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# Observation of isoprene hydroxynitrates in the Southeastern United States and implications for the fate of NO<sub>x</sub>

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## Abstract

Isoprene hydroxynitrates (IN) are tracers of the photochemical oxidation of isoprene in high  $\text{NO}_x$  environments. Production and loss of IN have a significant influence on the  $\text{NO}_x$  cycle and tropospheric  $\text{O}_3$  chemistry. To better understand IN chemistry, a series of photochemical reaction chamber experiments were conducted to determine the IN yield from isoprene photooxidation at high  $\text{NO}$  concentrations ( $> 100$  ppt). By combining experimental data and calculated isomer distributions, a total IN yield of  $9(+4/-3)\%$  was derived. The result was applied in a zero-dimensional model to simulate production and loss of ambient IN observed in a temperate forest atmosphere, during the Southern Oxidant and Aerosol Study (SOAS) field campaign, from 27 May to 11 July 2013. By comparing field observations with model simulations, we identified  $\text{NO}$  as the limiting factor for ambient IN production during SOAS, but vertical mixing at dawn might also contribute ( $\sim 27\%$ ) to IN dynamics. A close examination of isoprene's oxidation products indicates that its oxidation transitioned from a high- $\text{NO}$  dominant chemical regime in the morning into a low- $\text{NO}$  dominant regime in the afternoon. A significant amount of IN produced in the morning high  $\text{NO}$  regime could be oxidized in the low  $\text{NO}$  regime, and a possible reaction scheme was proposed.

## 1 Introduction

Isoprene ( $\text{C}_5\text{H}_8$ ) accounts for approximately half of the global non-methane biogenic volatile organic compound (BVOC) emissions (Guenther et al., 2006) and has a significant influence on the budgets of  $\text{OH}$ ,  $\text{O}_3$  and  $\text{NO}_x$  (Horowitz et al., 2007). Isoprene oxidation by  $\text{OH}$  in the presence of  $\text{NO}_x$  can lead to the formation of isoprene hydroxynitrates (IN), as described in Reactions (R1) and (R2). The chain-terminating Reaction (R2a) removes peroxy radicals ( $\text{RO}_2$ ) and  $\text{NO}$  from the atmosphere and decreases tropospheric  $\text{O}_3$  production (Carter and Atkinson, 1996). IN serves as a temporary  $\text{NO}_x$  reservoir, and the transport and photo-oxidative decomposition of these

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compounds can further modulate  $\text{NO}_x$  and  $\text{O}_3$  concentrations (Horowitz et al., 2007; Paulot et al., 2012; Xie et al., 2013). Gas-phase organic nitrates can also partition into the particle phase and undergo hydrolysis, contributing to the growth of secondary organic aerosols (SOA) (Jacobs et al., 2014; Rindelaub et al., 2015).



The initial OH addition (followed by  $\text{O}_2$ ) to isoprene (Reaction R1) produces eight isomeric  $\text{RO}_2$  radicals. Reaction of these  $\text{RO}_2$  radicals with NO proceeds primarily via two reaction pathways (Reaction R2a and b). Laboratory studies suggest that the nitrate formation channel (Reaction R2a) is minor compared to the alkoxy radical (RO) formation channel (Reaction R2b), with reported total IN yields ranging from 4 to 14 % (Chen et al., 1998; Patchen et al., 2007; Lockwood et al., 2010; Paulot et al., 2009; Sprengnether et al., 2002; Tuazon and Atkinson, 1990). Reaction (R2a) leads to the formation of eight IN isomers, including four  $\beta$ -IN isomers and four  $\delta$ -IN isomers (Table 1). The wide range of reported IN yields has led to uncertainty in quantifying isoprene's influence on the  $\text{NO}_x$  cycle and  $\text{O}_3$  enhancement (Xie et al., 2013; Horowitz et al., 2007; Paulot et al., 2012). IN can also be produced at night through  $\text{NO}_3$ -initiated isoprene oxidation with a yield around 20 %, adding to a total organic nitrate yield of 65–70 % (Rollins et al., 2009; Perring et al., 2009; Kwan et al., 2012). The major daytime IN sink is reaction with OH, which leads to a lifetime of 2.5 to 6.5 h, according to a recent kinetics study (L. Lee et al., 2014). At night, IN is more susceptible to loss from ozonolysis, and potentially  $\text{NO}_3$  oxidation when the  $\text{NO}_x$  concentration is high (Xie et al., 2013). IN have been observed in the ambient environment, primarily in forested areas under the influence of anthropogenic  $\text{NO}_x$  plumes (Grossenbacher et al., 2001, 2004; Giacomelli et al., 2005; Beaver et al., 2012; B. H. Lee et al., 2014). During the BEARPEX 2009 study conducted in the Sierra Nevada Mountains of California, IN constituted 38 % of the total organic nitrates (Beaver et al., 2012).

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Methods to quantify organic nitrates include infrared spectroscopy (IR), thermal dissociation-laser induced fluorescence (TD-LIF) spectroscopy, chemiluminescence, gas chromatography (GC)-based separation and detection techniques, and mass spectrometry (MS) (Rollins et al., 2010; Tuazon and Atkinson, 1990; Sprengnether et al., 2002; Day et al., 2002; O'Brien et al., 1995; Beaver et al., 2012; B. H. Lee et al., 2014; Lockwood et al., 2010; Paulot et al., 2009; Giacobelli et al., 2005; Grossenbacher et al., 2004; Patchen et al., 2007; Hartsell et al., 1994; Kwan et al., 2012; Teng et al., 2015). IR, TD-LIF, and chemiluminescence can only measure total organic nitrates because they respond solely to the nitrooxy functional group (Day et al., 2002; Rollins et al., 2010; Tuazon and Atkinson, 1990; Sprengnether et al., 2002; O'Brien et al., 1995; Hartsell et al., 1994). GC- and MS-based methods can speciate organic nitrates and have been employed previously to quantify IN in both laboratory and field studies (Lockwood et al., 2010; Patchen et al., 2007; Giacobelli et al., 2005; Paulot et al., 2009; B. H. Lee et al., 2014; Grossenbacher et al., 2004; Beaver et al., 2012; Kwan et al., 2012). For MS-based techniques, the fragile O-NO<sub>2</sub> bond in organic nitrates often fragments during ionization (Perring et al., 2009), so soft-ionization methods with reagent ion such as H<sup>+</sup>(H<sub>2</sub>O)<sub>4</sub>, CF<sub>3</sub>O<sup>-</sup>, and I<sup>-</sup> are necessary to detect the molecular ion for organic nitrates (Patchen et al., 2007; Beaver et al., 2012; B. H. Lee et al., 2014; Crouse et al., 2006).

Here we present a comprehensive laboratory and field study of the formation of IN from isoprene reaction with OH. In the summer of 2013, we quantified ambient IN in rural Alabama for 6 weeks during the Southern Oxidant and Aerosol Studies (SOAS, <http://soas2013.rutgers.edu/>). In parallel with the field study, laboratory experiments were conducted to determine the yield of IN from isoprene oxidation. For laboratory experiments, we synthesized authentic standards for the quantification of IN, using multiple calibration techniques. The IN yield obtained from lab experiments was applied in a zero-dimensional model to simulate IN production and loss in the atmosphere, which was then compared with the measurements from SOAS, to examine our understanding of atmospheric IN chemistry.

## 2 Experiment

### 2.1 CIMS IN calibration

A chemical ionization mass spectrometer (CIMS) was used to measure IN concentrations during the chamber experiments and the SOAS field study. The instrument is similar to the one described by Liao et al. (2011), which uses  $I(H_2O)_n^-$  to form iodide clusters with the analyte compounds.

Two authentic standards, 4,3-IN and 1,4-IN (a mixture of *trans*- and *cis*-1,4-IN), were synthesized to determine the sensitivity of CIMS toward IN isomers. 1,4-IN was prepared using the nitrification method described by L. Lee et al. (2014), and the sample was used after flash column chromatography without further purification to separate the *trans* and *cis* isomers. 4,3-IN was prepared by nitrification of (1-methylethenyl)oxirane, and the epoxide was synthesized following Harwood et al. (1990).

The IN gas-phase sample for CIMS calibration was prepared by evaporating an IN standard solution of known volume into 50 L of clean air. The IN concentration in the standard solution was determined with NMR and FTIR, and the results from the two methods were consistent within 15%. Multiple CIMS calibrations for 4,3-IN were performed, and the results did not deviate more than 15% after 1.5 years (Supplement Sect. 1). The average sensitivity of 4,3-IN normalized to the reagent ion signal was  $2.3(\pm 0.3) \times 10^{-3} \text{ ppt}^{-1}$  and was used as the surrogate sensitivity for the  $\beta$ -IN isomers except 1,2-IN.

The 1,4-IN calibration was conducted following the same procedures. Since the 1,4-IN standard contained a mixture of *trans*- and *cis*-1,4-IN, the measured sensitivity was a weighted average of both isomers. The relative abundance of the *trans*- and *cis*-1,4-IN isomers was obtained from NMR, and their individual sensitivities were estimated using a least-squares method (Supplement Sect. 2). The sensitivity for *trans*-1,4-IN was  $3(\pm 2) \times 10^{-4} \text{ ppt}^{-1}$ , and it was used as surrogate sensitivity for *trans*-4,1-IN. The sensitivity for *cis*-1,4-IN was  $1.3(\pm 0.3) \times 10^{-3} \text{ ppt}^{-1}$ , and it was used as surrogate sensitivity for *cis*-4,1-IN.

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5 estimate the relative abundance of IN isomers. The distribution of IN isomers during the chamber experiments was estimated using an iterative method (Supplement Sect. 3.1). For IN measurement during SOAS, a diurnal average of the changing IN isomer distribution was estimated and applied to calibrate IN data for each individual day. The isomer-weighted IN sensitivity changed by less than 20 % throughout the day (Supplement Sect. 3.2).

## 2.2 Isoprene chamber experiments

10 Seven experiments were conducted in the 5500 L Purdue photochemical reaction chamber (Chen et al., 1998) to determine the yield of IN from OH-initiated isoprene oxidation in the presence of  $\text{NO}_x$ . OH was generated from the photolysis of isopropyl nitrite. The starting conditions for the experiments are listed in Table 2. Each experiment was initiated by switching on the UV lamps and was considered complete when half of the isoprene was consumed or the NO concentration dropped to around 5 ppb.

15 The IN concentration was measured continuously during each experiment with the CIMS. Chamber air was sampled through a 5.2 m long inlet, made of 0.8 cm ID heated (constant 50 °C) FEP Teflon tubing. A total flow of 5 liters per minute ( $\text{L min}^{-1}$ ) was pulled through the inlet into a custom-built three-way valve system (Liao et al., 2011), where  $2 \text{ L min}^{-1}$  was sub-sampled into the CIMS through a 0.51 mm orifice. Water vapor was added downstream of the orifice to humidify the sample air to reduce the influence that variations in ambient RH and temperature have on the distribution of  $\text{I}(\text{H}_2\text{O})_n^-$  clusters. Laboratory tests showed that with constant  $\text{H}_2\text{O}$  addition, the CIMS sensitivity is not dependent on ambient air humidity (Supplement Sect. 6). The IN loss in the 50 °C sampling inlet was measured to be 5% for the 4,3-IN isomer. However, for the 1,2-IN isomer, it is more susceptible loss under high temperature. This is reflected in the chromatograms in Fig. 2a and b, as the ECD peaks of 1,2-IN and 4,3-IN have approximately the same height, while OH would preferentially add to C1 than C4 (Peeters et al., 2007), leading to a theoretical relative yield of 1.8–2 for 1,2-IN to 4,3-IN. Therefore, it is likely 1,2-IN decomposed in the GC oven with an elution temperature of

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80 °C. The loss of 1,2-IN is unclear as it flows through the 50 °C inlet with a residence time of 3s, so an upper limit of 50% was estimated, based on the loss of 1,2-IN inside the GC system.

Isoprene and its oxidation products, methyl vinyl ketone (MVK) and methacrolein (MACR), were quantified with a proton-transfer reaction linear ion trap mass spectrometer (PTR-LIT MS), with measurement precision of 3 ppb and accuracy of  $\pm 17\%$  (Mielke et al., 2010). MVK and MACR were observed as the same nominal mass without further differentiation for relative isomeric abundance. The NO concentration was measured through chemiluminescence using the total reactive nitrogen instrument (TRENI) (Lockwood et al., 2010), and the addition of isopropyl nitrite did not cause any interference signal for TRENI during the chamber experiments.

One wall loss experiment was conducted by keeping the IN isomers produced from isoprene oxidation in the dark chamber and sampling the chamber air with CIMS periodically for four hours. No significant IN loss was observed, so wall loss was not corrected for IN measurement.

## 2.3 CIMS SOAS measurement

During SOAS, the CIMS was used to measure ambient IN concentrations continuously from 26 May to 11 July 2013 at the Centerville (CTR) site (32.90° N, 87.25° W). The CTR site is located about 50 miles south of Birmingham and Tuscaloosa near the Talladega National Forest, a region abundant with pine and oak trees. The CIMS was operated under the same conditions as those during the chamber experiments. Air was sampled from 5.3m above the ground, with the same inlet (heated to constant 50 °C) and valve system that were used for chamber experiments. The CIMS three-way valve system was used to allow automated background measurement and in-situ Br<sub>2</sub> calibration to monitor instrument stability. The background was determined by passing ambient air through nylon wool coated with sodium bicarbonate for 2 min every 15 min. Br<sub>2</sub> calibration was performed hourly by adding a 30 sccm Br<sub>2</sub>/N<sub>2</sub> flow from a Br<sub>2</sub> permeation device to the ambient air being sampled into the CIMS for 2

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min. The CIMS sensitivity to IN was calibrated relative to the Br<sub>2</sub> sensitivity, which were both normalized to the reagent ion signal I(H<sub>2</sub><sup>18</sup>O)<sup>-</sup>. The Br<sub>2</sub> output rate from the permeation device was determined daily with the optical absorption method following Liao et al. (2011). The averaged Br<sub>2</sub> output of the permeation source throughout the campaign was 60(±8) ng min<sup>-1</sup>, which was 1.8(±0.2) ppb when diluted with ambient air.

## 2.4 0-D Model for IN data interpretation

A zero-dimensional (0-D) model based on the Master Chemical Mechanism (MCMv3.2) (Jenkin et al., 1997; Saunders et al., 2003) was used to investigate the production and loss of IN in the chamber and in the SOAS field study. The mechanism was updated for recent experimental and theoretical studies of isoprene chemistry, including the inter-conversion of isomeric isoprene RO<sub>2</sub> radicals (LIM1) (Peeters et al., 2014), IN reaction rate constants for OH and O<sub>3</sub> (L. Lee et al., 2014), IEPOX reaction rate constants for OH (Bates et al., 2014) and the branching ratio for NO<sub>3</sub> addition to isoprene (Fan and Zhang, 2004).

For the IN observations during SOAS, our analysis is focused on the production and loss of IN. Therefore, the 0-D model for the SOAS data analysis was constrained to the observed concentrations of the major species involved in the IN chemistry, including isoprene, HO<sub>x</sub>, O<sub>3</sub>, NO<sub>x</sub>, α-pinene, β-pinene and limonene. The NO<sub>2</sub> photolysis frequency in the 0-D model ( $J_{\text{NO}_2}$ ) was calculated using the Tropospheric Ultraviolet & Visible (TUV) Radiation Model (Madronich and Flocke, 1998) for clear sky conditions with 300 DU ozone, and the model input was scaled relative to observed radiation. The photolysis frequencies for all the other species were scaled relative to  $J_{\text{NO}_2}$  at zero-degree solar zenith angle.

Because the 0-D model does not take into account the changes in IN concentration as IN was transported to and out of the measurement site both vertically and horizontally, the ratio of total IN concentration to the sum of methyl vinyl ketone (MVK) and

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observed after sunrise. On average, the concentration rose to peak around 70 ppt at 10:00 a.m. (Fig. 5) and then decreased to a minimum around 10 ppt by 6:00 a.m. the next day, as a result of vertical mixing, boundary layer expansion, dry deposition and further oxidation. IN concentrations were significantly lower from 04 to 08 July, due to wet deposition and less photochemical reactivity caused by continuous rain events.

In contrast to the IN average diurnal profile (Fig. 5), the diurnal profiles for isoprene, OH, and NO<sub>x</sub> and MVK + MACR, each peaked at different times of the day (Fig. 6). The decrease in IN, and continued increase of MVK and MACR around 10:00 a.m. can be attributed to the competition among the four RO<sub>2</sub> loss channels (Reactions R2–R5).



The fraction of RO<sub>2</sub> loss to NO reaction is defined as  $\gamma$ , which is calculated with the following equation.

$$\gamma = \frac{k_{\text{RO}_2+\text{NO}}[\text{NO}]}{k_{\text{RO}_2+\text{NO}}[\text{NO}] + k_{\text{RO}_2+\text{HO}_2}[\text{HO}_2] + k_{\text{RO}_2+\text{RO}_2}[\text{RO}_2] + k_{\text{isomerize}}} \quad (1)$$

Isoprene RO<sub>2</sub> loss to permutation reactions (R4) was calculated assuming [RO<sub>2</sub>] = [HO<sub>2</sub>], and the rate constant  $1.6 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  was used (Jenkin et al., 1997). Isoprene RO<sub>2</sub> loss rates for reaction with NO and HO<sub>2</sub> (Reactions R2 and R3) were calculated based on observed NO and HO<sub>2</sub> concentrations, using rate constants  $k_{\text{RO}_2+\text{NO}} = 9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and  $k_{\text{RO}_2+\text{HO}_2} = 1.61 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Saunders et al., 2003; Stevens et al., 1999). The sum of the first-order RO<sub>2</sub> loss rate for reaction with NO, HO<sub>2</sub> and RO<sub>2</sub> was 0.01–0.07 s<sup>-1</sup> (Fig. 7a). Therefore, contribution from 1,5-H shift for  $\beta$ -RO<sub>2</sub> was negligible, due to the small isomerization rate constant (Peeters et al., 2014). However, for isoprene *cis*- $\delta$ -RO<sub>2</sub>, the 1,6-H shift rate constant is on the order of 0.1–1 s<sup>-1</sup> (Peeters et al., 2009,

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2014; Crounse et al., 2011). This fast isomerization depletes *cis*- $\delta$ -RO<sub>2</sub> radicals rapidly to form closed-shell products, e.g. hydroperoxy aldehyde (HPALD), and makes the relative abundance of *cis*- $\delta$ -RO<sub>2</sub> radicals very small ( $\sim 1\%$ , Supplement Sect. 4). For this reason,  $k_{\text{isomerize}}$  was omitted from the calculation of  $\gamma$ , but the yield of total RO<sub>2</sub> was incorporated when estimating the production rate of total IN, to account for rapid loss of *cis*- $\delta$ -RO<sub>2</sub> to 1,6-H shift.

The calculated diurnal average of the  $\gamma$  value is shown in Fig. 7b. For RO<sub>2</sub> radicals that were lost to reaction with NO or HO<sub>2</sub>, the RO<sub>2</sub> + NO reaction was the sole contributor in the early morning, but it was surpassed by RO<sub>2</sub> + HO<sub>2</sub> reaction before noon, as the NO concentration decreased steadily throughout the day. The IN production rate was calculated with the following equation.

$$P_{\text{IN}} = k_{\text{ISOP}+\text{OH}}[\text{OH}][\text{ISOP}] \cdot \Phi \cdot \gamma \cdot \alpha \quad (2)$$

$\Phi$  is the yield of total RO<sub>2</sub> from OH addition to isoprene that are available to react with NO, HO<sub>2</sub> and RO<sub>2</sub>, with an RO<sub>2</sub> lifetime in the range of 10–20 s. The calculated  $\Phi$  is 0.83 (Supplement Sect. 4), with contribution from  $\beta$ -RO<sub>2</sub> being 0.81, *cis*- $\delta$ -RO<sub>2</sub> being 0.01 and *trans*- $\delta$ -RO<sub>2</sub> being 0.02, and the remaining 17% products from isoprene OH oxidation are closed-shell species such as HPALD. The IN production rate decreased with the declining  $\gamma$  value (Fig. 7b), even though the concentrations of OH and isoprene each peaked at  $\sim 1:00$  p.m. This could lead to IN loss from OH oxidation to exceed IN production, making IN peak around the time when HO<sub>2</sub> reaction became the major RO<sub>2</sub> loss channel ( $\gamma < 0.5$ ). In this relatively clean environment, MVK and MACR production continued through isoprene ozonolysis (Grosjean et al., 1993) and OH oxidation in the low NO regime (Liu et al., 2013). The MVK + MACR production rate was calculated using the following equation.

$$P_{\text{MVK}+\text{MACR}} = k_{\text{ISOP}+\text{OH}}[\text{OH}][\text{ISOP}] \cdot \Phi_{\beta} \cdot \gamma \cdot (1 - \alpha) + k_{\text{ISOP}+\text{OH}}[\text{OH}][\text{ISOP}] \cdot \Phi \cdot (1 - \gamma) \cdot 0.06 + k_{\text{ISOP}+\text{O}_3}[\text{O}_3][\text{ISOP}] \cdot 0.61 \quad (3)$$

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$\Phi_{\beta}$  denotes the yield of isoprene  $\beta$ -RO<sub>2</sub>, the precursors for MVK + MACR, and the calculated  $\Phi_{\beta}$  was 0.81 (Supplement Sect. 4). The term  $k_{\text{ISOP}+\text{OH}}[\text{OH}][\text{ISOP}] \cdot \Phi_{\beta} \cdot \gamma \cdot (1 - \alpha)$  is the production rate of MVK + MACR with the isoprene  $\beta$ -RO<sub>2</sub> undergoing the RO<sub>2</sub> + NO reaction pathway. The term  $k_{\text{ISOP}+\text{OH}}[\text{OH}][\text{ISOP}] \cdot \Phi \cdot (1 - \gamma) \cdot 0.06$  is the production rate of MVK + MACR when the isoprene RO<sub>2</sub> proceeds via HO<sub>2</sub> reaction pathways to form MVK + MACR with an overall yield of 6 % (Liu et al., 2013). The term  $k_{\text{ISOP}+\text{O}_3}[\text{O}_3][\text{ISOP}] \cdot 0.61$  is the production rate of MVK + MACR from isoprene ozonolysis, with a total yield of 61 % (Grosjean et al., 1993).

As shown in Fig. 7b, the production rates of IN and MVK + MACR both plateaued around 10:00 a.m. For MVK + MACR, the decrease was later compensated with production from the HO<sub>2</sub> and O<sub>3</sub> pathway, and the production rate peaked around 2:00 p.m. when radiation was strong. For IN, however, its production rate did not increase with radiation due the limited availability of NO (small  $\gamma$  value). Therefore, the change in the relative importance of the two RO<sub>2</sub> sinks, RO<sub>2</sub> + NO and RO<sub>2</sub> + HO<sub>2</sub>, is likely one of the reasons that IN concentration peaked earlier than MVK + MACR concentration during SOAS.

The early morning increase in IN concentration could imply significant contribution from downward mixing of accumulated IN in the residual layer (RL), as the inversion is broken up after dawn (Hastie et al., 1993). When the earth surface cools in the evening, the remnants of the upper daytime boundary layer are isolated from the lower region near the ground, and the RL forms. The RL contains the same amount of isoprene, IN, and NO<sub>x</sub> as is found near the ground around sunset, thus serving as an IN reservoir at night (Neu et al., 1994). While IN in the nighttime boundary layer (NBL) is slowly lost to dry deposition, IN in the RL, which is isolated from the ground, is better preserved. In addition, IN production from reaction of isoprene with NO<sub>3</sub> may also contribute to RL IN, but this process is not as important in the NBL, because NO<sub>3</sub> is likely to be titrated by reaction with NO near ground (Stutz, 2004). As a result, the IN concentration in the RL is expected to be higher than that in the NBL before dawn. During sunrise, IN in the RL can mix downward, which in combination with photochemical IN production leads

to an increase in IN near the ground. The relative importance of these two processes will be assessed with our 0-D model in the following section.

### 3.3 0-D model for IN photochemistry during SOAS

Due to limited availability of overlapping data for model input from multiple instruments, ambient data for the following 12 days were used: 14 June, 16 June, 22 June, 23 June, 25 June–01 July and 03 July. For each day, only the daytime chemistry (5:00 a.m.–7:00 p.m.) was simulated, when photochemical reactivity was high. The observed IN and MVK + MACR concentrations at 5:00 a.m. were used as the initial concentrations for modeling. For isoprene,  $\alpha$ -pinene,  $\beta$ -pinene, limonene, NO, NO<sub>2</sub>, OH, HO<sub>2</sub>, and O<sub>3</sub>, the model concentrations were constrained to observations for the entire modeling period. The branching ratio for IN formation resulting from the isoprene RO<sub>2</sub> with NO reaction was set to 0.09 for all isomers, which is based on our measured 9% yield from the chamber experiments. As mentioned above, to avoid the complication in the simulation of absolute concentrations caused by transport and changing boundary layer height, we compared the simulated and observed  $[IN]/([MVK]+[MACR])$  ratio to evaluate the model.

Figure 8a shows the temporal profiles of the modeled and observed  $[IN]/([MVK]+[MACR])$  ratio for the selected 12 days. To gain a statistical overview of the model and observation comparison, the 12 day average was calculated (Fig. 8b). The 0-D model generally agrees with the observed ratio, lending support to the IN branching ratio determined in the chamber experiments. However, the morning increase was underestimated by the model on certain days (14, 16, 29 June, 01 and 03 July), while on other days (23 and 25–27 June), the decrease rate for the  $[IN]/([MVK]+[MACR])$  ratio was underestimated in the afternoon. Since the IN yield applied in the 0-D model has 36% uncertainty, a sensitivity test on the yield was performed. As shown in Fig. 8c, the simulated  $[IN]/([MVK]+[MACR])$  ratio is highly sensitive to the yield used in the model as expected. The 6% yield significantly underestimated the ratio in the morning, and the 12% yield significantly overestimated the ratio in the afternoon.

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## 4 Discussion

### 4.1 Model-observation comparison for SOAS data

As shown in Fig. 8c, the modeled results deviated from observations from 10:00 a.m. to 12:00 p.m. for the three yields applied, as the simulated  $[IN]/([MVK]+[MACR])$  ratio decreased slowly while the observed ratio dropped rapidly. The fast decrease in the  $[IN]/([MVK]+[MACR])$  ratio implies either fast production of MVK + MACR, or fast consumption of IN. In terms of fast production of MVK + MACR, the formation of MVK + MACR from OH and O<sub>3</sub> have been characterized in the model, and the model was capable of simulating MVK + MACR concentration to within measurement uncertainty for the chamber experiments (Supplement Sect. 3.1). Therefore, the discrepancy between model and observation is more likely associated with underestimated loss rate of IN. The model results with the 6% yield were lower than observations, despite potential underestimated IN loss rate, so a higher yield (9–12%) may be more accurate to describe the branching ratio for isoprene RO<sub>2</sub> + NO reaction.

The model overestimation in the afternoon can be caused collectively by measurement uncertainties for model input, uncertainties in the IN loss rates for OH oxidation and deposition, uncertainties in ambient IN and MVK + MACR measurement, and other missing IN loss processes. A recent study found that isoprene hydroperoxide (ISOPOOH) could interfere with MVK and MACR measurement when standard PTR-MS and GC methods are used (Rivera-Rios et al., 2014). We found that the model appeared to agree better with observations in the afternoon, if the ISOPOOH + IEPOX concentration was subtracted from MVK + MACR measurement data (Fig. 8d). However, the exact influence of ISOPOOH + IEPOX on the observations of MVK + MACR is unclear, as the ISOPOOH conversion efficiency is highly dependent on instrumental sampling configuration, and the interference of IEPOX has not been characterized.

We also considered that an underestimated IN photolysis rate could be one of the reasons for the model-observation discrepancy. The photolysis rate for IN was set to be identical as the photolysis rate for alkyl nitrates in MCMv3.2, but IN isomers have

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breakup. By combining the observations of IN and MVK + MACR during SOAS and the results from the 0-D model, we can calculate the growth rate of ambient IN concentration caused solely by isoprene photochemistry in the daytime (Supplement Sect. 7). This photochemical IN growth rate was compared with the observed IN growth rate, and we estimate that downward mixing can contribute to 27(±16) % of the fast IN increase in the morning, where the large uncertainty originates from the 30 % uncertainty in the IN yield.

The residual layer IN concentration before mixing (6:00 a.m.) was estimated with the 0-D model, using the same initial input as the ground-level observation on the previous day at 8:00 p.m. The chemical processes involved are IN production from isoprene oxidation by NO<sub>3</sub> (Reactions R5 and R6b) and IN consumption by OH, O<sub>3</sub> and NO<sub>3</sub>. Based on our model calculation, the steady-state NO<sub>3</sub> concentration at night was on the order of 1 × 10<sup>6</sup> molecules cm<sup>-3</sup>. Nighttime OH was generated through BVOC ozonolysis, and the simulated concentration was on the order of 5 × 10<sup>4</sup> molecules cm<sup>-3</sup>. Even though the OH concentration was very low at night, it was still the dominant IN loss pathway, as a result of the fast IN + OH reaction rate constants. It is worth noting that RO<sub>2</sub> produced from isoprene + NO<sub>3</sub> (Reaction R6) also has competing loss channels for reaction with RO<sub>2</sub> (Reaction R7) and with HO<sub>2</sub> (Reaction R8). Therefore, only a fraction of the isoprene nitrooxy peroxy radicals (ONO<sub>2</sub>RO<sub>2</sub>) can react with other peroxy radicals to produce IN through Reaction (R7b).

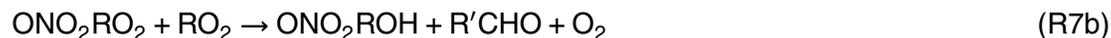
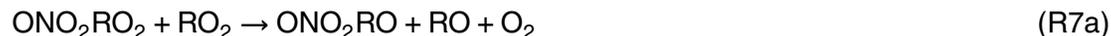


Figure 9 shows the simulated IN concentration in the RL and IN observed near ground before dawn, assuming the RL was completely stable at night with no depositional loss for IN from the RL. The simulated IN concentration in the RL before dawn was greater



a small  $\gamma$  value ( $\sim 0.3$ , Fig. 7b), significant amount of IN would be oxidized following the  $\text{HO}_2$  pathway. A possible reaction scheme is illustrated in Fig. 11 with 1,2-IN as an example.

Experimental studies by Jacobs et al. (2014) suggest that OH addition to IN can invoke IEPOX formation with a yield of 13% at atmospheric pressure, which simultaneously releases  $\text{NO}_2$ . For  $\text{RO}_2$  radicals produced from OH addition to IN, 30% will react with NO and 70% will react with  $\text{HO}_2$  for a  $\gamma$  value of 0.3 at 1:00 p.m.

For the  $\text{RO}_2 + \text{NO}$  reaction, L. Lee et al. (2014) observed the formation of dinitrate for  $\delta$  isomers of IN and estimated a branching ratio of less than 18% for  $\beta$ -4,3-IN based on missing carbon in the gas phase. The RO radicals from the  $\text{RO}_2 + \text{NO}$  reaction will dissociate to make either MACR nitrate or lose  $\text{NO}_2$  to form hydroxyacetone and glycoaldehyde. Both Jacobs et al. (2014) and L. Lee et al. (2014) reported MACR nitrate being the dominant product with an overall yield of 70%, thus making the corresponding branching ratio for the RO radical to be around 80%.

The  $\text{RO}_2 + \text{HO}_2$  products from IN oxidation are less understood. Alkyl peroxy radical reaction with  $\text{HO}_2$  can undergo two reaction channels to afford either hydroperoxide or RO radical and OH. The branching ratio is highly structure dependent. Simple alkyl peroxy radicals, such as  $\text{CH}_3\text{CH}_2\text{O}_2$ , can form hydroperoxide with almost unity yield (Hasson et al., 2004). However, for peroxy radicals with  $\beta$  carbonyl groups, such as  $\text{RC}(\text{O})\text{CH}_2\text{O}_2$ , the branching ratio for the OH formation pathway is more than 60% (Hasson et al., 2004, 2012). The  $\beta$  carbonyl oxygen can stabilize the reaction intermediate through internal hydrogen bonding, thus making the reaction favor the formation of OH and RO (Hasson et al., 2005). The  $\text{RO}_2$  from IN oxidation has a  $\beta$ -OH group and a  $\beta$ - $\text{NO}_3$  group, both capable of forming internal hydrogen bonding with the hydrogen of  $\text{HO}_2$ . Therefore, formation of OH and RO radicals may be a significant reaction channel when the  $\text{RO}_2$  radicals derived from IN react with  $\text{HO}_2$ . The closed-shell product from the  $\text{RO}_2 + \text{HO}_2$  reaction is dihydroxy hydroperoxy nitrate (DHHPN). This compound has not been identified in any laboratory studies. However, Lee et al. (2015) found a significant amount of compounds with the corresponding molecular formula of  $\text{C}_5\text{H}_{11}\text{O}_7\text{N}$

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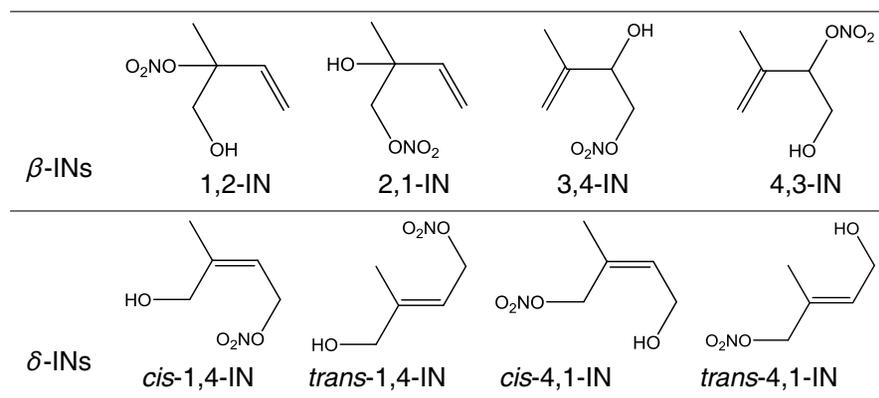
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**Table 1.** Hydroxynitrates from OH-initiated isoprene oxidation (high  $\text{NO}_x$ ).



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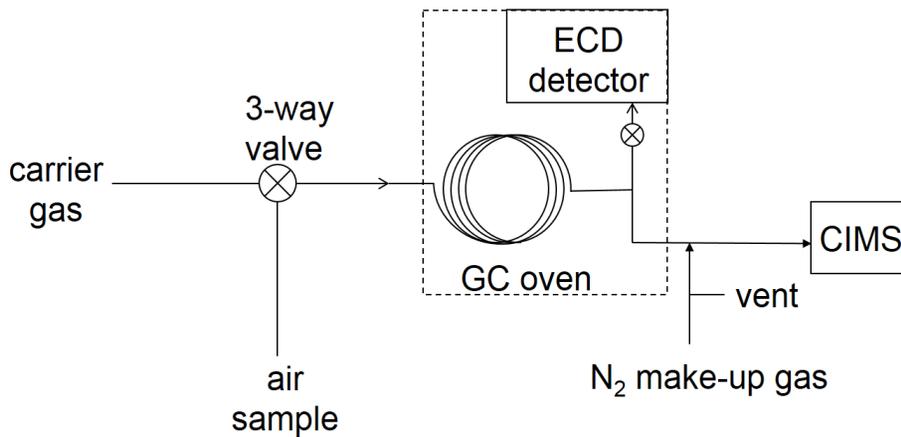
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**Table 2.** Initial conditions for IN yield experiments.

Expt. number	Isoprene (ppb)	Isopropyl nitrite (ppb)	NO (ppb)	Expt. duration (min)
1	140	180	160	16
2	80	180	130	15
3	70	180	130	12
4	120	180	125	14
5	90	180	220	14
6	75	180	210	12
7	85	180	2400	54



**Figure 1.** GC-ECD/CIMS setup for the CIMS sensitivity of 1,2-IN relative to 4,3-IN.

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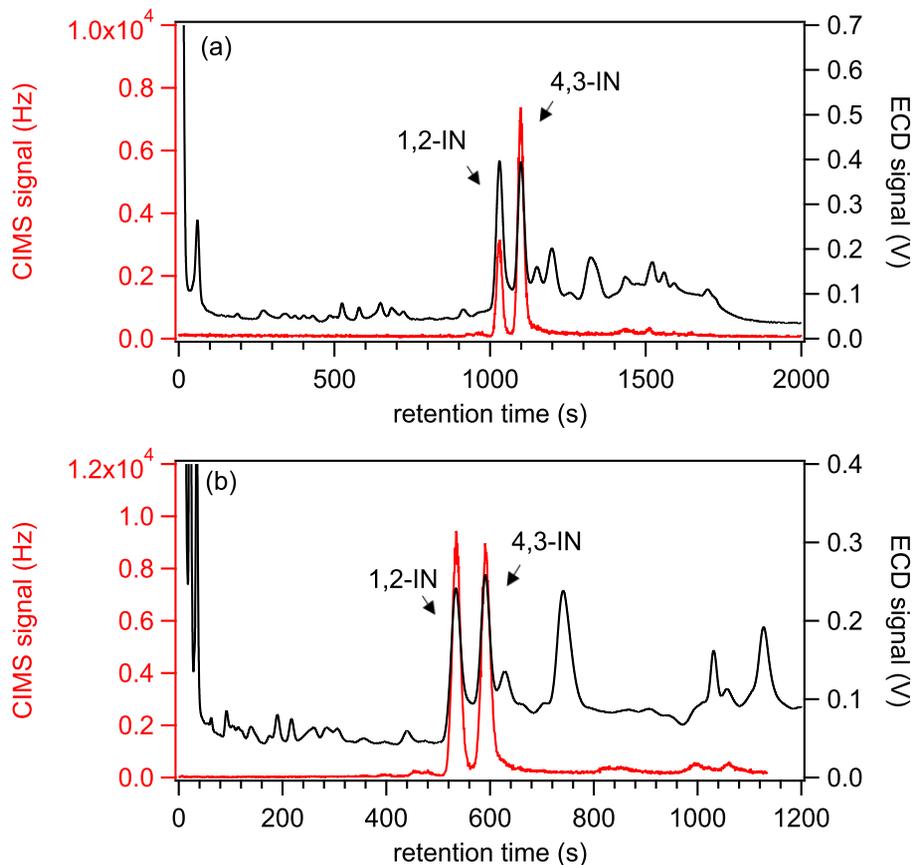
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**Figure 2.** GC-ECD/CIMS chromatogram with water (a) and without water (b) added to the CIMS. The ECD signal is in black and the CIMS signal is in red.

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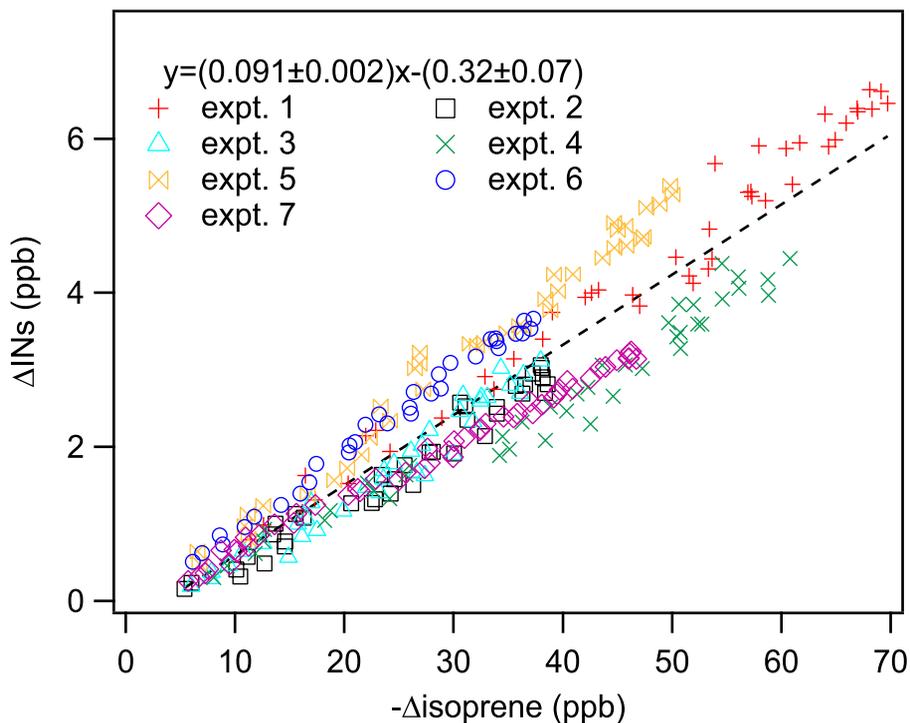
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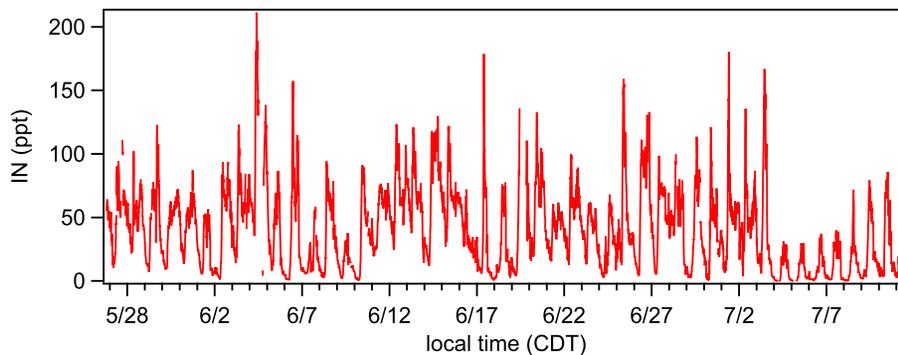
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**Figure 3.** IN and isoprene data for chamber experiments. An average yield of 9% was obtained from data of the seven experiments.

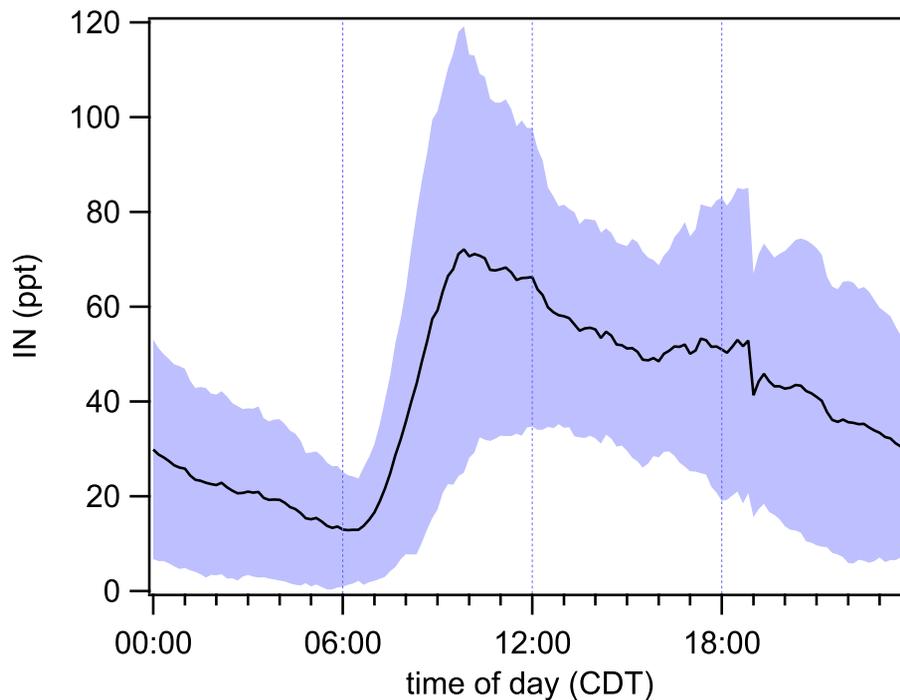
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**Figure 4.** IN observed during SOAS.[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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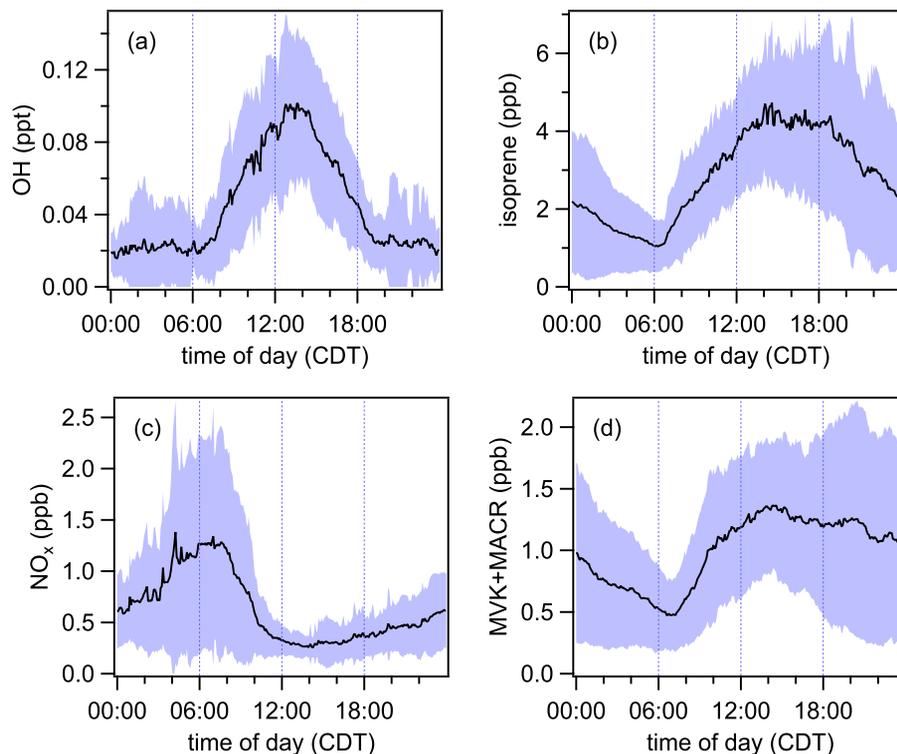


**Figure 5.** IN diurnal average from 28 May to 11 July. The blue shade indicates day-to-day variation ( $1\sigma$ ). The abrupt drop of concentration at 7:00 p.m. is caused by instrument fluctuation during its daily maintenance.

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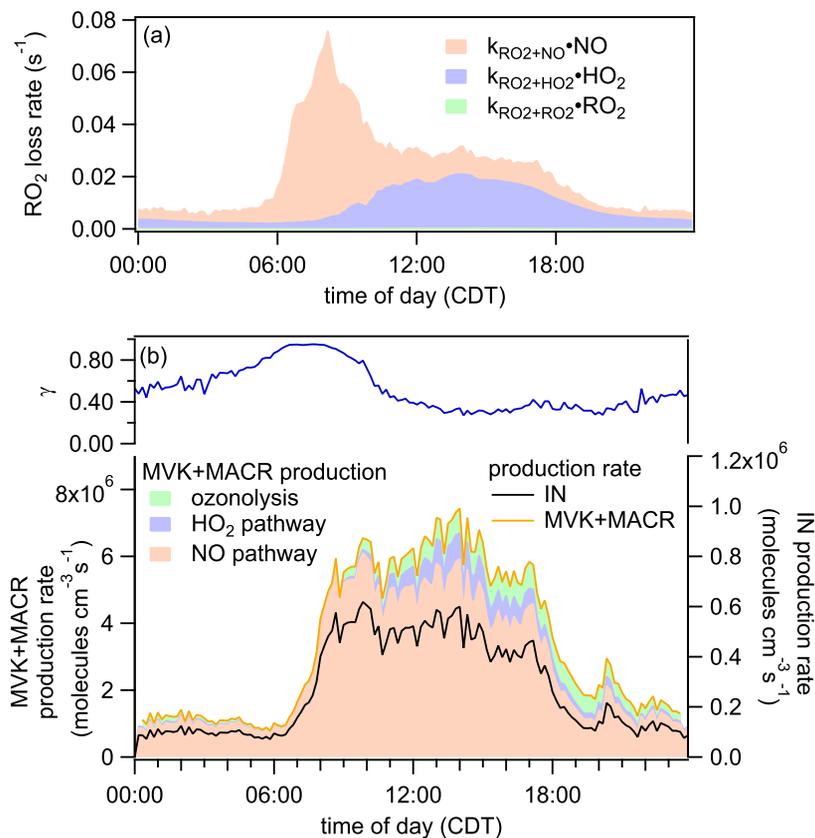


**Figure 6.** Diurnal average of OH (a, 13 June–03 July), isoprene (b, 16 June–11 July), NO<sub>x</sub> (c, 01 June–15 July) and sum of MVK and MACR (d, 16 June–11 July).

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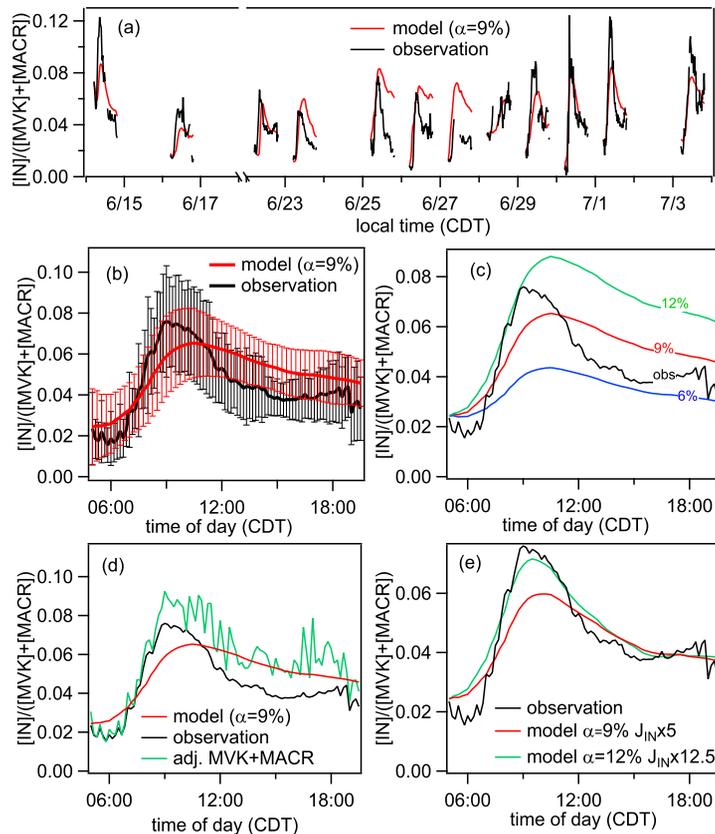
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**Figure 7.** (a) Diurnal average of  $\text{RO}_2$  loss rates for reaction with  $\text{NO}$ ,  $\text{HO}_2$  and  $\text{RO}_2$  from 22 June to 07 July. (b) Diurnal average of  $\gamma$  value and production rates of IN and MVK + MACR from 22 June to 07 July. For MVK + MACR, production from the three reaction channels are shown in different colors.

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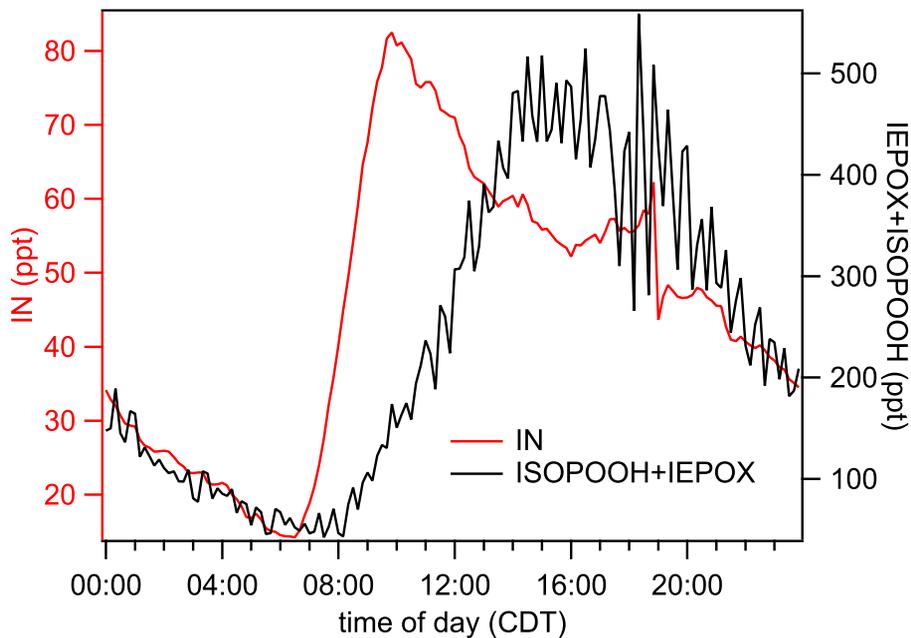


**Figure 8.** Simulated and observed  $[IN]/([MVK]+[MACR])$  ratio. **(a)** Results for each selected days. **(b)** Averaged results over the 12 days. The error bars represent day-to-day variation. **(c)** Sensitivity test with IN yield set as 6, 9 and 12% in the model. **(d)** MVK + MACR data was adjusted by subtracting observed IEPOX+ISOPOOH concentration from observed MVK + MACR concentration. **(e)** Results with enhanced IN photolysis rate.



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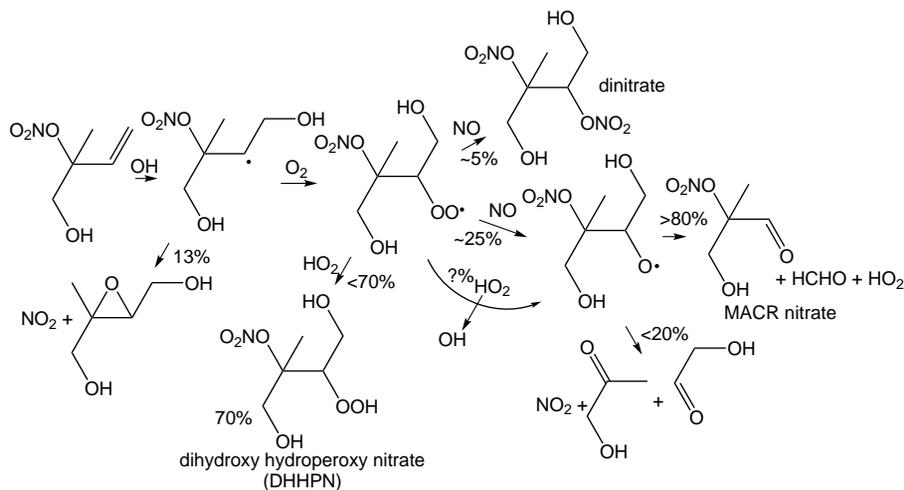


**Figure 10.** Diurnal averages of IN and ISOPOOH+IEPOX from 30 May to 04 July.

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**Figure 11.** Possible oxidation mechanism for 1,2-IN with  $\gamma = 0.3$ .