO3 System: Effect of Humidity and Peroxy Radical Fate. Atmos. Chem. Phys. 2015, 15 (13), 7497–7522. 10.5194/acp-15-7497-2015.

(45). Schwantes RH; Teng AP; Nguyen TB; Coggon MM; Crounse JD; St. Clair JM; Zhang X; Schilling KA; Seinfeld JH; Wennberg PO Isoprene NO3 Oxidation Products from the RO2 + HO2 Pathway. J. Phys. Chem. A 2015 10.1021/acs.jpca.5b06355.

(46). Wennberg PO; Bates KH; Crounse JD; Dodson LG; McVay RC; Mertens LA; Nguyen TB; Praske E; Schwantes RH; Smarte MD; et al. Gas-Phase Reactions of Isoprene and Its Major Oxidation Products. Chem. Rev. 2018, 118 (7), 3337–3390. 10.1021/acs.chemrev.7b00439. [PubMed: 29522327]

(47). Bates KH; Jacob DJ A New Model Mechanism for Atmospheric Oxidation of Isoprene: Global Effects on Oxidants, Nitrogen Oxides, Organic Products, and Secondary Organic Aerosol. Atmospheric Chemistry and Physics Discussions 2019, 1–46. 10.5194/acp-2019-328.

(48). Kwan AJ; Chan AWH; Ng NL; Kjaergaard HG; Seinfeld JH; Wennberg PO Peroxy Radical Chemistry and OH Radical Production during the NO3-Initiated Oxidation of Isoprene. Atmos. Chem. Phys. 2012, 12 (16), 7499–7515. 10.5194/acp-12-7499-2012.

(49). Compernolle S; Ceulemans K; Müller J-F EVAPORATION: A New Vapour Pressure Estimation Methodfor Organic Molecules Including Non-Additivity and Intramolecular Interactions. Atmospheric Chemistry and Physics 2011, 11 (18), 9431–9450. 10.5194/acp-11-9431-2011.

(50). Pankow JF; Asher WE SIMPOL.1: A Simple Group Contribution Method for Predicting Vapor Pressures and Enthalpies of Vaporization of Multifunctional Organic Compounds. Atmospheric Chemistry and Physics 2008, 8 (10), 2773–2796. 10.5194/acp-8-2773-2008.

(51). Myrdal PB; Yalkowsky SH Estimating Pure Component Vapor Pressures of Complex Organic Molecules. Ind. Eng. Chem. Res. 1997, 36 (6), 2494–2499. 10.1021/ie950242l.

(52). Nannoolal Y; Rarey J; Ramjugernath D; Cordes W Estimation of Pure Component Properties: Part 1. Estimation of the Normal Boiling Point of Non-Electrolyte Organic Compounds via Group Contributions and Group Interactions. Fluid Phase Equilibria 2004, 226, 45–63. 10.1016/j.fluid.2004.09.001.

(53). Saunders SM; Jenkin ME; Derwent RG; Pilling MJ Protocol for the Development of the Master Chemical Mechanism, MCM v3 (Part A): Tropospheric Degradation of Non-Aromatic Volatile Organic Compounds. Atmos. Chem. Phys. 2003, 3 (1), 161–180. 10.5194/acp-3-161-2003.

(54). Fry JL; Kiendler-Scharr A; Rollins AW; Brauers T; Brown SS; Dorn H-P; Dubé WP; Fuchs H; Mensah A; Rohrer F; et al. SOA from Limonene: Role of NO3 in Its Generation and Degradation. Atmos. Chem. Phys. 2011, 11 (8), 3879–3894. 10.5194/acp-11-3879-2011.

(55). D'Ambro EL; Lee BH; Liu J; Shilling JE; Gaston CJ; Lopez-Hilfiker FD; Schobesberger S; Zaveri RA; Mohr C; Lutz A; et al. Molecular Composition and Volatility of Isoprene Photochemical Oxidation Secondary Organic Aerosol under Low- and High-NO$_x$ Conditions. Atmospheric Chemistry and Physics 2017, 17 (1), 159–174. 10.5194/acp-17-159-2017.

(56). Pye HOT; D'Ambro EL; Lee BH; Schobesberger S; Takeuchi M; Zhao Y; Lopez-Hilfiker F; Liu J; Shilling JE; Xing J; et al. Anthropogenic Enhancements to Production of Highly Oxygenated Molecules from Autoxidation. PNAS 2019, 116 (14), 6641–6646. 10.1073/pnas.1810774116. [PubMed: 30886090]

(57). Pye HOT; Pinder RW; Piletic IR; Xie Y; Capps SL; Lin Y-H; Surratt JD; Zhang Z; Gold A; Luecken DJ; et al. Epoxide Pathways Improve Model Predictions of Isoprene Markers and Reveal Key Role of Acidity in Aerosol Formation. Environ. Sci. Technol. 2013, 47 (19), 11056–11064. 10.1021/es402106h. [PubMed: 24024583]

(58). Hanson DR; Ravishankara AR; Solomon S Heterogeneous Reactions in Sulfuric Acid Aerosols: A Framework for Model Calculations. J. Geophys. Res. 1994, 99 (D2), 3615–3629. 10.1029/93JD02932.

(59). Jacob DJ Heterogeneous Chemistry and Tropospheric Ozone, Atmos. Environ 2000, 34, 2131–2159.

(60). Meylan WM; Howard PH Bond Contribution Method for Estimating Henry's Law Constants. Environmental Toxicology and Chemistry 1991, 10 (10), 1283–1293. 10.1002/etc.5620101007.

(61). Hilal SH; Karickhoff SW; Carreira LA Prediction of the Vapor Pressure Boiling Point, Heat of Vaporization and Diffusion Coefficient of Organic Compounds. QSAR & Combinatorial Science 2003, 22 (6), 565–574. 10.1002/qsar.200330812.

(62). Surratt JD; Lewandowski M; Offenberg JH; Jaoui M; Kleindienst TE; Edney EO; Seinfeld JH Effect of Acidity on Secondary Organic Aerosol Formation from Isoprene. Environ. Sci. Technol. 2007, 41 (15), 5363–5369. 10.1021/es0704176. [PubMed: 17822103]

(63). Sato K Detection of Nitrooxypolyols in Secondary Organic Aerosol Formed from the Photooxidation of Conjugated Dienes under High-NOx Conditions. Atmospheric Environment 2008, 42 (28), 6851–6861. 10.1016/j.atmosenv.2008.05.010.

(64). Szmigielski R; Vermeylen R; Dommen J; Metzger A; Maenhaut W; Baltensperger U; Claeys M The Acid Effect in the Formation of 2-Methyltetrols from the Photooxidation of Isoprene in the Presence of NOx. Atmospheric Research 2010, 98 (2), 183–189. 10.1016/j.atmosres.2010.02.012.

(65). Rindelaub JD; Borca CH; Hostetler MA; Slade JH; Lipton MA; Slipchenko LV; Shepson PB The Acid-Catalyzed Hydrolysis of an α-Pinene-Derived Organic Nitrate: Kinetics, Products, Reaction Mechanisms, and Atmospheric Impact. Atmos. Chem. Phys. 2016, 16 (23), 15425–15432. 10.5194/acp-16-15425-2016.

(66). McNeill VF; Woo JL; Kim DD; Schwier AN; Wannell NJ; Sumner AJ; Barakat JM Aqueous-Phase Secondary Organic Aerosol and Organosulfate Formation in Atmospheric Aerosols: A Modeling Study. Environ. Sci. Technol. 2012, 46 (15), 8075–8081. 10.1021/es3002986. [PubMed: 22788757]

(67). Fahey KM; Carlton AG; Pye HOT; Baek J; Hutzell WT; Stanier CO; Baker KR; Appel KW; Jaoui M; Offenberg JH A Framework for Expanding Aqueous Chemistry in the Community Multiscale Air Quality (CMAQ) Model Version 5.1. Geoscientific Model Development 2017, 10 (4), 1587–1605. 10.5194/gmd-10-1587-2017. [PubMed: 30147851]

(68). Budisulistiorini SH; Nenes A; Carlton AMG; Surratt JD; McNeill VF; Pye HOT Simulating Aqueous-Phase Isoprene-Epoxydiol (IEPOX) Secondary Organic Aerosol Production During the 2013 Southern Oxidant and Aerosol Study (SOAS). Environ. Sci. Technol. 2017 10.1021/acs.est.6b05750.

(69). Carlton AG; Turpin BJ; Altieri KE; Seitzinger SP; Mathur R; Roselle SJ; Weber RJ CMAQ Model Performance Enhanced When In-Cloud Secondary Organic Aerosol Is Included: Comparisons of Organic Carbon Predictions with Measurements. Environ. Sci. Technol. 2008, 42 (23), 8798–8802. 10.1021/es801192n. [PubMed: 19192800]

(70). Liu S; Shilling JE; Song C; Hiranuma N; Zaveri RA; Russell LM Hydrolysis of Organonitrate Functional Groups in Aerosol Particles. Aerosol Science and Technology 2012, 46 (12), 1359–1369. 10.1080/02786826.2012.716175.

(71). Hu KS; Darer AI; Elrod MJ Thermodynamics and Kinetics of the Hydrolysis of Atmospherically Relevant Organonitrates and Organosulfates. Atmos. Chem. Phys. 2011, 11 (16), 8307–8320. 10.5194/acp-11-8307-2011.

(72). Jacobs MI; Burke WJ; Elrod MJ Kinetics of the Reactions of Isoprene-Derived Hydroxynitrates: Gas Phase Epoxide Formation and Solution Phase Hydrolysis. Atmos. Chem. Phys. 2014, 14 (17), 8933–8946. 10.5194/acp-14-8933-2014.

(73). Bean JK; Hildebrandt Ruiz L Gas–Particle Partitioning and Hydrolysis of Organic Nitrates Formed from the Oxidation of α-Pinene in Environmental Chamber Experiments. Atmos. Chem. Phys. 2016, 16 (4), 2175–2184. 10.5194/acp-16-2175-2016.

(74). Rindelaub JD; McAvey KM; Shepson PB The Photochemical Production of Organic Nitrates from α-Pinene and Loss via Acid-Dependent Particle Phase Hydrolysis. Atmospheric Environment 2015, 100, 193–201. 10.1016/j.atmosenv.2014.11.010.

(75). Eddingsaas NC; VanderVelde DG; Wennberg PO Kinetics and Products of the Acid-Catalyzed Ring-Opening of Atmospherically Relevant Butyl Epoxy Alcohols. J Phys Chem A 2010, 114 (31), 8106–8113. 10.1021/jp103907c. [PubMed: 20684583]

(76). Fountoukis C; Nenes A ISORROPIA II: A Computationally Efficient Thermodynamic Equilibrium Model for K^+–Ca^{2+}–Mg^{2+}–NH_4^+–Na^+–SO_4^{2-}–NO_3^-–Cl^-–H_2O Aerosols. Atmospheric Chemistry and Physics 2007, 7 (17), 4639–4659. 10.5194/acp-7-4639-2007.

(77). Hodzic A; Aumont B; Knote C; Lee-Taylor J; Madronich S; Tyndall G Volatility Dependence of Henry's Law Constants of Condensable Organics: Application to Estimate Depositional Loss of Secondary Organic Aerosols. Geophysical Research Letters 2014, 41 (13), 4795–4804. 10.1002/2014GL060649.

(78). Pye HOT; Murphy BN; Xu L; Ng NL; Carlton AG; Guo H; Weber R; Vasilakos P; Appel KW; Budisulistiorini SH; et al. On the Implications of Aerosol Liquid Water and Phase Separation for Organic Aerosol Mass. Atmospheric Chemistry and Physics 2017, 17 (1), 343–369. 10.5194/acp-17-343-2017. [PubMed: 30147709]

(79). Nguyen TB; Crounse JD; Teng AP; Clair JMS; Paulot F; Wolfe GM; Wennberg PO Rapid Deposition of Oxidized Biogenic Compounds to a Temperate Forest. PNAS 2015, 112 (5), E392–E401. 10.1073/pnas.1418702112. [PubMed: 25605913]

(80). Lin Y-H; Zhang H; Pye HOT; Zhang Z; Marth WJ; Park S; Arashiro M; Cui T; Budisulistiorini SH; Sexton KG; et al. Epoxide as a Precursor to Secondary Organic Aerosol Formation from Isoprene Photooxidation in the Presence of Nitrogen Oxides. PNAS 2013, 110 (17), 6718–6723. 10.1073/pnas.1221150110. [PubMed: 23553832]

(81). Rollins AW; Pusede S; Wooldridge P; Min K-E; Gentner DR; Goldstein AH; Liu S; Day DA; Russell LM; Rubitschun CL; et al. Gas/Particle Partitioning of Total Alkyl Nitrates Observed with TD-LIF in Bakersfield. Journal of Geophysical Research: Atmospheres 2013, 118 (12), 6651–6662. 10.1002/jgrd.50522.

(82). Ng NL; Brown SS; Archibald AT; Atlas E; Cohen RC; Crowley JN; Day DA; Donahue NM; Fry JL; Fuchs H; et al. Nitrate Radicals and Biogenic Volatile Organic Compounds: Oxidation, Mechanisms, and Organic Aerosol. Atmospheric Chemistry and Physics 2017, 17 (3), 2103–2162. 10.5194/acp-17-2103-2017. [PubMed: 30147712]

(83). Zhang H; Yee LD; Lee BH; Curtis MP; Worton DR; Isaacman-VanWertz G; Offenberg JH; Lewandowski M; Kleindienst TE; Beaver MR; et al. Monoterpenes Are the Largest Source of Summertime Organic Aerosol in the Southeastern United States. PNAS 2018, 115 (9), 2038–2043. 10.1073/pnas.1717513115. [PubMed: 29440409]

(84). Ayres BR; Allen HM; Draper DC; Brown SS; Wild RJ; Jimenez JL; Day DA; Campuzano-Jost P; Hu W; de Gouw J; et al. Organic Nitrate Aerosol Formation via NO3 + Biogenic Volatile Organic Compounds in the Southeastern United States. Atmos. Chem. Phys. 2015, 15 (23), 13377–13392. 10.5194/acp-15-13377-2015.

(85). Day DA; Wooldridge PJ; Dillon MB; Thornton JA; Cohen RC A Thermal Dissociation Laser-Induced Fluorescence Instrument for in Situ Detection of NO2, Peroxy Nitrates, Alkyl Nitrates, and HNO3. J. Geophys. Res. 2002, 107 (D6), ACH 4-1 10.1029/2001JD000779.
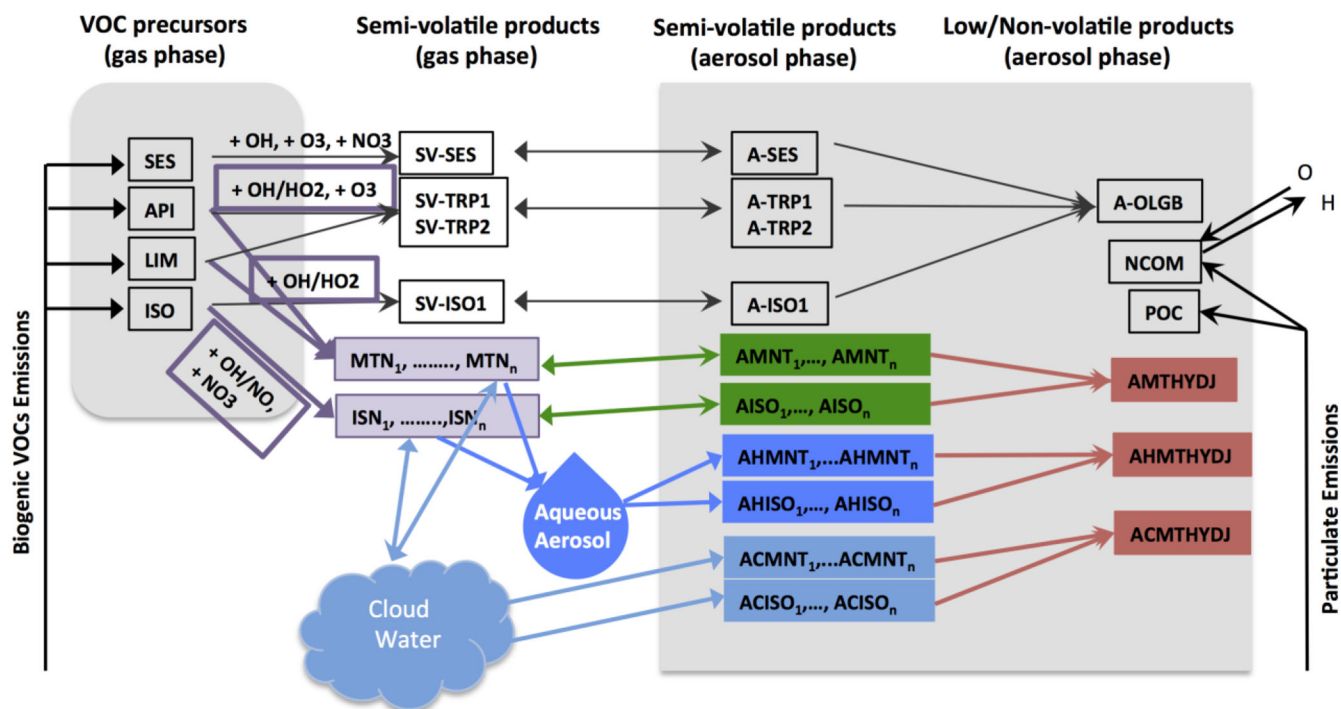
Figure 1.
Schematic of organic aerosol treatment and PON formation pathways in CMAQ. Purple boxes show the revised oxidation pathways for separation of the particle formation from monoterpenes and isoprene in low and high NO_x conditions. Shaded purples boxes show the gas phase monoterpenes and isoprene nitrates produced from NO_3 oxidation and photooxidation in high NO_x conditions. Shaded purples boxes show the gas phase monoterpenes and isoprene nitrates produced from NO_3 oxidation and photooxidation in high NO_x conditions. The particle organic nitrates that are in the equilibrium between gas and aerosol phases based on vapor-pressure driven partitioning to an organic phase are shown in green. Blue reflects the aqueous particle organic nitrates formed through heterogeneous uptake in cloud droplets and aerosol water and non-volatile organic aerosols from hydrolysis of particle organic nitrates are in red. Primary condensed-phase organics available for partitioning include NCOM (non-carbon organic matter) and POC (primary organic carbon).
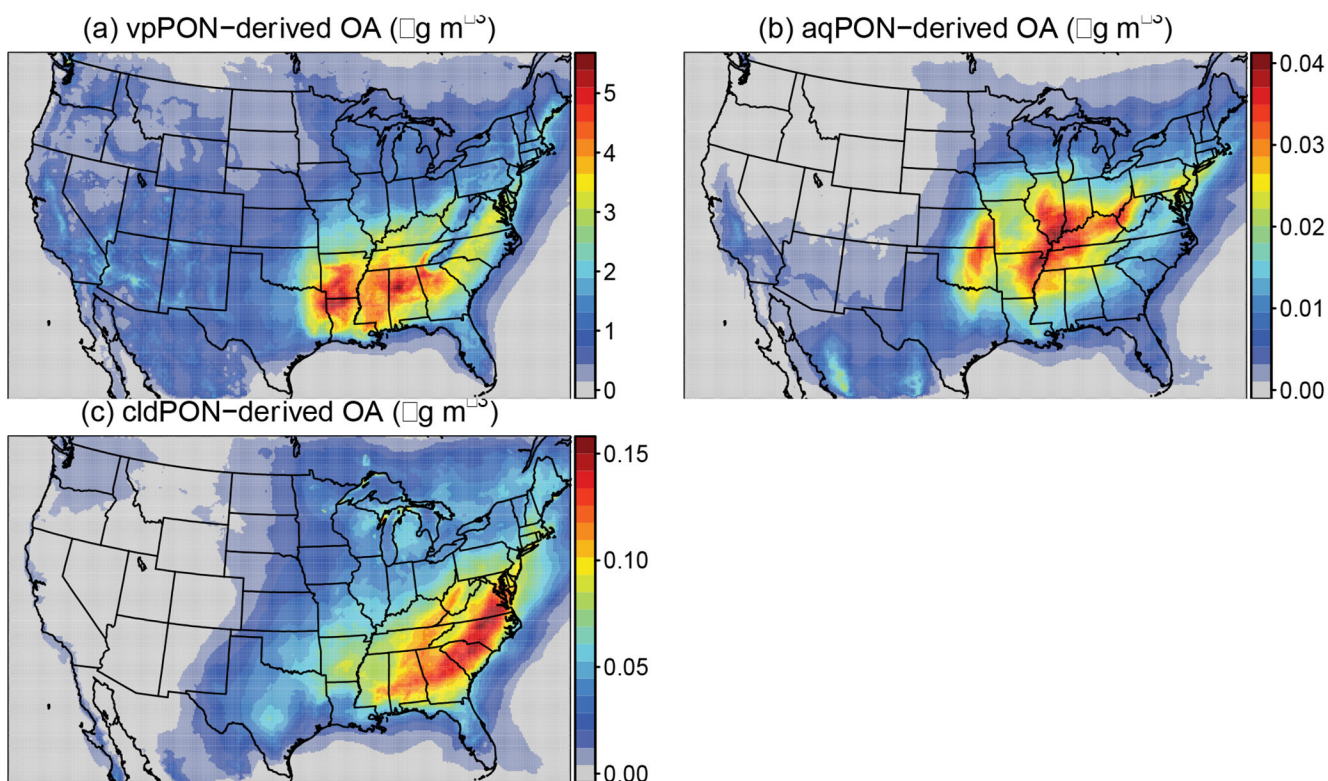
Figure 2.
Mean predicted (a) vpPON-derived, (b) aqPON-derived and (c) cldPON-derived OA concentrations (μg m^{-3}) for the model simulation period (June 2013) at the surface.
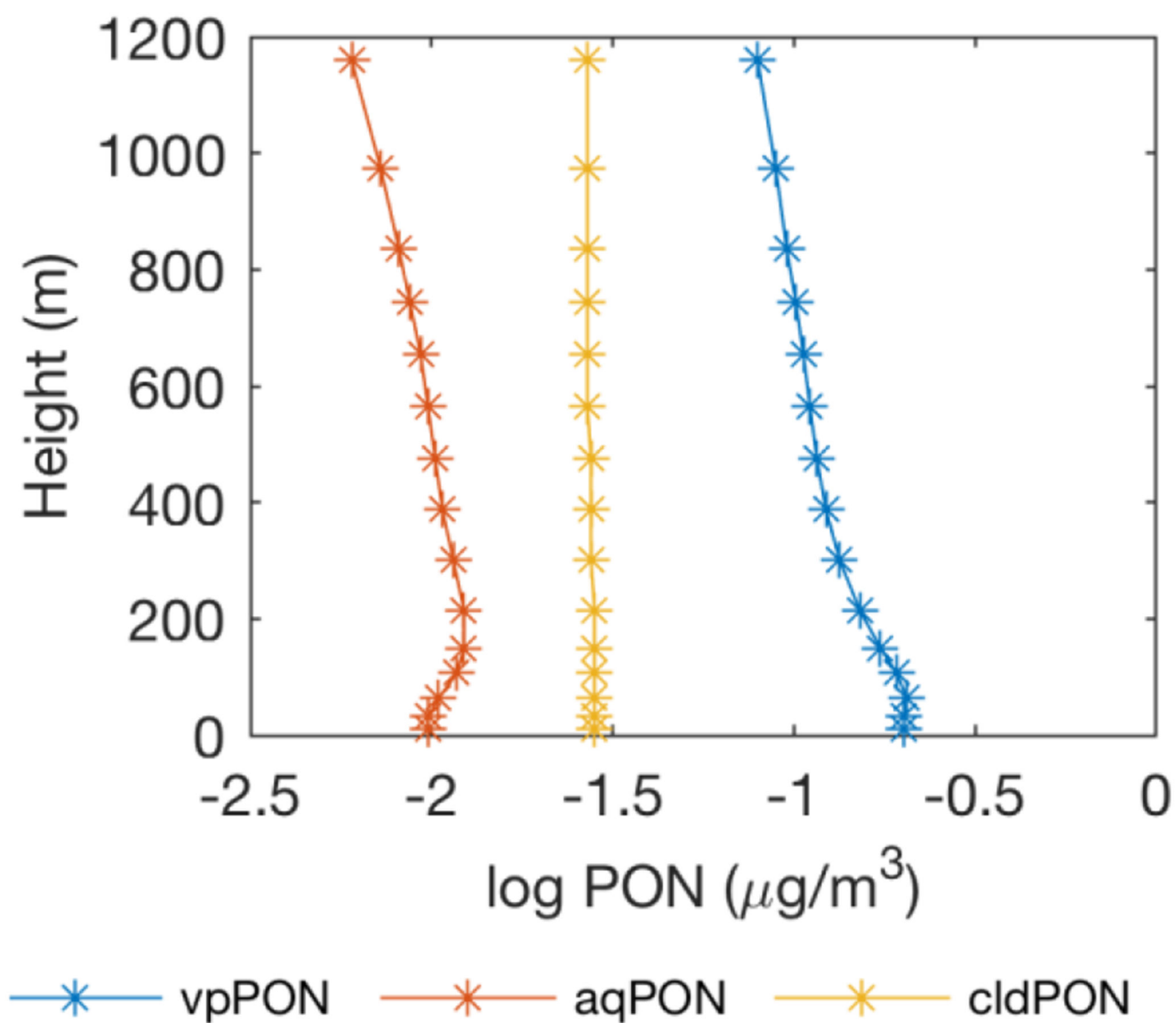
Figure 3.
Vertical profile of June 2013 mean predicted vpPON, aqPON and cldPON in the boundary
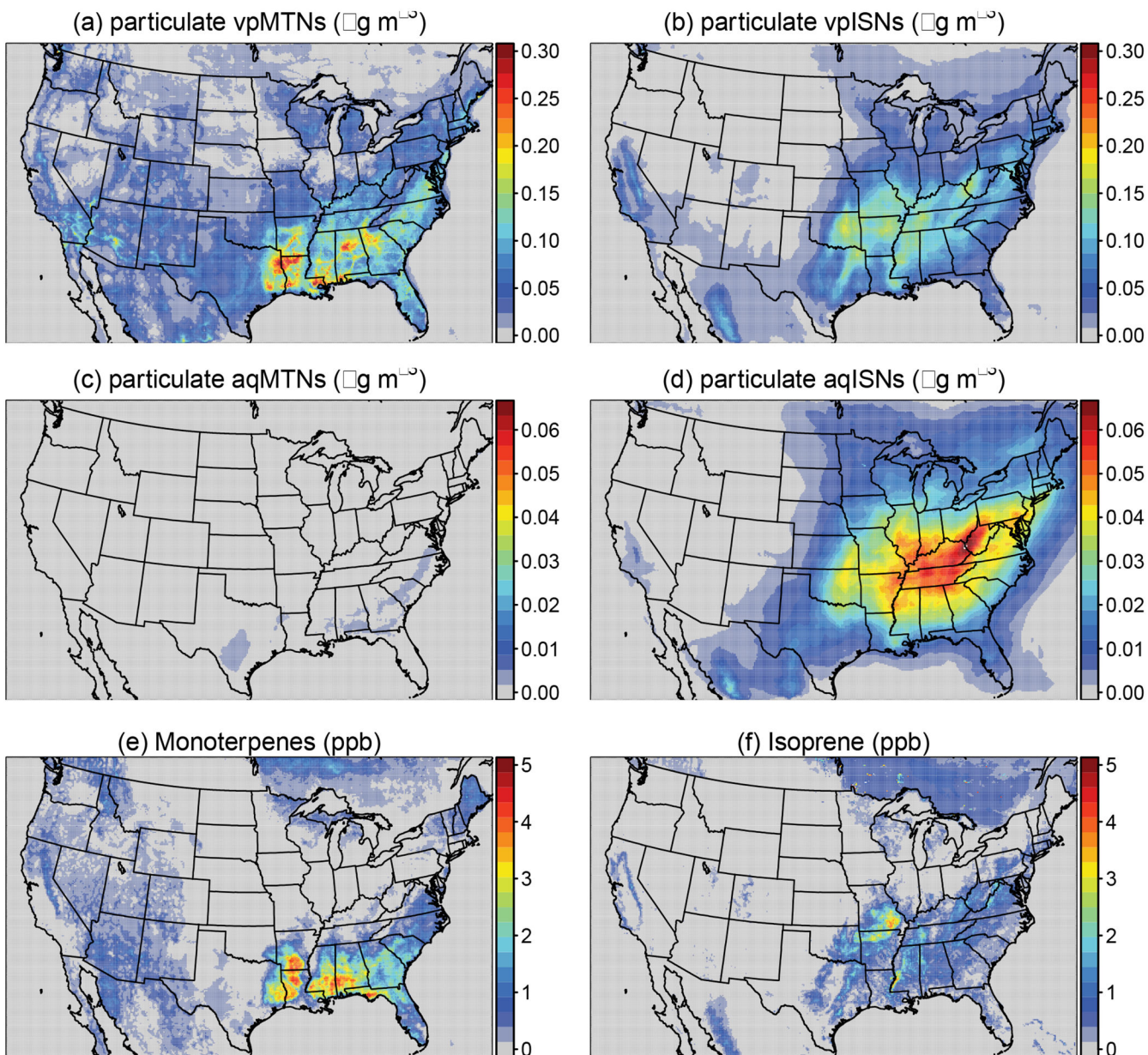layer at the CTR site (with an averaged daytime height 1200 m).

Figure 4.
June 2013 mean predicted (a, b) vpPON and (c, d) aqPON (µg m^{-3}) from (a, c) monoterpenes and (b, d) isoprene precursors. (e, f) June 2013 mean predicted concentrations of monoterpenes and isoprene.
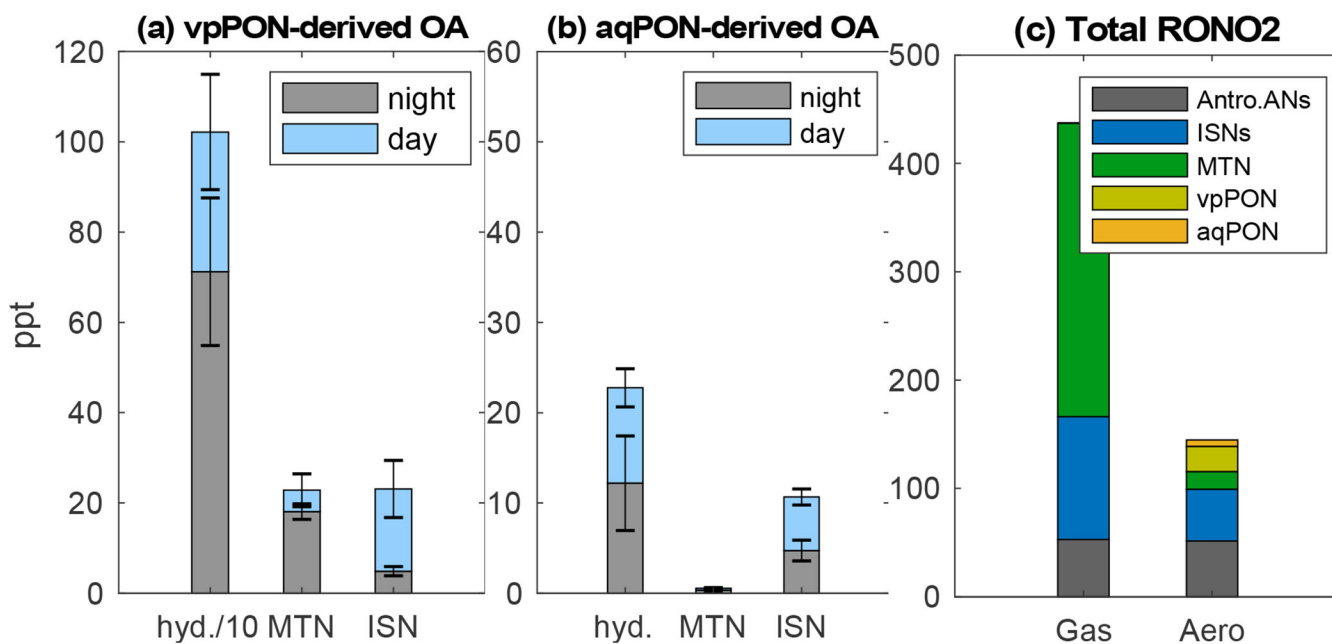
Figure 5.
(a) Mean of vpPON and (b) aqPON from monoterpenes (MTN) and isoprene (ISN) and hydrolysis product aerosols (hyd) from daytime and nighttime for the model simulation period at the CTR site. The hydrolysis product aerosols are predicted to be about a factor of 10 higher than the parent PONs associated with vapor pressure-driven partitioning. (c) Composition of total alkyl nitrates at CTR for two runs with the updated gas-phase RACM2_Berkeley2.1 mechanism with (Aero) and without (Gas) explicit representation of PON formation.
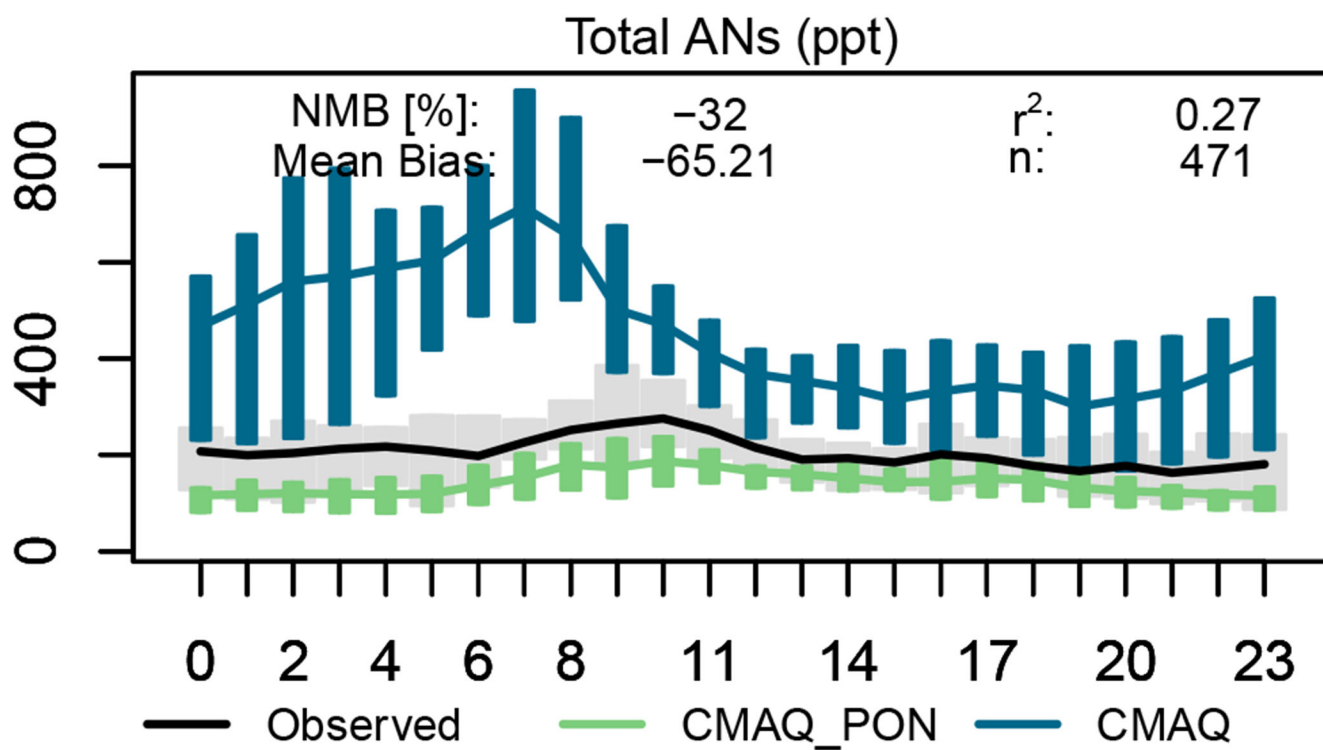
Figure 6.
Diurnal cycle of median predicted total alkyl nitrates (gas+ aerosol) in CMAQ at CTR site in June 2013 for two runs with the updated gas-phase RACM2_Berkeley2.1 mechanism with and without explicit representation of PON formation (in green (named as CMAQ_PON) and blue (named as CMAQ), respectively). Black line indicates the observations. Metrics including normalized mean bias (NMB) are for the simulation with PON formation and observations.