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Supplement of

Observation of isoprene hydroxynitrates in the southeastern United States and implications for the fate of NO_x

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1 CIMS calibration results for 4,3-IN

Multiple CIMS calibrations for 4,3-IN have been conducted overtime, and the results were stable (Figure S1).

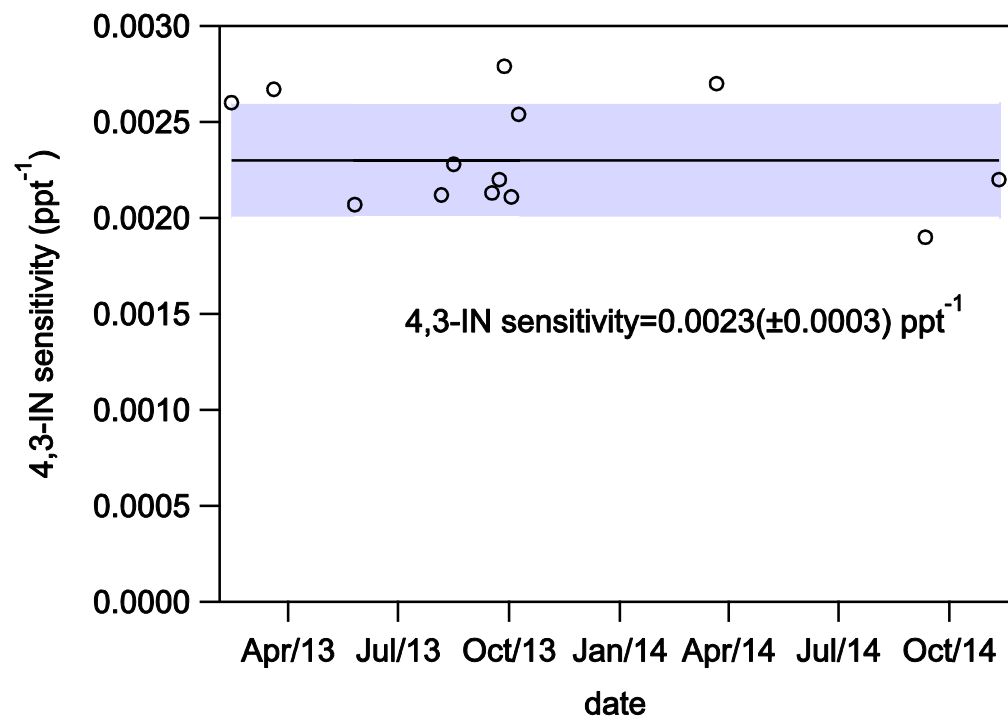


Figure S1. Calibration results for 4,3-IN. Each data point represents one calibration curve. The blue shade shows 1 σ standard deviation of the measured sensitivity.

2 CIMS sensitivities for *cis*- and *trans*-1,4-IN

Three CIMS calibrations were conducted using standard solutions that contained a mixture of *cis*- and *trans*-1,4-IN. The relative abundance of the *cis* and *trans* isomers was determined from NMR spectra. The overall sensitivity and relative isomer abundance are listed in Table S1.

Table S1. Overall sensitivity and isomer composition for *cis*- and *trans*-1,4-IN calibration.

Calibration	Sensitivity (ppt ⁻¹)	Isomer composition (<i>trans</i> relative to <i>cis</i>)
1	5.0(±0.5)×10 ⁻⁴	3.4±0.2
2	5.0(±0.8)×10 ⁻⁴	4.1±0.3
3	5.6(±0.8)×10 ⁻⁴	3.4±0.2

If we assume x is the sensitivity for *trans*-1,4-IN and y is the sensitivity for *cis*-1,4-IN, the isomer-weighted sensitivity measured by CIMS can be written as following. The coefficients on the left side of the equations are calculated from the relative isomer composition list in Table S1.

$$0.77x+0.23y=5.0\times 10^{-4} \quad (1)$$

$$0.80x+0.20y=5.0\times 10^{-4} \quad (2)$$

$$0.77x+0.23y=5.6\times 10^{-4} \quad (3)$$

Due to the uncertainties in the coefficients in equation (1) to (3), x and y in the above equation system cannot be solved. Therefore, we define function z through the following expression.

$$z=[5.0\times 10^{-4}-(0.77x+0.23y)]^2+[5.0\times 10^{-4}-(0.80x+0.20y)]^2+[5.6\times 10^{-4}-(0.77x+0.23y)]^2 \quad (4)$$

The true values of x and y can be approximated by finding the minimum of z . Using this method, we calculate the sensitivity for *trans*-1,4-IN to be 3(±2)×10⁻⁴ppt⁻¹ and the sensitivity for *cis*-1,4-IN to be 1.3(±0.3)×10⁻³ppt⁻¹.

3 IN isomer distribution in chamber and field studies

3.1 Model simulation for chamber studies

The relative yields of IN isomers depend on the relative yields of their corresponding precursor RO₂ radicals. However, the IN isomeric distribution can deviate from the RO₂ isomeric distribution, because the IN isomers have different loss rates, due to their different reactivities toward OH and O₃. To account for the influence of IN oxidation loss during the chamber studies, an iterative method was used to determine the IN isomeric distribution. The iterative process is illustrated in Figure S2.

The relative yield of the eight isoprene RO₂ radicals was used as the initial guess. The RO₂ isomeric distribution was calculated with the Kintecus simulation software (website <http://www.kintecus.com/>), based on the RO₂ interconversion and H-shift reaction rate constants proposed in the LIM1 mechanism (Peeters et al., 2014). An isomer-weighted IN sensitivity was derived from the calculated RO₂ isomer distribution. This sensitivity was used to calculate the initial guess value for the total IN yield (Figure S2).

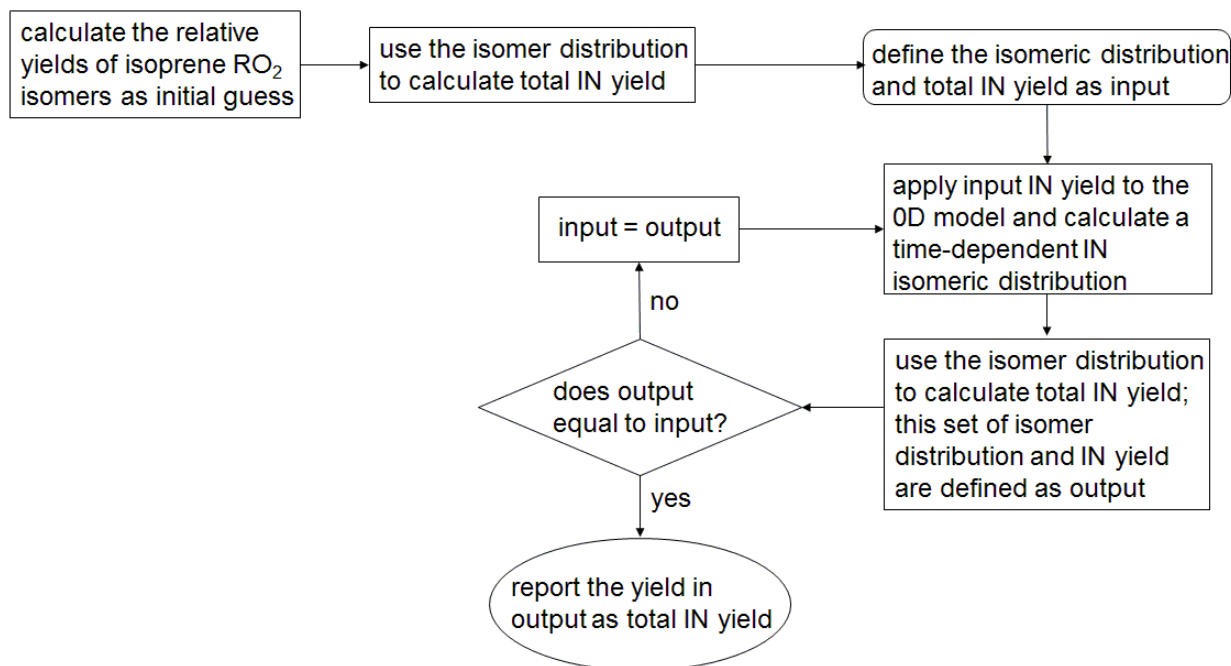


Figure S2. The iterative process to obtain a self-consistent set of IN yield and IN isomeric distribution data from the chamber experiments.

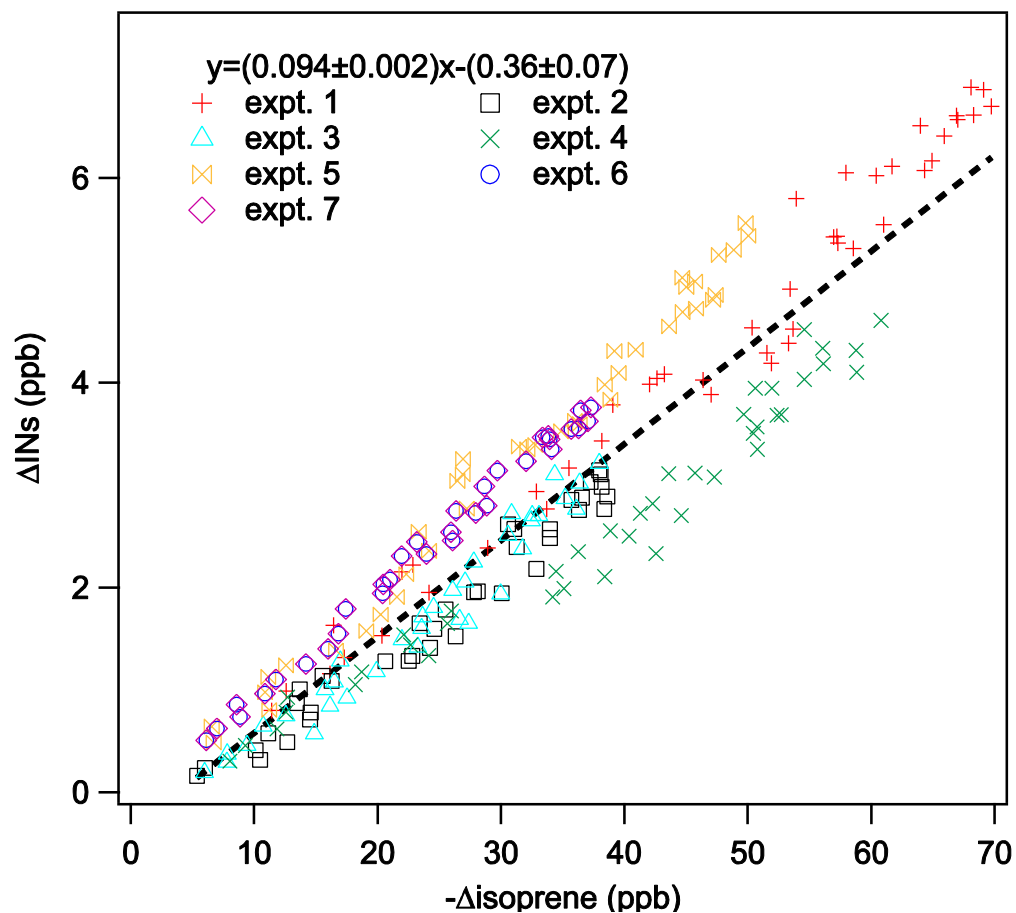


Figure S3. Initial guess value for IN yield, with IN sensitivity calculated based on RO₂ isomer distribution.

The iterative process was started by applying the guess value for the IN yield in the MCM-based 0D model and simulating the production and loss of IN isomers in the chamber. From the model a time-dependent IN isomer distribution was obtained, which was then used to calculate the new isomer-weighted IN sensitivity and IN yield. The new IN yield was applied in the 0D model again, which generated an IN isomer distribution identical to the IN isomer distribution from which this new input IN yield was derived. Figure S4 shows the changing IN sensitivity derived from the 0D model.

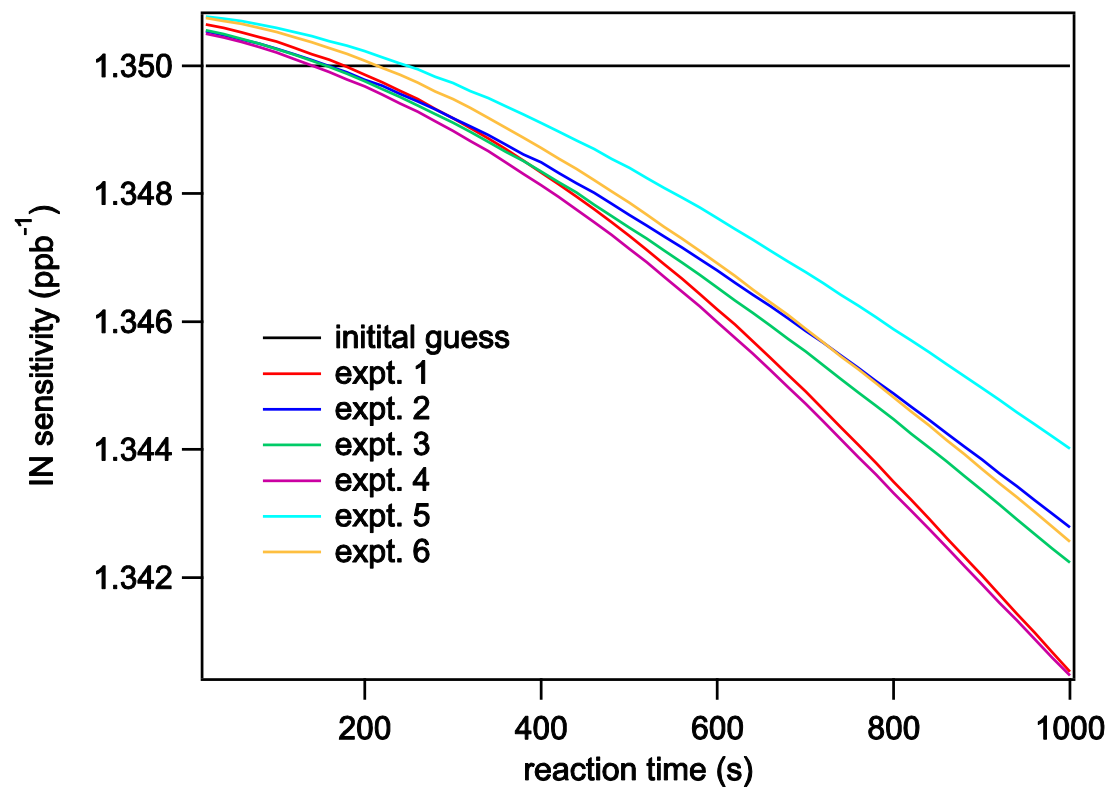


Figure S4. IN sensitivity with reaction time. The constant black line is the initial guess value derived from RO₂ isomer distribution. Only the first six experiments are shown, as the duration of the 7th experiment was 3600s and out of scale.

Figures S4~S7 show the model-observation comparison of isoprene, MVK+MACR, IN and NO for the chamber experiments. The red markers represent measurement data and the black markers represent model results. Each marker shape indicates one experiment.

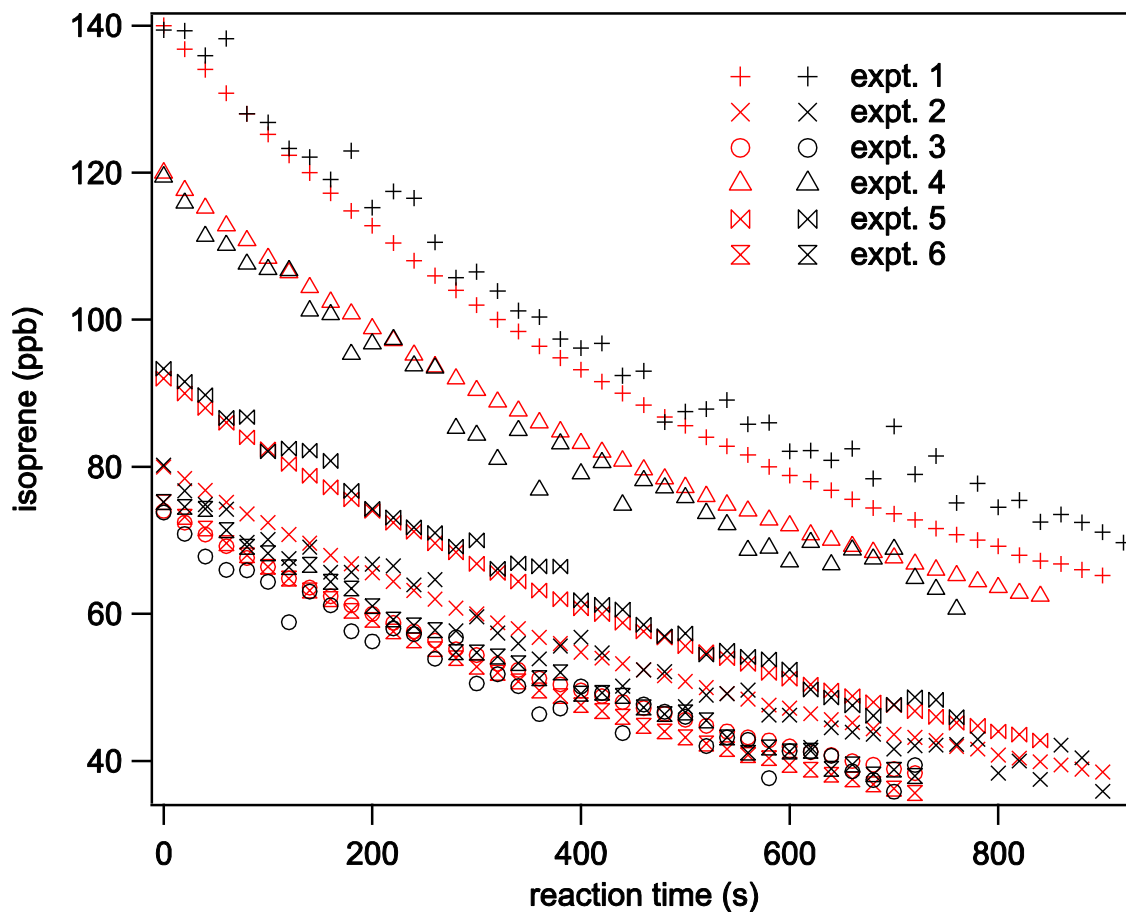


Figure S5. Model and measurement results of isoprene for chamber experiments. The red markers represent measurement data and the black markers represent model results.

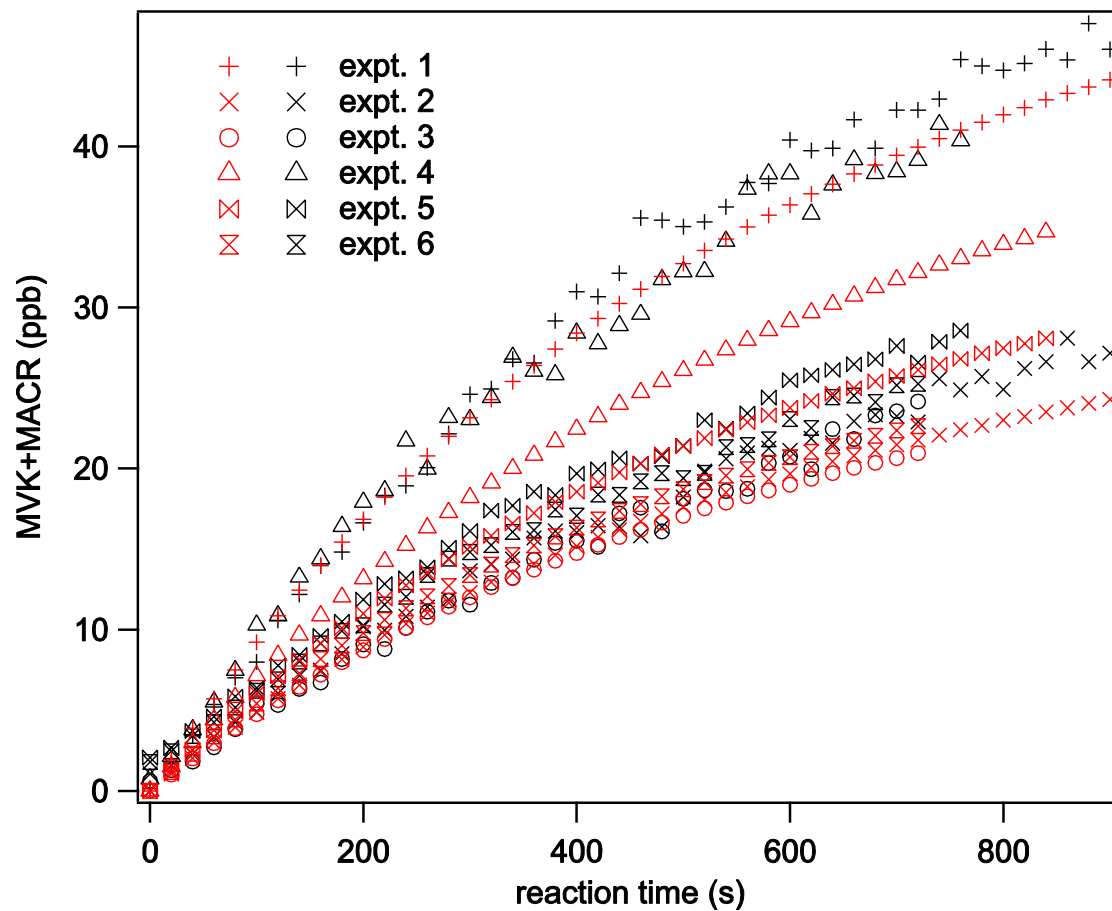


Figure S6. Model and measurement results of the sum of MVK and MACR for chamber experiments. The red markers represent measurement data and the black markers represent model results.

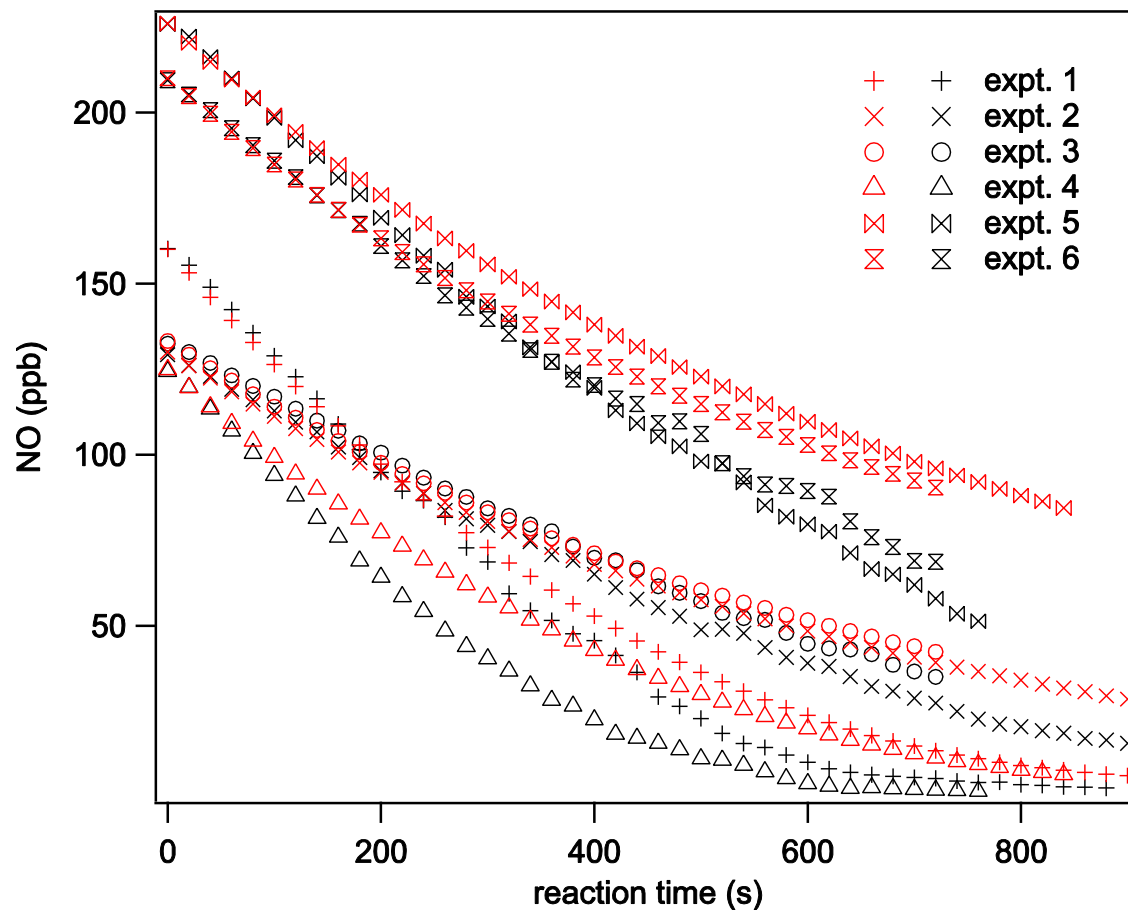


Figure S7. Model and measurement results of NO for chamber experiments. The red markers represent measurement data and the black markers represent model results. Each marker shape indicates one experiment.

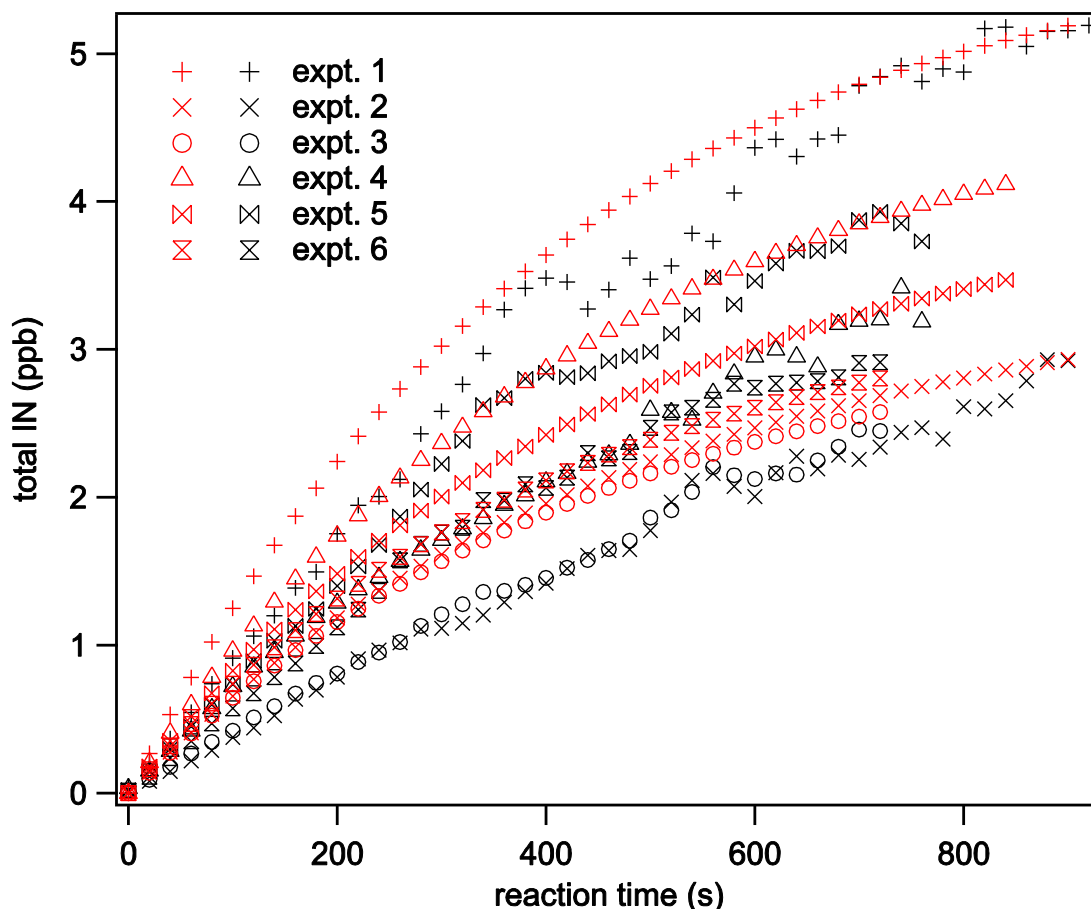


Figure S8. Model and measurement results of total IN for chamber experiments. The red markers represent measurement data and the black markers represent model results.

3.2 Isomer distribution for IN during SOAS

The 0D model was used to estimate the relative abundance of IN isomers during the SOAS study. The diurnal average of isoprene, OH, NO, NO₂, O₃ and HO₂ were calculated and the 0D model was used to simulate the relative concentrations of the IN isomers as they were produced from isoprene oxidation and lost to OH, O₃ and deposition throughout the day. The reaction was initiated at 6:00 AM (reaction time equals 0) and the duration was 24 hours. The simulated IN isomer composition is shown in Figure S9. A diurnal isomer-weighted IN sensitivity was calculated based on the simulated IN isomer distribution (Figure S10). The same diurnal calibration factors were applied to interpret IN raw data for each individual day.

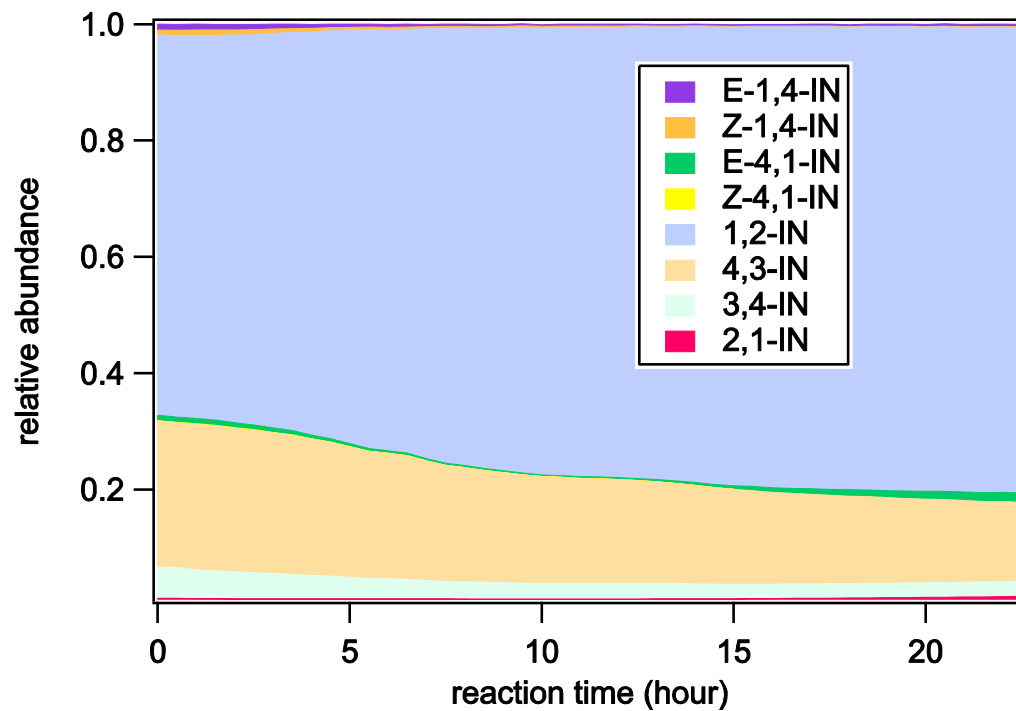


Figure S9. Simulated diurnal IN isomer distribution during SOAS.

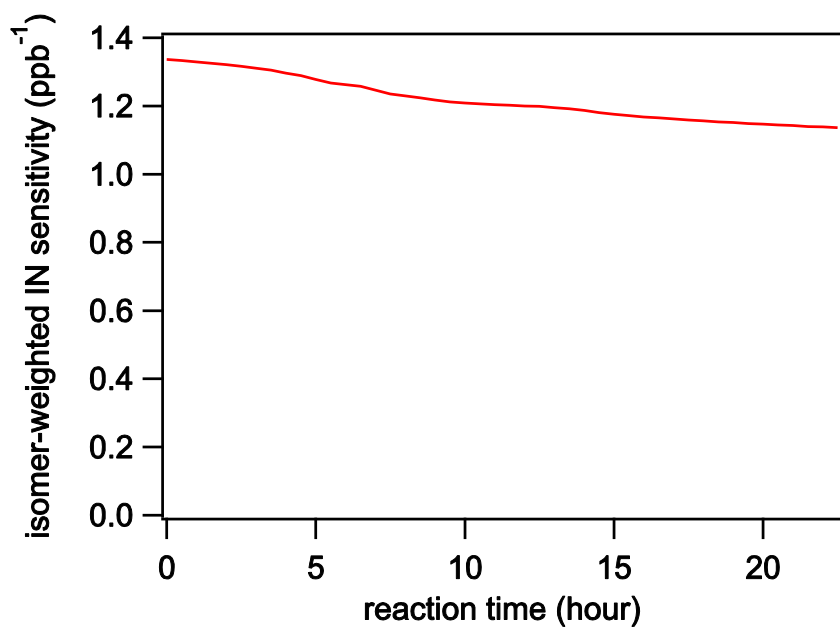


Figure S10. The diurnal isomer-weighted IN sensitivity during SOAS

4 Isoprene RO₂ distribution and RO₂ lifetime

During SOAS, the RO₂ loss rates to NO and HO₂ are slow, compared with 1,6-H shift rate constant for the *cis*- δ -RO₂. As a result, the yield of total RO₂ from OH addition to isoprene, defined as the amount of RO₂ produced relative to the amount of isoprene consumed, can decrease with RO₂ lifetime, as *cis*- δ -RO₂ radicals isomerize into hydroperoxy aldehyde (HPALD) and other RO₂ convert to *cis*- δ -RO₂ through O₂ loss and addition (Peeters et al., 2014). The yield of the products with respect to RO₂ lifetime was calculated with the Kintecus software, and the result is shown in Figure S11. The *cis*- δ -RO₂ radicals become less important with longer RO₂ lifetime. Besides RO₂ and HPALD, OH addition to isoprene also forms a stable carbonyl product, with a yield of 2% (Fan and Zhang, 2004; Peeters et al., 2014). The daytime total RO₂ loss rate to NO and HO₂ was on the order of 0.05 s⁻¹, so the RO₂ yield at 20 s was chosen to calculate the IN production rate during SOAS. With an RO₂ lifetime of 20 s, the isoprene oxidation products consist of 83% RO₂, 15% HPALD and 2% carbonyl product. The 83% RO₂ products include 1% *cis*- δ -RO₂, 2% *trans*- δ -RO₂ and 81% β -RO₂.

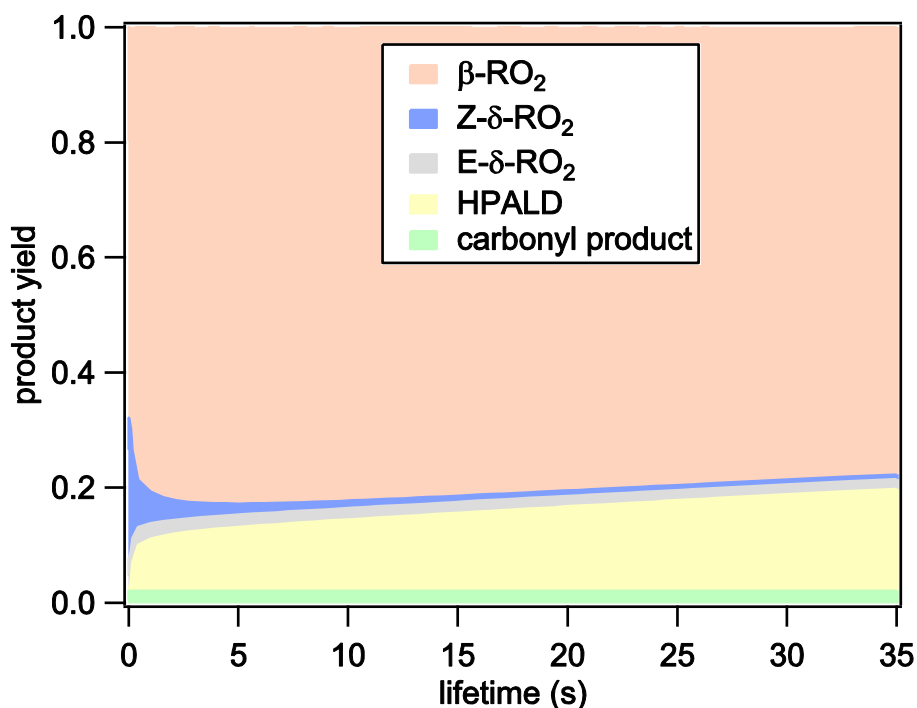


Figure S11. Product yield from OH addition to isoprene.

5 Sensitivity tests on LIM1 mechanism

The uncertainties in kinetics data for RO₂ interconversion and 1,6-H shift can cause error in the isoprene RO₂ and IN isomeric distribution. For the LIM1 mechanism, the uncertainties for the equilibrium constants $K_{eq}=k(+O_2)/k(-O_2)$ are a factor of 1.5, and the uncertainties for the 1,6-H shift rate constants $k_{1,6-H}$ are a factor of 2.4 (Peeters et al., 2014). Sensitivity tests were performed by varying the rate constants $k(+O_2)$ (or $k(-O_2)$) by 1.5 times and $k_{1,6-H}$ by 2.4 times, and calculating the relative abundance of the RO₂ isomers. We found changing $k_{1,6-H}$ had no influence on the relative abundance of RO₂ isomers, although it significantly influences the yield of HPALD. Changing $k(+O_2)$ or $k(-O_2)$ only affected the production rate of total RO₂, but had no influence on the relative abundance of RO₂ isomers. The isomeric distribution was affected most when $k(+O_2)$ or $k(-O_2)$ were varied differently for β -RO₂ and for δ -RO₂. When $k(+O_2)$ values for δ -RO₂ were increased by 1.5 times and $k(-O_2)$ values for β -RO₂ were decreased by 1.5 times, the product IN isomer distribution would favor formation of isomers with lower sensitivities. In this low sensitivity scenario, the MVK and MACR yields were 0.33 and 0.21, consistent with results from experimental studies (Jenkin et al., 1998; Zhao et al., 2004). When $k(+O_2)$ values for 1,2-RO₂ and cis-1,4-RO₂ were increased by 1.5 times and $k(-O_2)$ values the other RO₂ radicals were increased by 1.5 times, the product IN isomer distribution would favor formation of isomers with higher sensitivities. In this high sensitivity scenario, the MVK and MACR yields were 0.4 and 0.28, also consistent with experimental results (Liu et al., 2013). The high end of the isomer-weighted IN sensitivity is calculated with the isomer distribution obtained in the high sensitivity scenario and the high end of the sensitivities for the individual IN isomer, which deviates 20% from the sensitivity used for IN calibration. The low end of the isomer-weighted IN sensitivity is calculated with the isomer distribution obtained in the low sensitivity scenario and the low end of the sensitivities for the individual IN isomer, which deviates 23% from the sensitivity used for IN calibration. Therefore, the relative uncertainties for the IN measurements is +23%/-20%.

6 4,3-IN sensitivity and sample humidity

The stability of the CIMS signal for 4,3-IN under varying humidity was investigated with the setup in Figure S12a. A gas flow that contained constant 4,3-IN concentration and varying humidity was sampled by the CIMS. The constant 4,3-IN gas flow was generated by bubbling N_2 through a 4,3-IN solution kept at $0^\circ C$. The IN signal normalized to the signal of the reagent ion was stable with varying sample humidity (Figure S12b). The CIMS was configured with constant water vapor addition to the analyte compounds downstream the orifice.

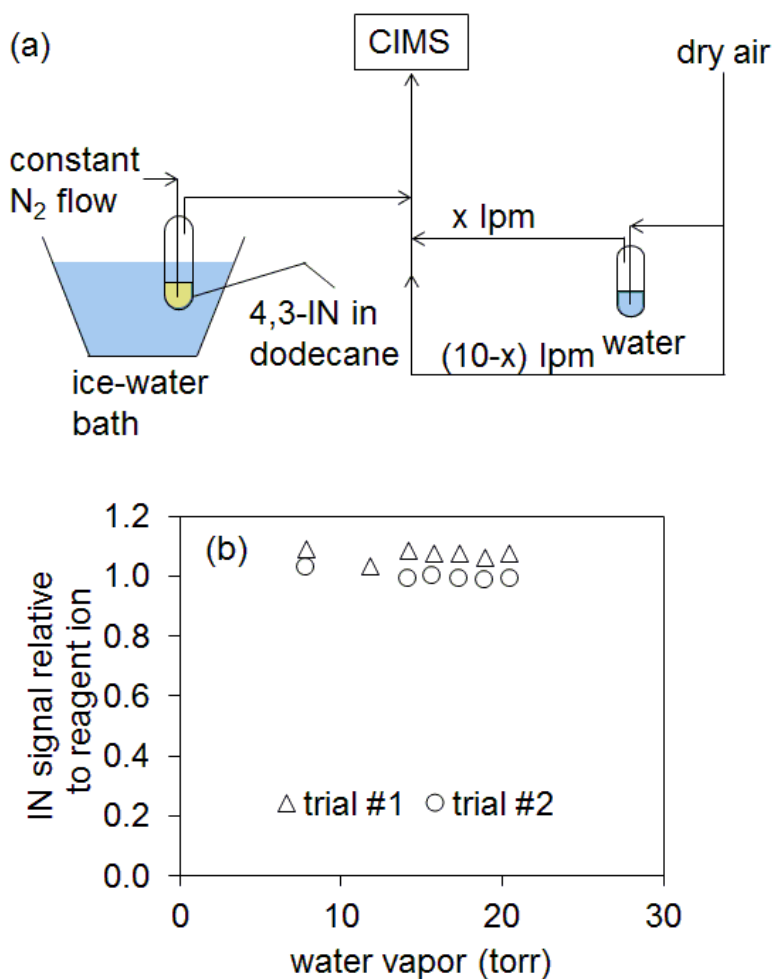


Figure S12. (a) Experimental setup for the CIMS humidity test. (b) Relative CIMS signal for 4,3-IN with varying sample humidity.

7 The influence of vertical mixing on morning [IN] increase

The rate at which $[IN]/([MVK]+[MACR])$ increased can be described using the following expression.

$$\text{rate} = \frac{d^{[IN]}/([MVK]+[MACR])}{dt} \quad (5)$$

If we define rate as variable r , the concentration of IN as x and the concentration of MVK+MACR as y , we will have the following expression.

$$r = \frac{dx/y}{dt} \quad (6)$$

Since the concentration of IN (x) and the concentration of MVK+MACR (y) both changed with time, Equation (6) can be written as the following.

$$r = -\frac{x}{y^2} \frac{dy}{dt} + \frac{1}{y} \frac{dx}{dt} \quad (7)$$

In Equation (7), dy/dt is the growth rate of MVK+MACR, and dx/dt is the growth rate of IN.

The 2-hour period from 7:00 AM to 9:00 AM for the 12-day average was chosen as the time window to estimate the contribution of downward mixing. To simplify the calculation, the average rate of change was used for IN and MVK+MACR, instead of the instantaneous rate. That modifies Equation (7) to the form of Equation (8) below.

$$r = -\frac{\bar{x}}{\bar{y}^2} \frac{\Delta y}{\Delta t} + \frac{1}{\bar{y}} \frac{\Delta x}{\Delta t} \quad (8)$$

\bar{x} and \bar{y} are the average concentrations of IN and MVK+MACR between 7:00 AM and 9:00 AM. $\Delta x/\Delta t$ and $\Delta y/\Delta t$ are the average growth rate for IN and for MVK+MACR with respect to time. The growth rate of the $[IN]/([MVK]+[MACR])$ ratio was controlled by the growth rate of MVK+MACR and the growth rate of IN. The growth rate of the $[IN]/([MVK]+[MACR])$ ratio for measurement data r_{obs} (Figure S13a) was higher than the growth rate of the $[IN]/([MVK]+[MACR])$ ratio for simulated results r_{mod} (Figure S13b). This is consistent with the hypothesis that the observed increase in the $[IN]/([MVK]+[MACR])$ ratio has contribution from downward mixing. The growth rate of $[MVK]+[MACR]$ was less likely to be affected by downward mixing, because MVK+MACR could be produced at night in both the NBL and the

residual layer through isoprene ozonolysis. Therefore, the difference between r_{obs} and r_{mod} was assumed to be caused only by the difference in $\Delta x/\Delta t$, the growth rate of [IN].

The growth rate of [IN] can be calculated from Equation (9). Using r_{mod} in Equation (9), the calculated [IN] growth rate is the result of isoprene photochemistry during the 7:00 AM to 9:00 AM period for the current day. Using r_{obs} in Equation (9), the calculated [IN] growth rate is the sum of isoprene photochemistry and IN downward mixing. It is worth mentioning that when r_{mod} is used in Equation 5.5, the \bar{x} , \bar{y} and $\Delta y/\Delta t$ values used should also be the modeling result. However, since the 0D model could not simulate the absolute concentrations of MVK, MACR and IN, the measurement results for \bar{x} , \bar{y} and $\Delta y/\Delta t$ values were used instead. The growth rate of MVK+MACR, $\Delta y/\Delta t$, was obtained from Figure S13c as the slope for the linear regression of [MVK]+[MACR] vs time.

$$\frac{\Delta x}{\Delta t} = \bar{y} \left(r + \frac{\bar{x}}{\bar{y}^2} \frac{\Delta y}{\Delta t} \right) \quad (9)$$

To evaluate the validity of Equation (9), the total [IN] growth rate was calculated by plugging r_{obs} into Equation (9). The result 9.93×10^{-3} ppt/s was consistent with the [IN] growth rate of 9.45×10^{-3} ppt/s derived directly from IN measurement (Figure S13d). Therefore, the mathematical representation of Equation (9) was able to properly describe the dynamics of the relative and absolute increases in the concentrations of IN and MVK+MACR. When r_{mod} was applied in Equation (9), we could calculate [IN] growth caused by isoprene chemistry to be 5.65×10^{-3} ppt/s, 7.28×10^{-3} ppt/s and 8.98×10^{-3} ppt/s, for IN yield of 6%, 9% and 12%. The difference between total [IN] growth rate and [IN] growth rate caused by photochemistry was attributed to downward mixing. On average, the influence of downward mixing was estimated to be $27(\pm 16)\%$.

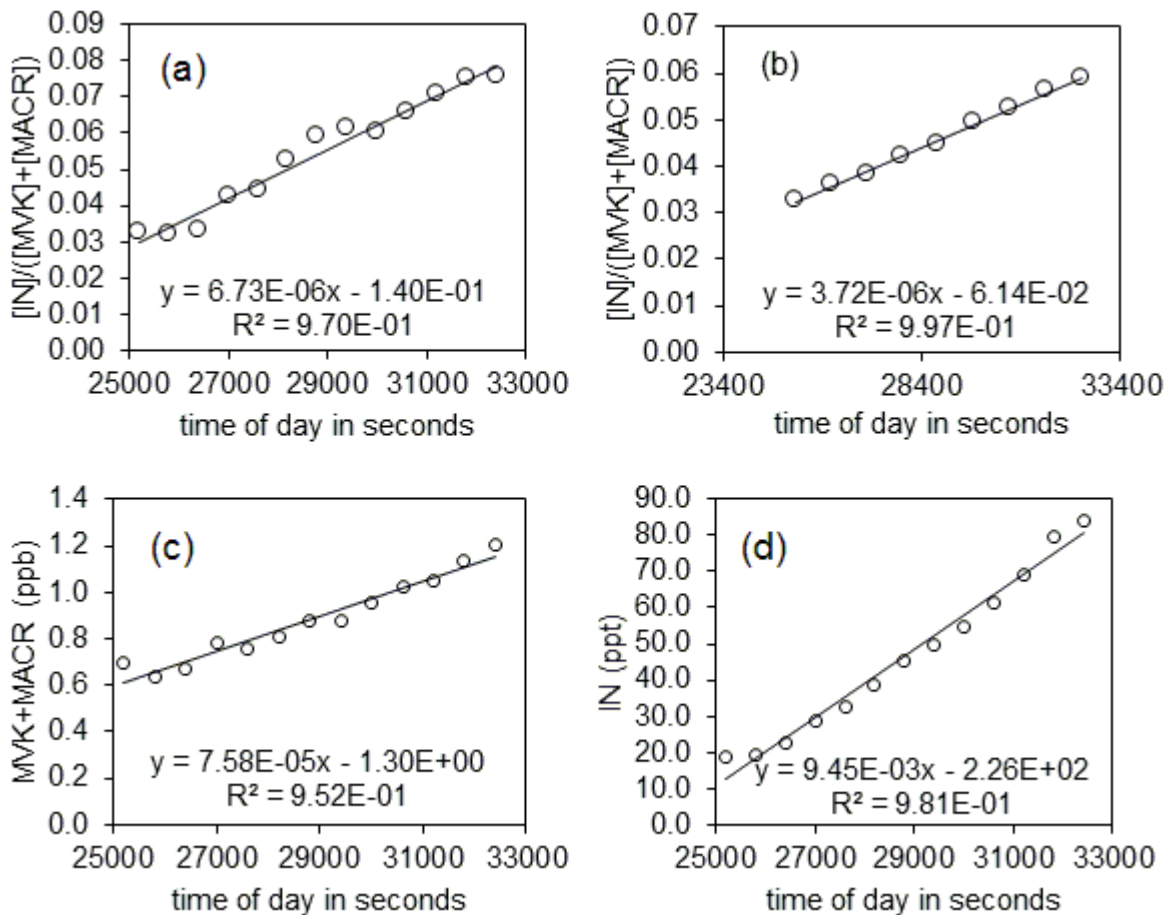


Figure S13. Growth rate of the (a) observed and (b) simulated $\frac{[IN]}{[MVK]+[MACR]}$ ratio. The simulated ratio is derived with a 9% IN yield in the model. (c) Growth rate of observed MVK+MACR concentration. (d) Growth rate of observed IN concentration.

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