

Auxiliary Material for:

Conversion of hydroperoxides to carbonyls in field and laboratory instrumentation:
observational bias in diagnosing pristine versus anthropogenically-controlled atmospheric
chemistry.

J. C. Rivera-Rios¹, T. B. Nguyen², J. D. Crounse², W. Jud³, J. M. St. Clair², T. Mikoviny⁴, J.
B. Gilman^{5,6}, B. M. Lerner^{5,6}, J. B. Kaiser¹, J. de Gouw^{5,6}, A. Wisthaler^{3,4}, A. Hansel³, P. O.
Wennberg^{2,7}, J. H. Seinfeld^{7,8} and F. N. Keutsch^{1,*}

¹ Department of Chemistry, University of Wisconsin-Madison, Wisconsin, USA

² Division of Geological and Planetary Sciences, California Institute of Technology,
Pasadena, California, USA

³ Institute of Ion Physics and Applied Physics, University of Innsbruck, Innsbruck, Austria

⁴ Department of Chemistry, University of Oslo, Oslo, Norway

⁵ NOAA Earth System Research Laboratory, R/CSD7, 325 Broadway, Boulder, Colorado,
USA

⁶ Cooperative Institute for Research in Environmental Sciences, University of Colorado,
Boulder, Colorado, USA

⁷ Division of Engineering and Applied Science, California Institute of Technology, Pasadena,
California, USA

⁸ Division of Chemistry and Chemical Engineering, California Institute of Technology,
Pasadena, CA, USA

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1. Characterization of 1,2- and 4,3-ISOPOOH

^1H and ^{13}C NMR spectra were recorded on either a Bruker AV-400 or a Varian MercuryPlus 300 NMR spectrometer. Samples were quantified by preparing an NMR sample with a known amount of TMSPh, a compound that does not interfere with any of the signals from ISOPOOH.

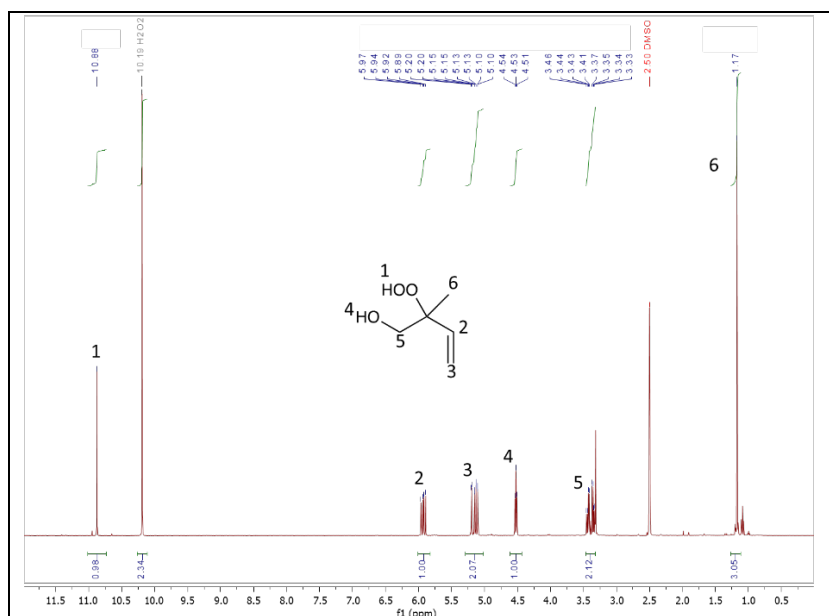


Figure S1: Proton NMR spectrum of 1,2-ISOPOOH. ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 10.88 (s, 1H), 5.93 (dd, $J = 17.9, 11.1$ Hz, 1H), 5.18 (dd, $J = 17.8, 1.4$ Hz, 1H), 5.12 (dd, $J = 11.1, 1.4$ Hz, 1H), 4.53 (t, $J = 6.2$ Hz, 1H), 3.43 (dd, $J = 11.4, 5.9$ Hz, 1H), 3.35 (dd, $J = 11.5, 6.5$ Hz, 1H), 1.17 (s, 3H). ^{13}C NMR (75 MHz, $\text{DMSO}-d_6$) δ 140.36, 114.95, 83.71, 64.72, 19.01.

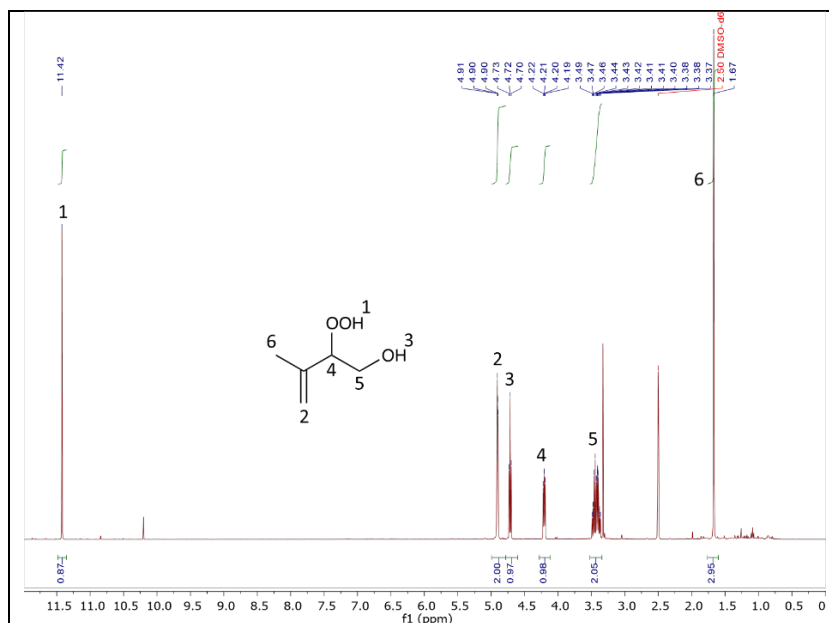


Figure S2: Proton NMR spectrum of 4,3-ISOPOOH. ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 11.42 (s, 1H), 4.94 – 4.83 (m, 2H), 4.72 (t, $J = 5.9$ Hz, 1H), 4.21 (dd, $J = 6.5, 4.9$ Hz, 1H), 3.52 – 3.34 (m, 2H), 1.67 (s, 3H). ^{13}C NMR (75 MHz, $\text{DMSO}-d_6$) δ 142.91, 113.19, 89.30, 61.12, 30.68.

Measurements of the synthetic standards with the Caltech triple quadrupole CF_3O^- CIMS instrument were consistent with previous measurements of ISOPOOH formed via low NO_x isoprene oxidation experiments, in agreement with the characterization via NMR spectroscopy. Sample degradation was tested either via CF_3O^- CIMS or NMR spectroscopy before experiments. Degradation of compounds was not significant when stored at -20°C , although the compounds are susceptible to this if stored at room temperature.

2.1 PTR-MS Study

The experiment was performed using a standard quadrupole-MS based PTR-MS instrument [de Gouw and Warneke, 2007]. This and similar instruments have been in use for MVK/MACR measurements since 1998 [Crutzen *et al.*, 2000]. The instrument is equipped with a second-generation drift tube [Steinbacher *et al.*, 2004] consisting of stainless steel rings separated by Teflon PTFE spacers. The drift tube was operated at conditions typically used for field measurements (drift tube pressure: 2.25 mbar, drift tube voltage: 560 V, drift tube temperature: 54°C). Inlet tubing to the drift tube exclusively consisted of Teflon PFA and PEEK. Liquid 1,2-ISOPOOH was injected into dry synthetic air in a 0.78 m^3 Teflon-FEP bag. While sampling from the bag, the PTR-MS instrument performed full mass scans in the m/z 20 to m/z 150 range to obtain the mass spectrum of 1,2-ISOPOOH. The 1,2-ISOPOOH concentration in the bag was 46.7 ppbV (accuracy: $\pm 25\%$) as simultaneously determined by the CIT-ToF-CIMS instrument.

2.2 SRI-ToF-MS studies

The SRI-ToF-MS (Selective Reagent Ionization Time-of-Flight Mass Spectrometer) combines the high resolution of PTR-ToF-MS developed at the University of Innsbruck [Graus *et al.*, 2010] with the capability of isomeric separation of certain functional groups. This is achieved by taking advantage of the different chemical ionization pathways of specific reagent ions (NO^+ and H_3O^+). For example, in the H_3O^+ mode aldehydes and ketones both exhibit proton transfer and thus both MVK and MACR are detected as $\text{C}_4\text{H}_7\text{O}^+$ (m/z 71.050). However, in the NO^+ mode ketones preferentially cluster with NO^+ whereas aldehydes are ionized via hydride ion transfer [Španěl *et al.*, 1997] and thus MVK is detected as $\text{C}_4\text{H}_6\text{O}\bullet\text{NO}^+$ (m/z 100.040), whereas MACR is detected as $\text{C}_4\text{H}_5\text{O}^+$ (m/z 69.034). The design of the custom built primary ion source of the Innsbruck SRI-ToF-MS allows fast switching between these primary ions and consequently for monitoring of VOC signals virtually in real-time.

The E/N in the instruments drift tube was periodically switched between 120 Td, 90 Td and 60 Td in H_3O^+ mode and 90 Td and 60 Td in NO^+ mode (E being the electric field strength and N the gas number density; $1\text{ Td} = 10^{-17}\text{ V cm}^2$). This helped to identify certain clusters and fragments.

The instrument was sampling from inflatable Teflon bags (300 – 400 L) containing the ISOPOOH standards. Gas standards were prepared by flushing a Teflon T piece containing a septum for ISOPOOH injection with 3 – 5 slm dry synthetic air (Messer Austria GmbH, 5.0 grade). For the first 30 min after droplet injection the air stream was directed into

the hood in order to eliminate residual high volatility contaminants in part used as solvents for ISOPOOH synthesis and purification. Afterwards the flow was directed into the bag, which had been previously filled with ca. 50 L of synthetic air to reduce possible wall losses of the samples.

For introduction of ISOPOOH samples into the SRI-ToF-MS special care was taken to prevent any contact of the sample stream (0.72 slm) with metallic surfaces between the Teflon bag and the drift tube inside the instrument. Therefore, only tubing and fittings made of either Teflon or PEEK were used and the drift tube represented the only metallic surface the sample came in contact with.

Both the ~1.35m long inlet line and the drift tube could be heated (maximum temperatures used were 50°C for the inlet line and 80°C for the drift tube). For the cold trap experiments, approximately half way between the bag and the SRI-ToF-MS the sampling line insulation was removed and a polystyrene box (20 x 20 x 20 cm), which could be filled with dry ice, was inserted. Before each experiment the Teflon bag was filled with pure synthetic air in order to determine the VOC background.

Major ion signals from the sample air could be unequivocally assigned to MVK in the case of 1,2-ISOPOOH and MACR in the case of 4,3-ISOPOOH: in H_3O^+ mode they were detected as $\text{C}_4\text{H}_7\text{O}^+$ (m/z 71.050), and in NO^+ mode 1,2-ISOPOOH was detected as $\text{C}_4\text{H}_6\text{O}\bullet\text{NO}^+$ (m/z 100.040), specific for MVK, whereas 4,3-ISOPOOH was detected as $\text{C}_4\text{H}_5\text{O}^+$ (m/z 69.034), specific for MACR. Negligible signals could be attributed to the parent compound (ISOPOOH) in both NO^+ and H_3O^+ mode independent of the E/N or inlet temperatures used.

In the cold trap experiments the MVK respectively MACR signals were largely eliminated, indicating that at least a major part of MVK and MACR is formed after the cold trap. Low volatility ISOPOOHs are expected to be largely frozen out in the cold trap, although this is a function of flow rate. These assumptions are supported by an 1,2-ISOPOOH experiment, in which the dry ice in the cold trap was removed after 75 min, resulting in a large burst of MVK as the cold trap warmed up.

3.1 Laboratory gas chromatography using Caltech GC-FID

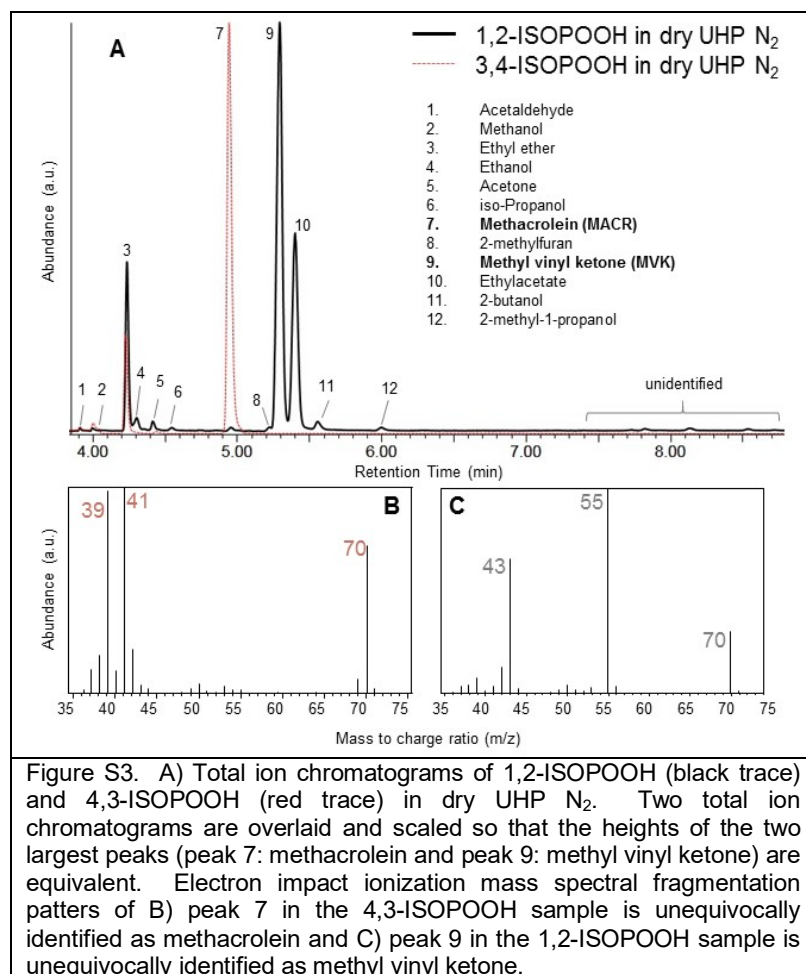
GC analyses were performed with a commercial gas chromatograph (6890N, Agilent Technologies) equipped with a flame-ionization detector (FID). The carrier gas was hydrogen (UHP H_2 , Air Liquide) and the make-up gas was nitrogen obtained from evaporated liquid nitrogen. The analyte gas was sampled through a 0.125" OD perfluoroalkoxy (PFA) Teflon inlet tube. An automatic 6-way stainless steel injection valve directed the analyte gas flow through a 10 mL uncoated stainless steel sample loop, toward either a purge line or the column inlet. The valve box was maintained at 150°C and the sample loop was continually flushed with the analyte gas mixture. The column inlet, maintained at 155°C, diluted the injected gas by a ratio of 5:1 with the carrier gas before elution through a bonded polystyrene-divinylbenzene capillary column (HP PLOT-Q, length 15 m, diameter 530 μm) with a nominal flow rate of 10 std. mL min^{-1} . The oven temperature program initiated at

60°C, and ramped to 250°C where the oven temperature was held for 3 minutes. The FID detection signals and the column retention times were calibrated with commercial standards of isoprene (Aldrich, > 99% purity), methacrolein (MACR, Aldrich, 95% purity) and methyl vinyl ketone (MVK, Aldrich, 99% purity). The standard compounds were quantified by volume injection, and diluted by calibrated mass flows of nitrogen gas.

Gas mixtures of synthesized 1,2-ISOPOOH and 4,3-ISOPOOH standards (~ 200 – 250 ppbv) were created by diluting a measured volume of headspace gas above the standards with nitrogen in inflatable fluorinated ethylene propylene (FEP) Teflon bags with 300 L capacity. The ISOPOOH standard mixture was quantified by CF_3O^- chemical ionization mass spectrometry (CIMS) [Crounse *et al.*, 2006], using the sensitivity calibrations previously described (Paulot, Crounse *et al.* 2009). Decomposition of ISOPOOH in the inlet does not occur with the Caltech CIMS as it samples exclusively through PFA Teflon tubing and fluoropolymer coated (Fluoropol, 801A, Cytonix) glass. 1,2-ISOPOOH and 4,3-ISOPOOH were converted to MVK and MACR in the GC, respectively, as evidenced by peaks with identical peak shape and retention times (Fig. 2). The conversion yields were determined by comparing the GC analyses, using the MVK and MACR calibrations under the assumption that the ISOPOOH decomposition occurred before reaching the GC column, with the CIMS analyses. The assumption that decomposition occurred pre-column was supported by the following observations: (1) ISOPOOH sampled by CIMS through a 3 m length of capillary column did not decompose (2) there was no peak broadening or retention time shift, compared to authentic MVK and MACR peaks, that would indicate chemical decomposition in the column, and (3) the most significant factor for conversion was the temperature of the valve box, which is the first metal component to come into contact with the analyte gas stream. Conversion yields of greater than 70% were obtained for the ISOPOOH isomers for the GC methodology described here based on ISOPOOH concentrations determined with the Caltech CF_3O^- CIMS. These experiments were performed during the Focused Isoprene eXperiments at California Institute of Technology (FIXCIT) campaign. [Nguyen *et al.*, 2014]

3.2 In-situ gas chromatography using NOAA GC-MS

The NOAA instrument is a custom-built, two-channel gas chromatograph coupled to an Agilent (5973N) electron impact (EI) ionization quadrupole mass spectrometer [Goldan and Kuster, 2004; Gilman *et al.*, 2010]. The NOAA GC-MS is designed for in-situ sampling of a range of volatile organic compounds (VOCs) with immediate analysis. All oxygenated VOCs including methacrolein (MACR) and methyl vinyl ketone (MVK) are detected on the second channel, which is detailed here following a brief description of sample preparation.



Purified liquid standards of 1,2-ISOPOOH and 4,3-ISOPOOH were shipped to NOAA's Earth Systems Research Laboratory in Boulder, CO under dry ice and refrigerated until use. Both standards were initially analyzed via ¹H-NMR (500 MHz) in DMSO-d₆ to ensure sample integrity. For analysis via GC-MS, a few microliters of the pure ISOPOOH standard were drawn into a borosilicate glass capillary tube (1.5 x 50 mm) open at both ends. The capillary tube was then placed inside a larger PFA sample line (0.25" OD x 10") with PFA bulkhead fittings on both ends. The analyte's gas-phase concentration was diluted by

continuously flushing the sample line with ~ 2 slpm of ultra-high purity dry nitrogen (UHP N₂).

A polytetrafluoroethylene (PTFE)-diaphragm stainless steel vacuum pump operating at < 2 slpm was used to draw the diluted ISOPOOH sample stream to the GC-MS at super-ambient pressure (1350 kPa). Downstream of the sample pump, 70 sccm of the sample stream is pushed thru a 0.125" OD PFA sample line and two unheated PTFE solenoid valves before entering an ozone trap made of 1 g sodium sulfite (Na₂SO₃) in a 0.25" OD glass tube maintained at 30°C with PTFE fittings and filters at both ends. From the sulfite trap, the sample stream is plumbed via a 0.125" OD PFA line to a valve oven at 75°C which contains a 10-port stainless steel switching valve with a polyetheretherketone (PEEK) rotor and then

to a water trap (0.125" OD PFA tubing with PFA fittings) at -35°C. The sample stream exiting the water trap is plumbed via a 0.125" OD PFA line to the aforementioned heated 10-port stainless steel valve, followed by 0.125" OD passivated stainless steel sample line to the sample trap. The sample trap consists of 10 cm of un-coated fused silica tubing (0.53mm ID) at -145°C via cryogenic cooling. Sample is acquired for 5 minutes at 70 sccm for a total sample size of 350 mL. Post sample acquisition, the sample trap is heated from -145°C to 35°C in 5 seconds while UHP He carrier gas flushes the sample from the sample trap to the cryofocus region (Restek Rxi-624Sil, 0.25mm ID, 4 cm) cooled to -165°C where it is held there for 307 seconds while the channel 1 sample is being analyzed. The cryofocus region then is rapidly heated effectively injecting the sample onto the remainder of the analytical column (Restek Rxi-624Sil, 0.25mm ID, 30m) while flushing with a He carrier gas flow rate of 2 sccm.

First, dry UHP N₂ without ISOPOOH was analyzed to ensure the sample stream was free of contaminants. Then 1,2-ISOPOOH in the glass capillary was added to the sample stream. The largest response measured by the NOAA GC-MS was identified as MVK by a) matching the observed retention time (5.30 minutes) to the known retention time of MVK from commercial gas standards and b) comparing the observed EI mass fragmentation pattern to the NIST mass spectral database (Figure S3). The largest peak identified in 4,3-ISOPOOH samples was MACR (retention time = 4.95 minutes, Figure S3). Bypassing the sample pump (i.e., completely removing it from the sample path) resulted in substantial decreases in MVK or MACR responses, consistent with the suggestion that the hot stainless steel surfaces, such as that present in the sample pump, may facilitate the conversion of 1,2-ISOPOOH to MVK and 4,3-ISOPOOH to MACR. Tests were repeated with humidified UHP nitrogen as a diluent with no change in results.

In order to determine if 1,2-ISOPOOH could be measured on the NOAA GC-MS, we bypassed the sodium sulfite trap and warmed the water trap from -45°C to +35°C; however, the parent analyte was never observed. This is in accordance with previous tests that have shown that VOCs containing more than one oxygen atom (e.g., organic acids, diols, or peroxides) cannot be detected by the NOAA GC-MS. We note that both ISOPOOH standards are unusually "sticky" such that the NOAA GC-MS required several days of continuous flushing to reduce the respective MVK or MACR signals to background after these experiments were performed.

4. ISOPOOH decomposition studies

Studies testing the effect of heated metal tubing on ISOPOOH decomposition were conducted using the Caltech CF₃O⁻ CIMS. ISOPOOH standard was sampled through a 7" long 1/4" O.D. stainless tube inserted into the sampling line at about 1 atm of dry zero air and a residence time of about 1 sec. Transmission changed from 76% at 30°C to less than 6% at 60°C, verifying that ISOPOOH readily decomposes on heated metal surfaces, although there appears to be a large passivation effect, as initially transmission was much less and slowly increased over 10's of minutes. In contrast, even at 60°C virtually no decomposition was observed for PFA Teflon tubing.

Similar experiments were also conducted by observing the amount of formaldehyde formed upon sampling through metal tubing as a function of temperature. With increasing temperature of the metal tubing there was a strongly increasing formaldehyde signal, consistent with the proposed interference mechanism. The conversion yield was not calculated as the amount of ISOPOOH introduced into the instrument was not known.

5. Vapor pressure calculations using SIMPOL [Pankow and Asher, 2008]

| Group | Value | # for ISOPOOH | # for MVK | # for MACR |
|---------------------------|--------|----------------------|----------------------|----------------------|
| constant term | 1.79 | 1 | 1 | 1 |
| carbon number | -0.438 | 5 | 4 | 4 |
| alkene | -0.105 | 1 | 1 | 1 |
| enone | -0.506 | 0 | 1 | 1 |
| hydroxyl | -2.23 | 1 | 0 | 0 |
| aldehyde | -1.35 | 0 | 0 | 1 |
| ketone | -0.935 | 0 | 1 | 0 |
| hydroperoxy | -2.48 | 1 | 0 | 0 |
| P_{vap} exponent | | -5.215 | -1.508 | -1.923 |
| P_{vap} (atm) | | 6.1×10^{-6} | 3.1×10^{-2} | 1.2×10^{-2} |

6. OH reactivity calculated from MCM v3.2

| Compound | $k_{\text{X}+\text{OH}}$ at 298K ^{a)} | relative yield ^{b)} | OH reactivity ^{d)} |
|--|--|------------------------------|---------------------------------------|
| MVK | 2.014×10^{-11} | 0.415 | $0.5 \text{ s}^{-1} \text{ ppb}^{-1}$ |
| MACR | 2.863×10^{-11} | 0.265 | $0.7 \text{ s}^{-1} \text{ ppb}^{-1}$ |
| (MVK+MACR) | 2.345×10^{-11} | | $0.6 \text{ s}^{-1} \text{ ppb}^{-1}$ |
| 1,2-ISOPOOH | 5.0×10^{-11} | 0.444 | $1.3 \text{ s}^{-1} \text{ ppb}^{-1}$ |
| 4,3-ISOPOOH | 1.15×10^{-10} | 0.306 | $2.9 \text{ s}^{-1} \text{ ppb}^{-1}$ |
| ISOPOOH ^{c)} | 8.85×10^{-11} | | $2.2 \text{ s}^{-1} \text{ ppb}^{-1}$ |
| $\Delta(\text{reactivity})$ | | | $1.6 \text{ s}^{-1} \text{ ppb}^{-1}$ |
| $\Delta(\text{scaled reactivity})$ ^{e)} | | | $2.9 \text{ s}^{-1} \text{ ppb}^{-1}$ |

a) in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

b) yield of 1,2-ISOPO₂ and 4,3-ISOPO₂ via reaction of isoprene with OH and accounting for nitrate formation for reaction with NO.

c) for this case the weighted average of 1,2-ISOPOOH and 4,3-ISOPOOH, as these isomers are detected as MVK/MACR assuming an air number density of 2.5×10^{19} molecules cm^{-3} scaled by a detection efficiency of 57%, the average determined for PTR and GC in this work.

7. Effect on estimated OH from MVK+MACR/isoprene ratios

The reaction rate of ISOPOOH with OH is 3-4 that for MVK/MACR and the yield of ISOPOOH from RO₂+HO₂ is >85%. The analytical expression for a sequential reaction (eq. 5a, 5b in ref. [Karl et al., 2007] was used by Karl et al. to estimate OH concentrations from the ratio of oxidation product to isoprene.

$$\frac{[MVK + MACR]}{[Isoprene]} = 0.55 \frac{k_{I+OH}}{k_{M+OH} - k_{I+OH}} \left(1 - e^{((k_{I+OH} - k_{M+OH})[OH]t)} \right) \quad (1)$$

$$t := \frac{z_i}{w^*} \quad (2)$$

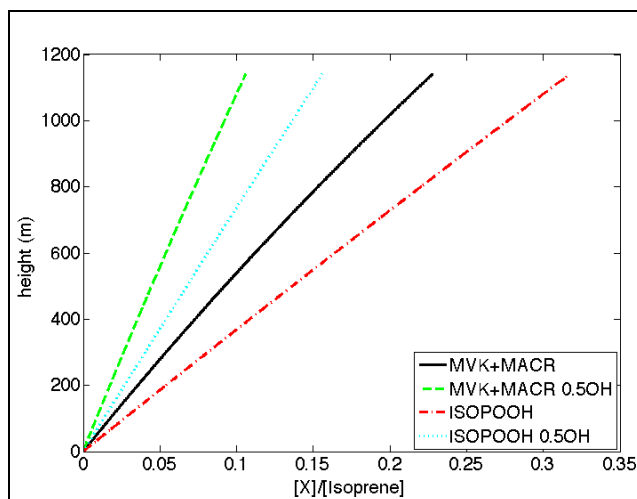


Figure S4: Calculated product/isoprene ratios.

k_I is the reaction rate constant of isoprene + OH, k_M is the average reaction rate constant of (MVK and MAC) + OH, z_i is the altitude, w^* is the convective velocity scale, estimated at 1.9 m/s, and t is the reaction time. The method assumes that the vertical transport is analogous to a flow tube reaction with a vertical velocity of 1.9 m/s.

Figure S4 shows the calculated ratios of [MVK+MACR]/isoprene for $[OH] = 6 \times 10^6 \text{ molecules cm}^{-3}$ and $[OH] = 3 \times 10^6 \text{ molecules cm}^{-3}$. Also shown are the

corresponding [ISOPOOH]/isoprene ratios calculated by substituting the average rate constant of MVK+MACR with OH with that of the mean value of 1,2- and 4,3-ISOPOOH of $8 \times 10^{-11} \text{ molec}^{-1} \text{ cm}^3 \text{ s}^{-1}$ (MCM). Also the yield of 55% for MVK+MACR used by Karl et al. is substituted by the yield of ISOPOOH, which is greater than 85%. Different ratios result for the same OH concentration ($6 \times 10^6 \text{ molec cm}^{-3}$) depending on which product is assumed. Clearly, conclusions drawn on the basis of MVK and MACR need to be reevaluated as the chemical properties of ISOPOOH differ from those of MVK and MACR.

8. OH recycling from MVK+MACR/isoprene ratios at NO = 0, O:C ratio and OH reactivity

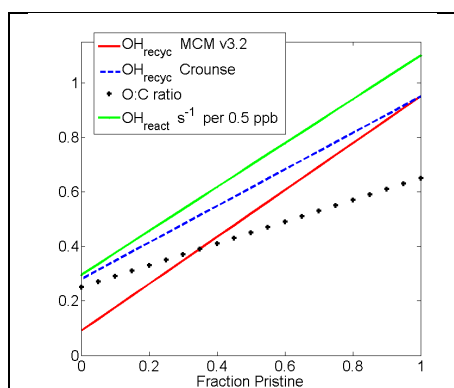


Figure S5: O:C ratio, OH recycling, and OH reactivity as a function of pristine contribution to observed products.

The reaction of ISOPOOH with OH fully recycles OH via formation of IEPOX. In contrast the oxidation of MVK and MACR by OH forms HO_2 and not OH according to the MCM v3.2 [Jenkin et al., 1997, 2003; Saunders et al., 2003]. The figure shows the difference in OH recycling under pristine conditions as a function of the contribution of ISOPOOH to the measurement. The blue dotted line includes the OH recycling mechanism from MACR described by Crounse et al. [Crounse et al., 2012; Kjaergaard et al., 2012], which is largely independent of NO. The effects on oxidative capacity via both the OH sink strength (reactivity) and the OH recycling fraction

vary strongly with the fraction of pristine product. Depending on the conditions the two might balance each other. The O:C ratio is much larger if the observed products are ISOPOOH than if they are MVK+MACR.

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