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## 2 **Supplementary Information for**

### 3 **Rapid hydrolysis of tertiary isoprene nitrate efficiently removes NO<sub>x</sub> from the atmosphere**

4 **K. T. Vasquez, J. D. Crouse, B. C. Schulze, K. H. Bates, A. P. Teng, L. Xu, H. M. Allen and P. O. Wennberg**

5 **Correspondence to:**

6 **P. O. Wennberg ([wennberg@caltech.edu](mailto:wennberg@caltech.edu))**

#### 7 **This PDF file includes:**

8 Supplementary text

9 Figs. S1 to S10

10 Table S1

11 References for SI reference citations

## 12 Supporting Information Text

### 13 1. Caltech Field Study

14 Data was obtained between 01 August and 17 August 2017. During this time, the GC-CIMS instrument was located atop the  
15 central library on the Caltech campus in Pasadena, CA (44 m above ground level, 34.1368 °N, 118.126 °W). Pasadena is a  
16 part of the Los Angeles Metropolitan area and the South Coast Air Basin (SoCAB). As such, it is located near a multitude of  
17 mobile and industrial sources of anthropogenic pollution. However, the field site is also in close proximity to local vegetation  
18 which is made up of known isoprene emitters, such as oak and eucalyptus trees (1). Thus, biogenic emissions also influence the  
19 area (2, 3).

20 During the study, the field site experienced daytime (10:00 - 20:00 PDT) relative humidities between 42 - 64% and warm  
21 temperatures (a mean low of 20°C and a mean high of 31°C). The instrument was placed on the southwest corner of the roof  
22 of the library and inlet protruded from the south face of the building, sampling into the majority of the daytime winds. Back  
23 trajectories (Fig. S1) show that, on average, air masses passed through downtown Los Angeles approximately one hour before  
24 reaching the field site in the early afternoon.

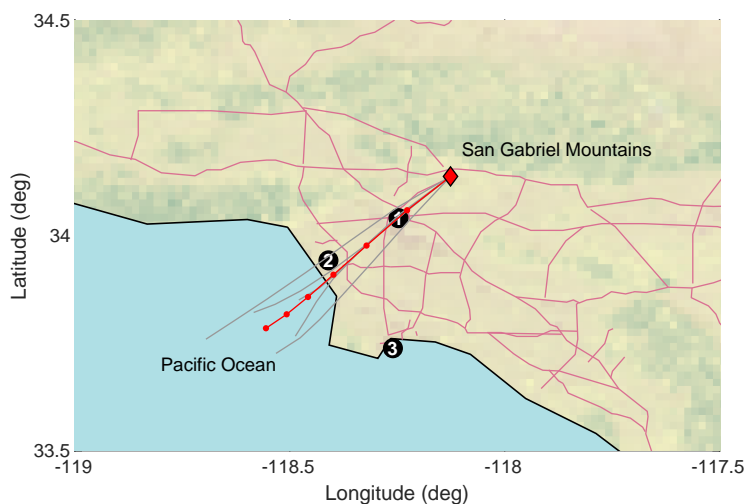


Fig. S1. Map of southern California indicating the location of the Caltech field site (red diamond), major highways (pink) and the following three locations: (1) downtown Los Angeles, (2) the Los Angeles International Airport and (3) the Port of Los Angeles. The average HYSPLIT back trajectory (4) for 15:00 PDT (red line) is shown for five randomly selected clear, sunny days during the study (gray lines). Each red circle on the average back trajectory represents 1 hour elapsed time.

### 25 2. Data Processing and Uncertainty

26 Data processing of the GC data presented in this work has been discussed by Vasquez et al. (5). As the 1,2-IHN and 4,3-IHN  
27 isomers are not completely separated with our GC configuration, we used a web-available MATLAB peakfit function (6) and  
28 modified it to support an exponentially modified gaussian peak shape, in which individual peaks had fixed widths and distinct  
29 tailing constants, to deconvolve the chromatogram. Peak parameters were chosen by minimizing the root mean square (rms)  
30 difference between the data and the peak fitting model. Sensitivity of the fitted peak area to the fitting parameters was  
31 estimated using a bootstrapping method (7). We varied both the chosen peak widths and tailing constants by  $\pm 40\%$  over  
32 1000 trials. Trials that degraded the fit beyond  $1\sigma$  of the rms error were disregarded. The calculated peak areas were then  
33 scaled by their relative CIMS sensitivities and GC transmission factors, before being normalized by the volume of air collected  
34 on the column in order to determine the corresponding ambient concentrations. The  $\text{CF}_3\text{O}^-$  CIMS sensitivities of 1,2-IHN  
35 and 4,3-IHN have previously been measured to be similar (8, 9). Both isomers have been shown to have GC transmission  
36 efficiencies near 100% provided water is not condensed during the trapping period (5, 8, 9).

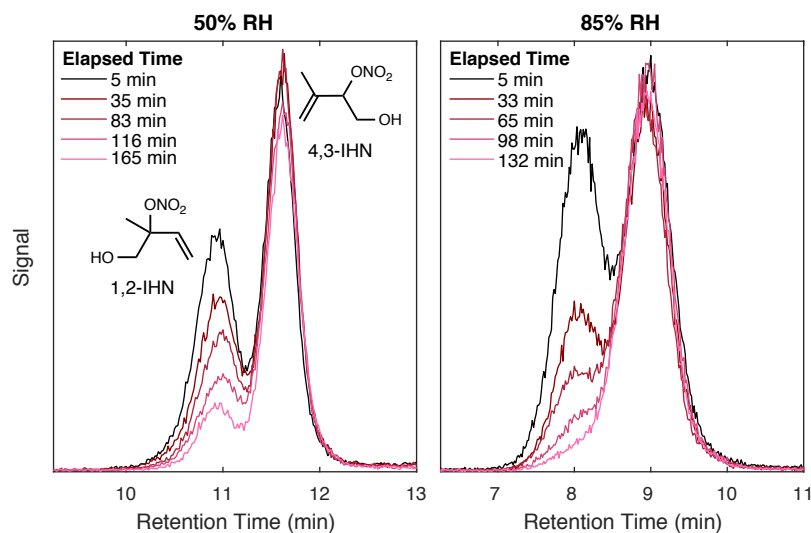
### 37 3. Hydrolysis Kinetics Experiments

38 **IHN Hydrolysis in a Humid Chamber.** Chamber experiments were conducted to probe the kinetics of condensed-phase hydrolysis  
39 of 1,2-IHN. For these experiments, isoprene, NO and methyl nitrite ( $\text{CH}_3\text{ONO}$ , OH source) were added to a 24  $\text{m}^3$  Teflon  
40 bag. UV lights were illuminated for a few minutes to oxidize approximately 10% of the isoprene in the chamber, limiting  
41 the production of second-generation products. Oxidation products were then observed in the dark using the GC-CIMS (see  
42 Materials and Methods in main text).

43 Experiments were performed at 50% and 85% relative humidity at 25°C (Fig. S2). During these experiments, a rapid decay  
44 of the 1,2-IHN isomer was observed and its lifetime was found to be strongly dependent on humidity levels, resulting in a

lifetime of 45 minutes at 50% RH and 15 minutes at 85% RH. In contrast, there was no observed decay of the 4,3-IHN isomer at either humidity during the course of the experiments, which is consistent with its longer lifetime against hydrolysis (10). Corresponding signal increases were observed at  $m/z$  187 ( $\text{CF}_3\text{O}^-$  cluster with neutral of mass of 102 amu), consistent with formation of isoprene diol, a product of IHN hydrolysis. In addition, we observed an initial small production of *E*-1,4-IHN isomer during the dark portion of the experiments, subsequently followed by first-order decay. We hypothesize this production arises from the condensed-phase isomerization of 1,2-IHN, similar to what has been previously observed during the GC-analysis of 1,2-IHN (8).

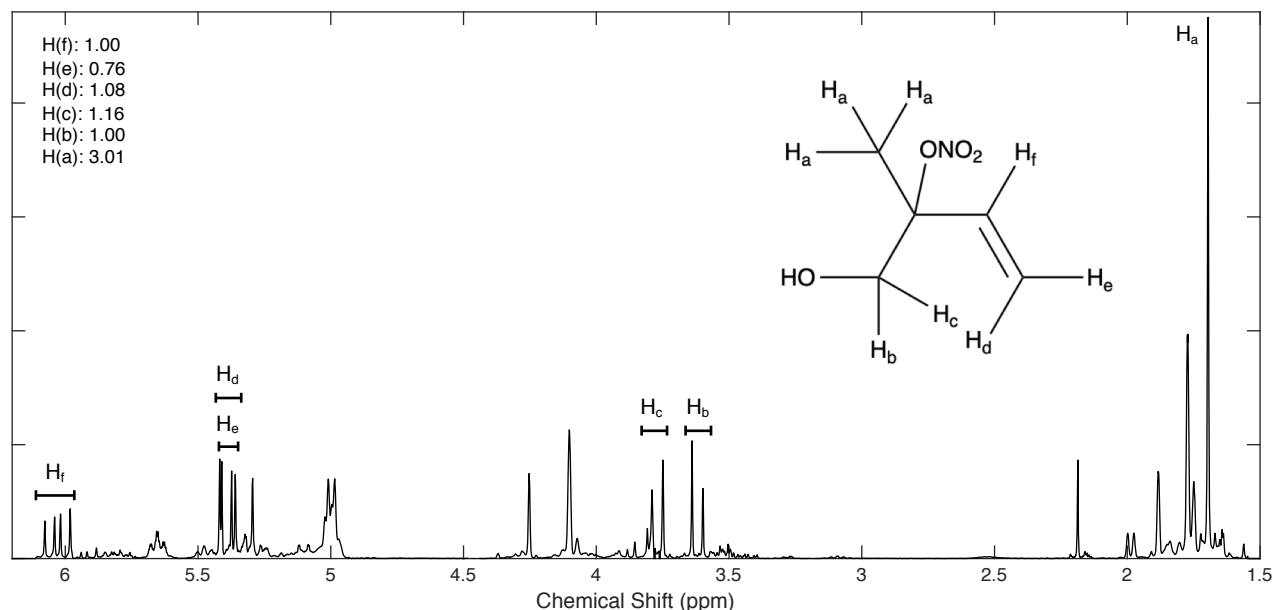
Hydrolysis was likely occurring on the chamber walls. Similar experiments with high levels (up to  $500 \mu\text{g m}^{-3}$ ) of ammonium sulfate particulate mass did not alter the decay rate in a measurable manner compared to experiments without seed. Experiments conducted under dry conditions (<5% RH) had significantly lower loss rates for 1,2-IHN. Experiments conducted in a smaller chamber ( $1 \text{ m}^3$ ) using a clean Teflon bag showed that the 1,2-IHN concentrations remained stable at elevated humidities (>80%) over a 12 hour period, despite a higher gas-wall interaction rate. We suggest that accumulation of deposited material on the walls of the large chamber (such as  $\text{H}_2\text{SO}_4$  and other salts derived from deposited seed particles, and possibly low-volatility organic material) can take up water under high humidity, creating a condensed-phase reservoir within which the hydrolysis can occur.



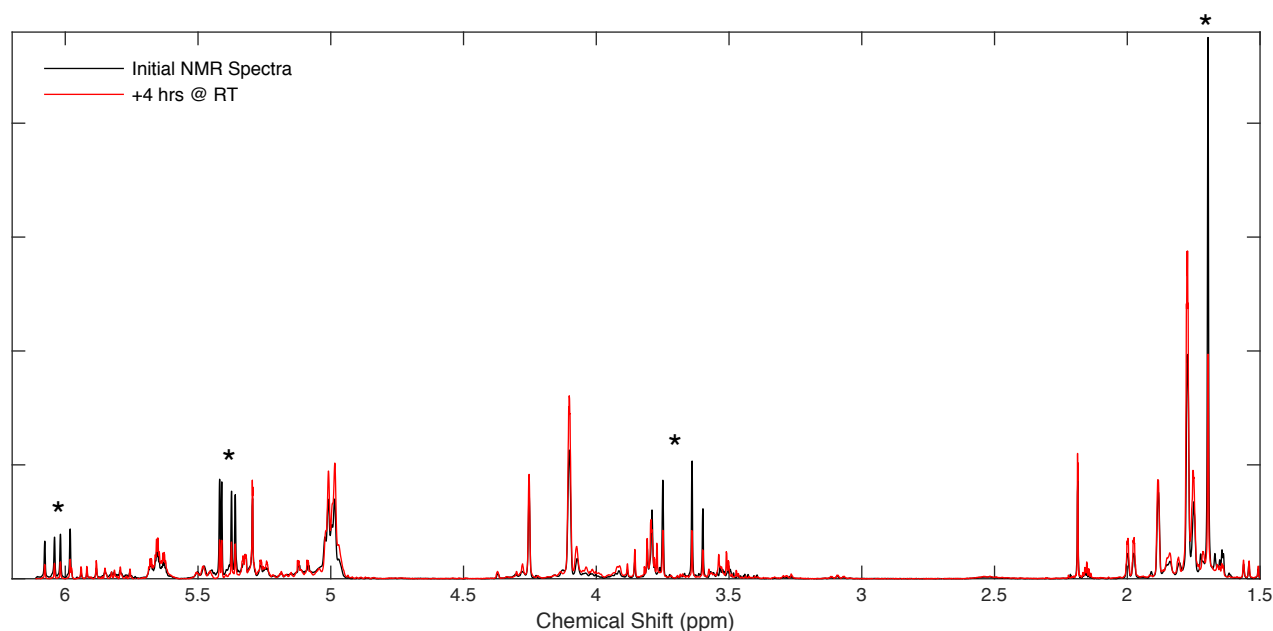
**Fig. S2.** High NOx isoprene oxidation experiments were performed at 50% (left) and 85% (right) RH. The lifetime of the 1,2-IHN isomers was found to be strongly dependent on humidity. Under completely dry conditions in a clean Teflon bag, the area of the 1,2-IHN isomer peak is 1.5 times that of 4,3-IHN with NO levels >500 ppbv, such that the  $\text{RO}_2$  distribution is near the kinetic limit. We note that different temperature programs were used for these two data sets. As a result, the resolution and retention time of these isomers are not identical.

**Synthesis of 1,2-IHN.** 1,2-IHN synthesis was performed by combining anhydrous nitric acid with 2-methyl-2-vinylloxirane (Sigma-Aldrich) in dry dichloromethane. Special care was taken to minimize the amount of  $\text{H}_2\text{O}$  present in the reaction mixture by purging the headspace of the reaction vessel with dry nitrogen. Typical synthesis: 330 mg (4.0 mmol) 2-methyl-2-vinylloxirane was dissolved 8 ml anhydrous methylene chloride (Sigma-Aldrich). This was placed in a 100 ml round bottom flask with a teflon-coated magnetic stir bar, briefly purged with dry  $\text{N}_2$ , and cooled to  $-10^\circ\text{C}$  using an isopropanol bath that was cooled with liquid nitrogen. With rapid stirring, a mixture of 250 mg (4.0 mmol) anhydrous  $\text{HNO}_3$  in 7 ml methylene chloride was slowly added (1-2 drops per second) with  $\text{N}_2$  purge. After  $\text{HNO}_3$  addition, the cold bath was removed, and the mixture was allowed to warm to room temperature with stirring. Anhydrous  $\text{HNO}_3$  was produced just before each synthesis using the reaction of  $\text{NaNO}_3$  with  $\text{H}_2\text{SO}_4$ , as described by McCabe, et al. (11). Products were analyzed by evaporating a small amount of the crude reaction mixture into a 100 L Teflon pillow bag and analyzing the gas composition with the GC-CIMS. Initially, 1,2-IHN was the most abundant IHN isomer (1,2-IHN >70% of total IHN). Using gas-phase quantification (GC-CIMS), total IHN yield was small (typically a few percent (mol/mol) of the starting epoxide). Separation of 1,2-IHN from other products in the reaction mixture was attempted using flash chromatography with silica gel, however, no 1,2-IHN was collected from the column. It is likely that residual  $\text{H}_2\text{O}$  or hydroxy groups attached directly to the silica gel is sufficient to hydrolyze the 1,2-IHN on the column.

$^1\text{H}$  NMR spectra of the crude reaction mixture (after removal of the methylene chloride by vacuum distillation at  $-15^\circ\text{C}$ ) is shown in Fig. S3. Signals arising from 1,2-IHN are identified by comparing the initial NMR spectra to one taken after leaving the reaction mixture at room temperature for 4 hours and observing which signals decayed (Fig. S4). 1,2-IHN is highly reactive. We observe that 1,2-IHN (crude reaction mixture) decays in dry methylene chloride at  $-15^\circ\text{C}$  with a lifetime of  $\sim 1$  day, likely through reactions with itself, or other species present in the reaction mixture.



**Fig. S3.**  $^1\text{H}$  NMR spectra (300 MHz) of 1,2-IHN in deuterated chloroform (Sigma Aldrich, 99.8% D).  $\delta$  6.03 (dd,  $J = 17.7, 11.0$  Hz, 1H- $\text{H}_f$ ), 5.394 (d,  $J = 11.0$ , Hz, 1H- $\text{H}_e$ ), 5.391 (d,  $J = 17.6$ , Hz, 1H- $\text{H}_d$ ), 3.77 (d,  $J = 12.2$ , Hz, 1H- $\text{H}_c$ ), 3.62 (d,  $J = 12.3$ , Hz, 1H- $\text{H}_b$ ), 1.70 (s, 3H- $\text{H}_a$ ). It appears that the geminal coupling between  $\text{H}_d$  and  $\text{H}_e$  is quite small and not resolved with this spectrometer.



**Fig. S4.**  $^1\text{H}$  NMR spectra of crude 1,2-IHN synthetic mixture taken 4 hours apart with sample resting at room temperature between analyses. Signals strongly decaying with time are believed to arise from 1,2-IHN hydrogens (\*).

80 **Synthesis of 4,3-IHN.** Synthesis of 4,3-IHN was conducted in a manner similar to the IHN synthesis described by Lee et al. (9)  
 81 In place of 2-methyl-2-vinyloxirane, (1-methylethenyl)oxirane was used. Because this epoxide is not commercially available it  
 82 was synthesized according to the method described by Harwood, et al.,(12) though scale was reduced by factor of 4. After  
 83 synthesis of the hydroxy nitrate, the crude reaction mixture was analyzed using GC-CIMS as described above for 1,2-IHN. The  
 84 distribution of the IHN isomers as analyzed in the gas-phase was: 89% 4,3-, 1% *Z*-4,1-, and 10% *E*-4,1-IHN. The overall IHN  
 85 molar yield was approximately 13% of the starting epoxide. After removal of methylene chloride at  $-15^\circ\text{C}$  using vacuum, the

86 crude mixture was purified using flash chromatography. A column composed of six inches of 400 mesh silica gel within a 2.54  
87 cm O.D. pyrex tube was prepared using a solvent mixture of 1:1 ethyl acetate:hexanes. After flowing about 1 column volume  
88 of solvent to condition the column, the concentrated crude reaction mixture was charged to the top of the column. The column  
89 was run under gravity for about 4 hours, collecting 5-15 ml aliquots, monitoring the output composition using TLC, and CIMS.  
90 A C<sub>5</sub>-diol was found to elute very rapidly (first 2-3 aliquots). The IHN isomers eluted much later, however, separation of the  
91 isomers was quite good when collecting 5 ml aliquots. Elution order was observed to be 4,3-, Z-4,1-, E-4,1-IHN, as verified by  
92 NMR and GC-CIMS. Aliquots containing the same isomers were combined, solvent was removed, and products were diluted  
93 with methylene chloride for storage.

94 **IHN Hydrolysis in D<sub>2</sub>O.** IHN hydrolysis kinetics in D<sub>2</sub>O were studied using <sup>1</sup>H NMR methods similar to experiments described  
95 by Eddingsaas et al. (13). NMR spectra were acquired using a Varian 600 MHz spectrometer with sample probe controlled to  
96 25° C. Additional reference spectra were collected in CDCl<sub>3</sub> using a Varian 300 MHz instrument. For the kinetics experiments,  
97 an NMR tube was charged with D<sub>2</sub>O and used to tune the spectrometer, collecting a single sample. The tube was then removed  
98 from the NMR and a small aliquot of the 1,2-IHN concentrated synthetic mixture was combined with the D<sub>2</sub>O in the NMR  
99 tube. The tube was inverted several times to promote mixing, and quickly reinserted into the NMR probe. Sequential spectra  
100 were collected over time with an acquisition period of 22.6 s. A period of approximately 45 s elapsed between addition of the  
101 synthetic mixture to the D<sub>2</sub>O and the end of acquisition for the first spectrum. While signals from 1,2-IHN, E and Z-1,4-IHN  
102 are readily apparent in reference spectra in CDCl<sub>3</sub>, no signals from 1,2-IHN are observed for spectra in D<sub>2</sub>O.

103 As no 1,2-IHN signals were observed in the NMR spectra of the D<sub>2</sub>O sample, we can only place lower limits on the hydrolysis  
104 rate of 1,2-IHN in D<sub>2</sub>O at 298 K. Using the signal to noise of the NMR spectra in D<sub>2</sub>O experiment, signals from the E and  
105 Z-1,4-IHN in the D<sub>2</sub>O experiment, the ratio of signals from 1,2-IHN to E- or Z-1,4-IHN, and assuming the initial distribution  
106 of isomers is the same between the reference and the D<sub>2</sub>O experiments, we constrain the hydrolysis lifetime of 1,2-IHN in D<sub>2</sub>O  
107 to be less than 10 s.

108 The hydrolysis rate coefficients of E and Z-1,4-IHN in D<sub>2</sub>O at 298 K were measured to be  $(10.1 \pm 0.4) \times 10^{-3} \text{ s}^{-1}$  and  
109  $(5.3 \pm 0.2) \times 10^{-3} \text{ s}^{-1}$ , respectively (Fig. S5). The bulk hydrolysis rate of E and Z-1,4-IHN has been previously reported by  
110 Jacobs et al. (10) as  $(6.76 \pm 0.09) \times 10^{-3} \text{ s}^{-1}$ . At the time, Jacobs et al. (10) could not resolve these two isomers. Subsequently,  
111 in CDCl<sub>3</sub> they determined that the mixture had a ratio of 2.6:1 (14). Using this initial ratio and the isomer specific rate  
112 constants to calculate the total 1,4-IHN amount over the time scale of the Jacob et al. (10) experiments, these two studies are  
113 in broad agreement.

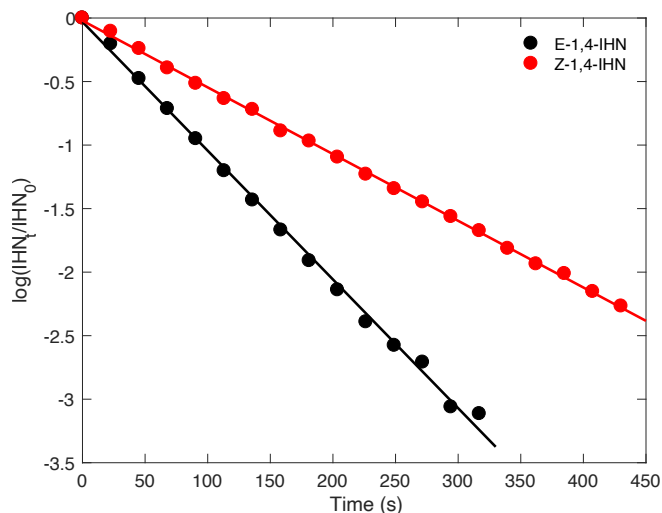


Fig. S5. First-order decay of NMR signal for E-1,4-IHN (black) and Z-1,4-IHN (red) in D<sub>2</sub>O at 298 K.

114 **4,3-IHN Henry's Law Constants.** A known volume of the 4,3-IHN solution was combined with 6 mL H<sub>2</sub>O in a multi-neck round  
115 bottom flask (RBF). The flask was cooled to 0°C in an ice bath with stir bars in both the RBF and the ice bath, slowly stirring.  
116 A small flow of N<sub>2</sub> was passed through the headspace of the RBF using a flow controller. After the RBF, a large flow of N<sub>2</sub>  
117 diluted the effluent from the RBF and carried the analytes to the CIMS where the 4,3-IHN was quantified. Using the ratio of  
118 the gas flows, the concentration above the solution was calculated. This, along with the assumption of headspace saturation  
119 (which was checked by reducing the flow through the RBF by a factor of 2), allowed for calculation of the Henry's Law constant.  
120 Similar methods were used to quantify the Henry's law constant of 4,3-IHN in octanol. The results from these experiments are  
121 listed in Table S1. It was not possible to determine the Henry's law constant for 1,2-IHN in water or octanol using this method.

**Table S1. Experimentally determined Henry's law constants ( $K_H$ ) for 4,3-IHN in water and octanol at 0°C**

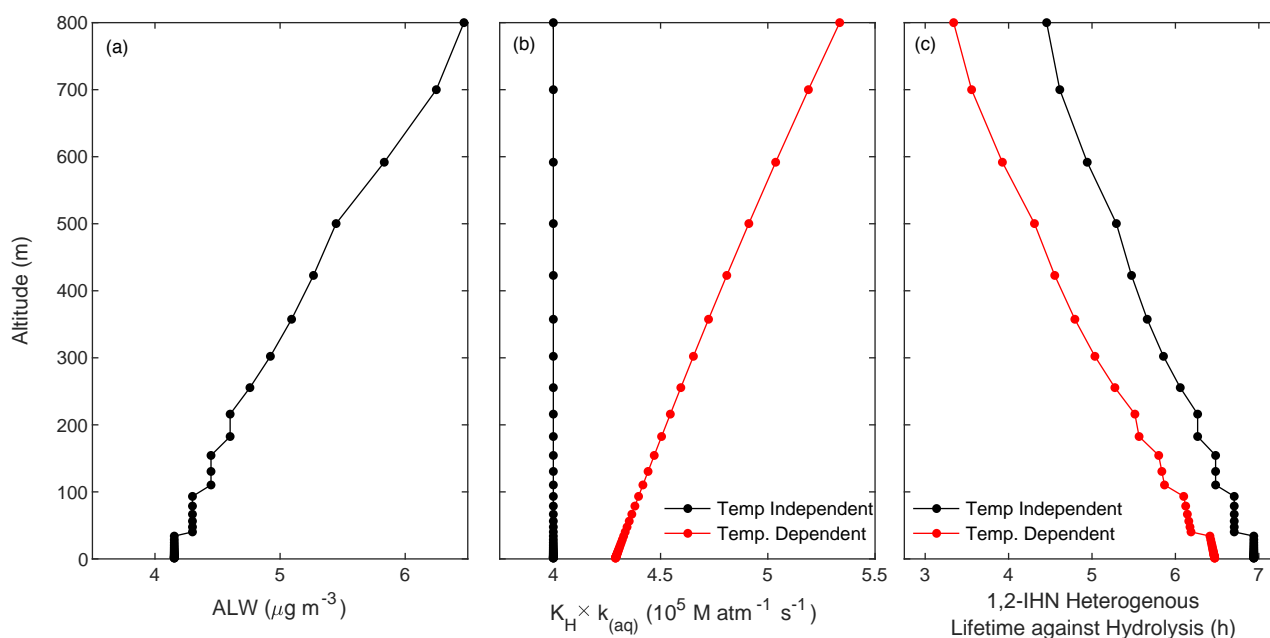
Isomer	$K_H$ ( $10^4$ M atm $^{-1}$ )	
	Water	Octanol
4,3-IHN	$3.1 \pm 0.8$	$0.9 \pm 0.3$

#### 122 4. IHN Photolysis

123 To estimate the photolysis rate, a 1 m<sup>3</sup> Teflon bag containing synthesized 1,2-IHN was placed in direct sunlight for five hours  
124 in Pasadena, CA on March 26, 2015 between 10:00 –15:00 local time. 50  $\mu$ L of the 1,2-IHN reaction mixture was combined  
125 with 650  $\mu$ L acetone and a droplet of this solution was placed in a three-way vial. Dry air was then blown over this droplet,  
126 and the evaporated reaction mixture was collected in a FEP Teflon pillow bag. Contents of the bag were measured with the  
127 GC-CIMS both before and after exposure to sunlight. Chromatograms show that 1,2-IHN, and *E* and *Z*-1,4-IHN were present  
128 in significant quantities and 4,3-IHN was present in trace amounts. 1,2-butanediol was added to the bag to estimate OH  
129 oxidation during the experiment. It is assumed that 1,2-butanediol did not photolyze significantly over the time scale of this  
130 experiment.

131 Over the course of five hours of exposure to sunlight, after correcting for OH oxidation (using butanediol signal), 1,2-IHN  
132 decreased by about 10%. This places an upper limit to the photolysis rate of  $(1.0 \pm 1.0) \times 10^{-5}$  s $^{-1}$  for this experiment.  
133 Adjusting this number for the difference in photon flux between March 26 and August 1, we calculate an upper limit to the  
134 1,2-IHN photolysis rate of  $1.2 \times 10^{-5}$  s $^{-1}$  or approximately 22 daylight hours.

#### 135 5. 1D Model Description



**Fig. S6.** Midday (noon local time) Los Angeles boundary layer profile of (a) the calculated aerosol liquid water (ALW) used to model IHN partitioning, (b) the product of the estimated 1,2-IHN Henry's law constant ( $K_H$ ) and aqueous hydrolysis rate ( $k_{(aq)}$ ) using both temperature independent (black) and dependent (red) values, and (c) the 1,2-IHN heterogenous lifetime against hydrolysis calculated from our model using temperature independent (black) and dependent (red) values of  $K_H$  and  $k_{(aq)}$ .

136 The one-dimensional (1D) atmospheric model used in this work simulates the emission, deposition, vertical transport, and  
137 photochemical oxidation of 250 chemical species in an atmospheric column tuned to replicate conditions observed during the  
138 2010 CalNex campaign (May–June, 2010). The model consists of 40 vertical layers ranging from the ground (0.05 m) to 800 m.  
139 The first 39 layers exist within the range of the daytime boundary layer, with the 40th layer representing the free troposphere.  
140 Depending on the time of day, the uppermost layers (33–40) represent either the boundary layer or the nocturnal residual  
141 layer. Layer heights within the boundary layer are calculated similarly to previous 1D models and increase exponentially with  
142 altitude (15, 16), while the free troposphere layer has a prescribed depth of 100 m. Simulations are run for 24 hours with a  
143 time step of one minute. Diurnal meteorological variables and emission rates are provided as model inputs, as explained in  
144 more detail subsequently.

145 Vertical transport is simulated in the model using K-theory, a first-order flux-gradient approach common to 1D atmospheric  
 146 models (15–17). Layer-specific K-values, or eddy diffusivities, are calculated using the following equation (16):

$$147 \quad K_i = l_i^2 \left| \frac{dv}{dz_i} \right| f \quad [1]$$

148 where  $l_i$  is the vertical length scale for eddies in each layer,  $\frac{dv}{dz_i}$  is the local vertical gradient of horizontal wind velocity, and  
 149  $f$  represents a stability parameter. From 10:00–17:00, the boundary layer is assumed to be fully developed and K-values  
 150 are calculated from the ground to 700 m using vertical wind profiles calculated from ground level measurements. At night  
 151 (20:00–06:00), mixing is effectively restricted to the bottom 250 m, meant to represent the nocturnal boundary layer in the Los  
 152 Angeles area. During development and decline of the boundary layer (06:00–10:00 and 17:00–20:00), K-values are interpolated  
 153 between those used at night and midday. Midday mixing between the top of the boundary layer and the free troposphere is  
 154 assigned a K-value of  $5 \text{ m}^2 \text{ s}^{-1}$ . Simulated IHN isomer ratios are insensitive to the free tropospheric layer depth and the mixing  
 155 rate between the boundary layer and the free troposphere.

156 The model combines the RACM2 chemical mechanism (18), which simulates oxidation of lumped VOC classes for use in  
 157 regional models, with the condensed isoprene oxidation mechanism from Wennberg et al. (19), resulting in a system with 250  
 158 chemical species and 583 chemical reactions. Photolysis rates provided by the individual mechanisms are scaled to achieve  
 159 agreement between modeled and measured values of the hydroxyl radical during CalNex 2010 (20) and the photolysis rate of  
 160  $\text{NO}_2$  ( $j_{\text{NO}_2}$ ). Emissions of non-biogenic lumped VOCs used in the RACM2 mechanism were obtained from the California Air  
 161 Resources Board (CARB) database. Emissions data were available for the week of July 22–28, 2012. While these data do not  
 162 correspond with the exact timeframe of the CalNex campaign, the use of data from June and the inclusion of an advective  
 163 term described below produce reasonable simulation of the lumped VOC concentrations and there is good agreement between  
 164 measured and modeled oxidant concentrations. Given uncertainty in local isoprene emissions due to vegetation heterogeneity  
 165 in and around the Pasadena area, we performed sensitivity tests to determine a reasonable peak emission rate that, when  
 166 diurnally scaled by the solar zenith angle, produced agreement between measured and modeled isoprene concentrations. This  
 167 process suggests a peak effective rate of  $\sim 0.3 \text{ mg m}^2 \text{ hr}^{-1}$ . This value agrees well with model estimates for the region using the  
 168 MEGAN model (21, 22).

169 Two types of advective processes are simulated within the model. Given the difficulty in quantifying the influence of  
 170 advection on local concentrations, we include an advective mixing term similarly to Wolfe and Thornton (15) that pushes  
 171 the model towards agreement with measured diurnal concentrations. The magnitude of this first order advective term is  
 172 proportional to the difference between the modeled and measured concentration at each step. This advective term is only  
 173 incorporated for parent VOCs, NO,  $\text{NO}_2$ , and  $\text{O}_3$  in the bottom 20 layers of the model, which encompasses the region from the  
 174 ground to  $\sim 20 \text{ m}$ . Importantly, this term is not included in the differential equations governing IHN isomer production and  
 175 loss. The model also includes an advective loss term to prevent unrealistic accumulation of oxidation products within the  
 176 column. The magnitude of this loss rate is based on layer-dependent horizontal wind velocities and an assumed width of the  
 177 Los Angeles basin ( $k_{\text{wind}} = v_i/125 \text{ km}$ ) (23).

178 Deposition velocities of IHN isomers are assumed to follow a diurnal pattern proportional to the cosine of the solar zenith  
 179 angle with peak (midday) value of  $2 \text{ cm s}^{-1}$ , following measurements by Nguyen et al. (24). Deposition velocities of other  
 180 species are calculated using the formula of Gao et al. (25) for deposition to the ground, with Henry’s law constants and  
 181 reactivity values taken from Ashworth et al. (17). The model assumes deposition occurs within the lowest 5 m of the domain,  
 182 and first-order deposition rates are calculated by dividing the deposition velocity by this 5 m sub-domain height (23).

183 Diurnal mass loadings of aerosol liquid water (ALW) used to model IHN partitioning were calculated using ISORROPIA-II  
 184 (26). Ground-level measurements of temperature, relative humidity, and mass loadings of inorganic aerosol components ( $\text{SO}_4$ ,  
 185  $\text{NH}_4$ , and  $\text{NO}_3$ ) collected during CalNex 2010 were used as model inputs. The CalNex data set for the LA ground site is  
 186 publicly available at <https://esrl.noaa.gov/csl/groups/csl7/measurements/2010calnex/Ground/DataDownload>. Organic aerosol  
 187 was not assumed to contribute to water uptake. Other salts not accurately quantified (e.g., Cl, Na, etc) were not included in  
 188 the ALW calculation given their small contribution to aerosol mass loadings in the Los Angeles region (27). Aerosol mass  
 189 loadings were assumed constant with altitude. The assumption of vertically invariant aerosol mass loadings is likely inaccurate  
 190 in the early morning, as vehicular emissions within a shallow boundary layer produce substantial inorganic nitrate aerosol (27),  
 191 increasing ALW in the boundary layer but not the residual layer. However, without additional constraints or more complex  
 192 modeling it is difficult to quantify the influence of this assumption. Nevertheless, assuming a constant aerosol vertical profile  
 193 should lead to an overestimate of the integrated amount of ALW within the column, rather than an underestimate, therefore  
 194 producing a conservative (i.e., low) estimate of the IHN  $K_H \times k_{(\text{aq})}$  product ( $k_{\text{hydro}}^*$ ).

195 Both Henry’s law coefficients ( $K_H$ ) as well as the aqueous hydrolysis rate ( $k_{(\text{aq})}$ ) are functions of temperature. Unfortunately,  
 196 these dependences are not well-known for the IHN isomers, therefore we provide the following estimates for these parameters:

$$197 \quad K_H(T) = K_H(273) \frac{e^{9622/T}}{e^{9622/273}} \quad [2]$$

$$198 \quad k_{(\text{aq})}(T) = k_{(\text{aq})}(298\text{K}) \frac{e^{-6000/T}}{e^{-6000/298}} \quad [3]$$

200 The temperature dependence for  $K_H$  is based on findings from Shepson et al. (28).  $k_{(\text{aq})}$  simply assumes a doubling in the  
 201 hydrolysis rate for every 10 degrees increase in temperature. For 4,3-IHN,  $k_{(\text{aq})}(298 \text{ K})$  is taken from Jacobs et al. (10) as

202  $1 \times 10^{-5} \text{ s}^{-1}$ . For 1,2-IHN, we only constrain  $k_{\text{hydro}}^*$ , the product of  $k_{(\text{aq})}$  and  $K_{\text{H}}$ . While the temperature dependences of  $k_{(\text{aq})}$   
203 and  $K_{\text{H}}$  are both large, they have opposite signs, and thus in the product,  $k_{\text{hydro}}^*$ , they largely cancel, increasing by only a  
204 factor of 1.25 from the ground to the top of the boundary layer for midday simulations (Fig. S6).

205 While we do not know the  $K_{\text{H}}$  for 1,2-IHN in water, we can estimate a likely range. The lower limit is likely the  $K_{\text{H}}$  of  
206 4,3-IHN, as polar functionalities near the methyl group will increase solvation in water. For example, Henry's law constant  
207 for 1,2-ISOPOOH is approximately an order of magnitude larger than 4,3-ISOPOOH (29). For the upper limit, we suggest  
208 the  $K_{\text{H}}$  of 4,3-IHN scaled by the ratio of the  $K_{\text{H}}$  for 1,2-ISOPOOH to 4,3-ISOPOOH. We hypothesize that due to hydrogen  
209 bonding, the hydroperoxide functionality acts as a better solvating group than the nitrate group, thus the difference for the  
210 solubility of the hydroperoxides in water will be larger than for the nitrates. Together, we estimate a range of  $K_{\text{H}}$  for 1,2-IHN  
211 of  $3.1 \times 10^4 - 3.1 \times 10^5 \text{ M atm}^{-1}$  at 273 K, or  $1.6 \times 10^3 - 1.6 \times 10^4 \text{ M atm}^{-1}$  at 298 K. From this range in  $K_{\text{H}}$ , along with our  
212 constraint for  $k_{\text{hydro}}^*$  (main text), the range in hydrolysis rate,  $k_{(\text{aq})}$ , for 1,2-IHN is likely between 25 and  $250 \text{ s}^{-1}$  at 298 K.  
213 While this implies a very fast hydrolysis rate for 1,2-IHN, it is not inconsistent with our observations.

214 Between the CalNex-LA observations and 2017 when these measurements were made,  $\text{NO}_x$  levels declined. We have  
215 performed sensitivity studies and find the best fit to the atmospheric data (Fig. 3, main text) is not significantly impacted by  
216 the  $\text{NO}_x$  reductions.

## 217 6. GEOS-Chem

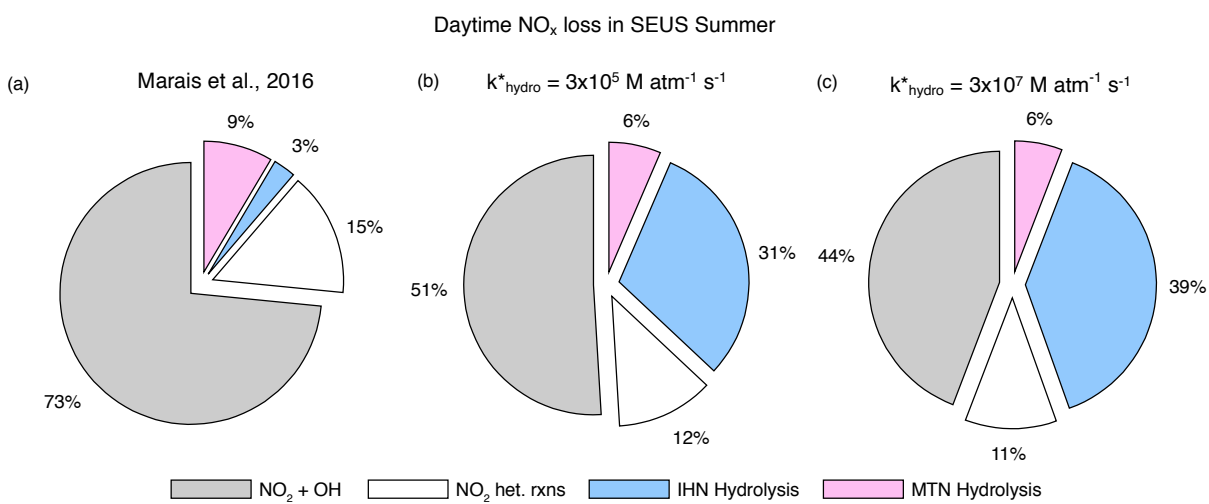
218 **Description of GEOS-Chem Simulations.** Simulations of 1,2-IHN hydrolysis and its effects were conducted using version 11-02c  
219 of the GEOS-Chem global chemical transport model (30), run at  $2^\circ \times 2.5^\circ$  horizontal resolution with 72 vertical layers extending  
220 through the stratosphere. GEOS-Chem incorporates assimilated meteorological observations from the NASA Goddard Earth  
221 Observing System - Forward Processing (GEOS-FP) data product from the NASA Global Modeling and Assimilation Office  
222 (GMAO). We used the standard HEMCO emissions (31), including isoprene emissions from the MEGAN v2.1 inventory scaled  
223 uniformly to  $535 \text{ Tg a}^{-1}$  (21), along with observationally fixed tropospheric methane. We conducted both month-long (1 - 31  
224 July 2014) and annual (1 August 2014 - 31 July 2015) simulations, following one year of initialization from 1 July 2013.

225 GEOS-Chem incorporates an editable chemical mechanism with gas-phase and heterogeneous chemistry. For all simulations  
226 performed herein, we replaced the default isoprene oxidation scheme with the Mini-CIM mechanism described in Bates et al.  
227 (32), which separates the 1,2- and 4,3-IHN isomers and incorporates a number of additional updates to isoprene chemistry  
228 based on the reduced mechanism compiled by Wennberg et al. (19). The aerosol uptake and hydrolysis of isoprene nitrates in  
229 GEOS-Chem is parameterized with an irreversible reactive uptake coefficient ( $\gamma$ ) onto the aqueous inorganic component of  
230 aerosol. In their analysis of organic nitrate chemistry in the Southeast United States, Fisher et al. (33) used a constant  $\gamma$   
231 of 0.005 for all isoprene nitrates. Marais et al. (34) introduced a mechanistic formulation for  $\gamma$  based on an effective overall  
232 hydrolysis rate,  $k_{\text{hydro}}^*$  ( $\text{M atm}^{-1} \text{ s}^{-1}$ ), which incorporates an effective Henry's law constant ( $K_{\text{H}}$ ,  $\text{M atm}^{-1}$ ), accounting for  
233 rapid dissociation or hydration equilibria in the aqueous phase) and a pseudo-first-order aqueous-phase reaction rate constant  
234 ( $k_{(\text{aq})}$ ,  $\text{s}^{-1}$ ). Marais et al. (34) used  $K_{\text{H}} = 3.3 \times 10^5 \text{ M atm}^{-1}$  for all isoprene-derived nitrates,  $k_{(\text{aq})} = 1.6 \times 10^{-5} \text{ s}^{-1}$  for  
235 lumped  $\beta$ -hydroxynitrates, and  $k_{(\text{aq})} = 6.8 \times 10^{-3} \text{ s}^{-1}$  for  $\delta$ -hydroxynitrates and dihydroxy-dinitrates. Here, we updated the  
236  $K_{\text{H}}$  of 4,3-IHN to match the value listed in Table S1, and reduce its  $k_{(\text{aq})}$  to  $1 \times 10^{-5} \text{ s}^{-1}$ . For 1,2-IHN, we perform individual  
237 simulations with  $k_{\text{hydro}}^*$  values of  $0$ ,  $3 \times 10^4$ ,  $3 \times 10^5$ ,  $3 \times 10^6$ , and  $3 \times 10^7 \text{ M atm}^{-1} \text{ s}^{-1}$ , all invariant with temperature. In  
238 our analysis, we compared the resulting mixing ratios as well as total production and loss of species of interest between these  
239 simulations employing different 1,2-IHN  $k_{\text{hydro}}^*$  values and against simulations using the baseline uptake parameterizations  
240 from Marais et al. (34) and Fisher et al. (33). We acknowledge that there is an inconsistency in the modeling of the 4,3-IHN  
241 hydrolysis loss and the experimental determinations of this quantity. The 273 K value for  $K_{\text{H}}$  is used in GEOS-Chem along  
242 with the 298 K value for  $k_{(\text{aq})}$ . Using the temperature dependencies above leads to a hydrolysis rate for the 4,3-IHN that  
243 is about 6 times too fast. We note, however, that this does not impact our results, as even using the faster hydrolysis rate,  
244 4,3-IHN hydrolysis is negligible compared to the overall loss rate.

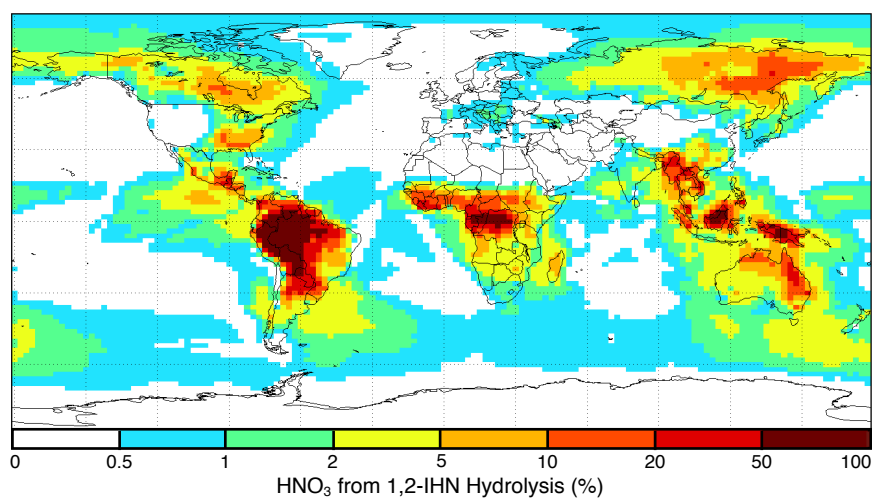
245 We also include the hydrolysis of monoterpene nitrates (MTN), as implemented in the current default GEOS-Chem set up.  
246 As currently described in Fisher et al. (33), this chemistry is largely based on the scheme developed by Browne et al. (35)  
247 for use in WRF-Chem, which was built on the RACM2 scheme developed by Goliff et al. (18). GEOS-Chem assumes a bulk  
248 lifetime of monoterpene nitrates against hydrolysis of 1 h (33), which was found to simulate measured particle organic nitrate  
249 mass during the SOAS and SEAC<sup>4</sup>RS campaigns better than the longer lifetimes estimated in field and laboratory analyses  
250 (36–38). However, this hydrolysis lifetime is poorly constrained and is rendered particularly uncertain by the many simplifying  
251 assumptions underlying the GEOS-Chem MTN parameterization, including the lumping of the parent monoterpenes into two  
252 representative precursor species, their heavily abridged oxidation mechanism, the lumping of MTN into two representative  
253 species (those with and without double bonds), and the fixed reactive uptake coefficient of  $\gamma = 0.01$  for all MTN. In light of  
254 the changes we make in this work to the budget of organic nitrates, the MTN parameterization in GEOS-Chem should be  
255 reassessed.

256 Lastly, in our simulations, we do not include fast tertiary nitrate hydrolysis of the other compounds besides IHN. Thus,  
257 these simulations may underestimate the contribution of hydrolysis towards shortening the  $\text{NO}_x$  lifetime. As one example, OH  
258 oxidation of 1,2-isoprene hydroperoxy nitrate (IPN) is thought to yield several second-generation tertiary nitrates (19), which  
259 will also likely undergo rapid hydrolysis.

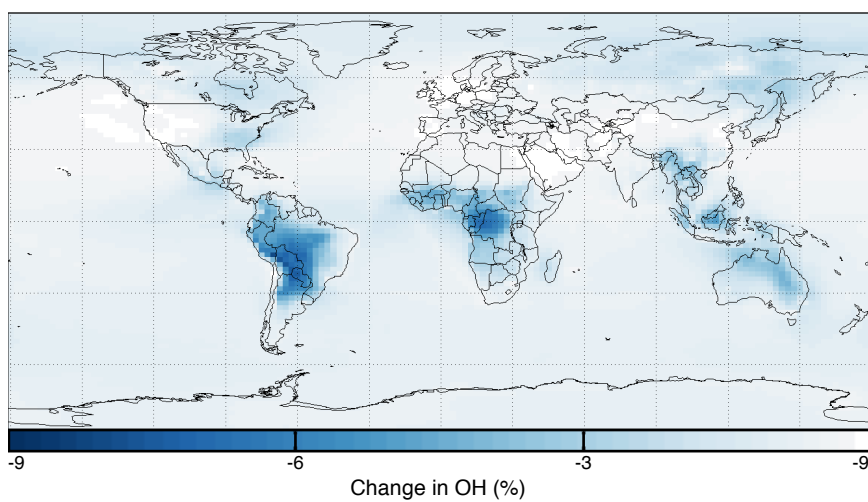




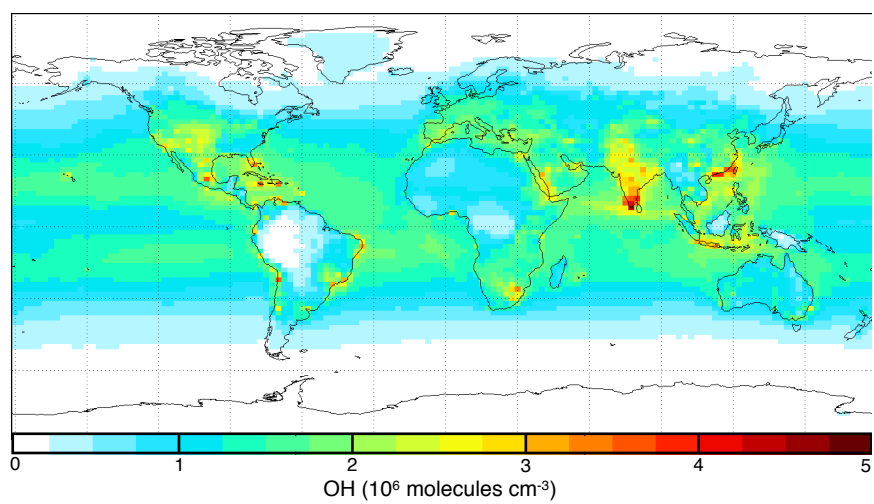
**Fig. S7.** Pie charts showing the global impact IHN hydrolysis has on the different daytime NO<sub>x</sub> pathways in the lower 1 km of the atmosphere over the southeast USA in the summer when (a) using parameters from Marais et al. (34), (b) setting  $k^*_{\text{hydro}}$  to  $3 \times 10^5 \text{ M atm}^{-1} \text{ s}^{-1}$ , and (c) setting  $k^*_{\text{hydro}}$  to  $3 \times 10^7 \text{ M atm}^{-1} \text{ s}^{-1}$ . The global impact of this chemistry remains largely unchanged when  $k^*_{\text{hydro}} > 3 \times 10^5 \text{ M atm}^{-1} \text{ s}^{-1}$ .



**Fig. S8.** Annually averaged fraction of HNO<sub>3</sub> attributed to 1,2-IHN hydrolysis in the lowest 1 km of the atmosphere, as calculated with GEOS-Chem when a 1,2-IHN hydrolysis rate of  $k_{\text{hydro}}^* = 3 \times 10^5 \text{ M atm}^{-1} \text{ s}^{-1}$  has been included.



**Fig. S9.** Annually averaged change in OH in the lowest 1 km of the atmosphere when comparing the standard GEOS-Chem model with one that includes a 1,2-IHN hydrolysis rate of  $k_{\text{hydro}}^* = 3 \times 10^5 \text{ M atm}^{-1} \text{ s}^{-1}$ .



**Fig. S10.** Annually averaged OH concentrations in the lowest 1 km of the atmosphere, as calculated with GEOS-Chem when a 1,2-IHN hydrolysis rate of  $k_{\text{hydro}}^* = 3 \times 10^5 \text{ M atm}^{-1} \text{ s}^{-1}$  has been included.

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