

We thank the editor for reading the paper carefully and providing thoughtful comments, which have resulted in improvements in the revised version of the manuscript.

We reply to each comment below in bold text.

1. Revisit reviewer#1's general comment 1, specifically for the diurnal cycles of OH_{bg} (at least in brief manner).

Following the reviewers suggestions we have included in the current version of the manuscript time series of the SCI obtained from the different estimates. We have now also included in the supplementary information a discussion of these time series, including some information on the diurnal profile. As extensively underlined in the text, the time series carry a large uncertainty due to the many unknowns encountered in their determination. We feel that an analysis of these time series beyond what is currently made available tends towards over-analysis, and certainly has diminished returns with respect to the focus of the paper.

2. Include authors' response to the reviewer#2's 3rd comment with more details than current version of the manuscript.

The authors' response to the 3rd comment from reviewer number 2 was added to the manuscript in more details (Section 4.5).

3. In section 3.3. editor suggests to use instantaneous O₃ concentration and redo the calculation than just using one number (7×10^{-17} molec/cm³) for the OH reactivity analysis.

In section 3.3, the instantaneous VOC_{unknown} and O₃ concentrations are used. We have rephrased the text to make this clearer.

4. For HOPE2012 missing OH reactivity and OH_{bg} analysis, this editor wonders about what if the authors separate the analysis into several periods (i.e. tree cutting, days and nights, 26-08th July, etc.) instead of full mission period. For me it is not convincing to say that the some portion of OH_{bg} is from SCI since two campaign report similar magnitude of SCI concentration but different dependencies of OH_{bg} on temperature and BVOC signature.

In the current version of the manuscript, for the HOPE 2012 campaign, there are some data periods separated from the rest of the campaign (i.e. tree cutting, 26th-28th of July) as they were characterized by peculiar behaviors (e.g. larger OH reactivity, instrument left unattended). We do not have valid reasons to divide the data into even more periods, nor do we feel that this would help give a better idea of the reasons for the discrepancy between the two environments.

Regarding SCI as a source of the OH_{bg} signal: we state in several places (Page 24, lines 18-19, Page 27, lines 21-22, Page 33, lines 23-24) that the discrepancy in the behavior of the OH_{bg} between the two

environments could be due to the contribution of more species to the OH_{bg} during the HOPE 2012 campaign compared to HUMPPA 2010, but likewise we do not believe that the evidence shown allows us to completely exclude a contribution of SCI to the OH_{bg} for either campaign. We show clearly that the OH_{bg} signals observed in the two environments cannot be compared from a point of view of absolute value. It is correct that during the night the amount of OH_{bg} observed in counts per second normalized on laser power in the two environments is similar, but this does not take into account the sensitivity towards the species causing the OH_{bg} , which could have been higher in the HOPE 2012 campaign compared to the HUMPPA 2010 one. In addition, as mentioned, in the night, during the HOPE 2012 campaign, there could have been additional interference caused by NO_3 . Finally, our paper also discusses the mechanistic discrepancy that arises from assigning an absolute OH concentration to the OH_{bg} signal (section 4.6), as this would imply a massive OH source in the atmosphere that is unsupported by any data.

Combined, we feel that the paper is very open about the fact that the OH_{bg} may not be fully caused by SCI, and that the SCI concentration derived by OH_{bg} is merely indicative for the hypothetical case where SCI are the sole interference. To date, no other interferences other than NO_3 have been unambiguously identified, such that this hypothesis remains plausible.

*Technical corrections

1. Double check significant figures

Checked

2. p19 line 5, OH reactivity ==> OH production

Corrected

1 **Estimating the atmospheric concentration of Criegee**
2 **intermediates and their possible interference in a FAGE-LIF**
3 **instrument**

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2 **Abstract**

3 We analysed the extensive dataset from the HUMPPA-COPEC 2010 and the HOPE 2012
4 field campaigns in the boreal forest and rural environments of Finland and Germany,
5 respectively, and estimated the abundance of stabilised Criegee intermediates (SCI) in the
6 lower troposphere. Based on laboratory tests, we propose that the background OH signal
7 observed in our IPI-LIF-FAGE instrument during the afore-mentioned campaigns is caused at
8 least partially by SCI. This hypothesis is based on observed correlations with temperature and
9 with concentrations of unsaturated volatile organic compounds and ozone. Just like SCI, the
10 background OH concentration can be removed through the addition of sulfur dioxide. SCI
11 also adds to the previously underestimated production rate of sulfuric acid. An average
12 estimate of the SCI concentration of $\sim 5.0 \times 10^4$ molecules cm^{-3} (with an order of magnitude
13 uncertainty) is calculated for the two environments. This implies a very low ambient
14 concentration of SCI, though, over the boreal forest, significant for the conversion of SO_2
15 into H_2SO_4 . The large uncertainties in these calculations, owing to the many unknowns in the
16 chemistry of Criegee intermediates, emphasise the need to better understand these processes
17 and their potential effect on the self-cleaning capacity of the atmosphere.

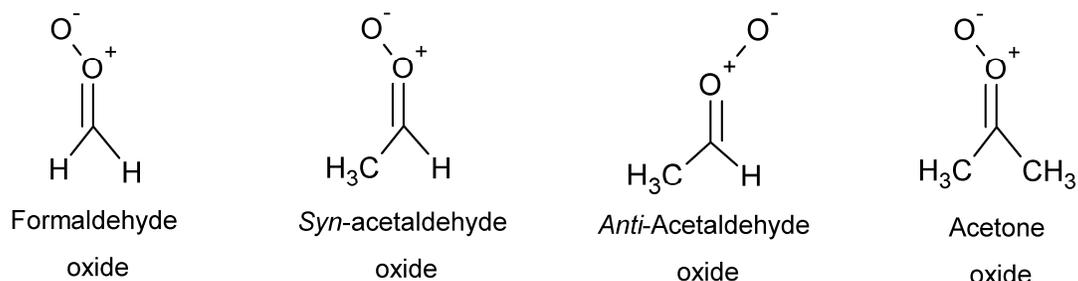
18

19 **1 Introduction**

20 Criegee intermediates (CI), or carbonyl oxides, are formed during the ozonolysis of
21 unsaturated organic compounds (Criegee, 1975; Johnson and Marston, 2008; Donahue et al.,
22 2011): in the gas phase ozone attaches to a double bond forming a primary ozonide (POZ)
23 that quickly decomposes forming a Criegee intermediate and a carbonyl compound. The CI

1 can exist as thermally stabilised CI (SCI) or as chemically activated CI (Kroll et al.,
 2 2001; Drozd et al., 2011), where the chemically activated CI have high energy content and in
 3 the atmosphere either undergo unimolecular decomposition, or are stabilised by collisional
 4 energy loss forming SCI.

5 For many decades the chemistry of Criegee intermediates was investigated both with
 6 theoretical and indirect experimental studies as reviewed in detail by Johnson and Marston
 7 (2008), Vereecken and Francisco (2012), and Vereecken et al. (2015). During the last few
 8 years, numerous experimental studies specifically on stabilised Criegee intermediates have
 9 been performed following their first detection by Welz et al. (2012). Many laboratories have
 10 now detected SCI with various techniques (Berndt et al., 2012; Mauldin III et al.,
 11 2012; Ouyang et al., 2013; Taatjes et al., 2013; Ahrens et al., 2014; Buras et al., 2014; Liu et al.,
 12 2014a; Sheps et al., 2014; Novelli et al., 2014b; Stone et al., 2014; Chhantyal-Pun et al.,
 13 2015; Lee, 2015; Newland et al., 2015a; Fang et al., 2016a; Smith et al., 2016) and have
 14 confirmed that they are very reactive towards many atmospheric trace gases. Currently, the
 15 most studied Criegee intermediates are formaldehyde oxide, CH_2OO , acetaldehyde oxide,
 16 CH_3CHOO (*syn* and *anti*, i.e. with the outer oxygen pointing towards or away from an alkyl
 17 group, respectively) and acetone oxide, $(\text{CH}_3)_2\text{COO}$.



18

19 The importance of stabilised Criegee intermediates as oxidants in the atmosphere depends on
 20 the rate coefficient of their reaction with water vapour as the latter is ubiquitously present in

1 relatively high concentrations in the boundary layer (between 10^{16} to 10^{17} molecules cm^{-3}).
2 The rate of this reaction strongly depends on the CI conformation (Aplincourt and Ruiz-
3 López, 2000;Tobias and Ziemann, 2001;Ryzhkov and Ariya, 2003;Kuwata et al.,
4 2010;Anglada et al., 2011;Anglada and Sole, 2016;Chen et al., 2016;Lin et al., 2016;Long et
5 al., 2016) and until now the rate coefficient has been measured for *anti*- CH_3CHOO (Taatjes
6 et al., 2013;Sheps et al., 2014) while lower limits have been determined for CH_2OO (Stone et
7 al., 2014), *syn*- CH_3CHOO (Taatjes et al., 2013;Sheps et al., 2014) and $(\text{CH}_3)_2\text{COO}$ (Huang et
8 al., 2015;Newland et al., 2015b). The uncertainties in these rate coefficients make it difficult
9 to estimate the importance of Criegee intermediates and the impact they may have as oxidants
10 in the atmosphere. Additionally, recent studies (Berndt et al., 2014b;Chao et al., 2015;Lewis
11 et al., 2015;Smith et al., 2015;Lin et al., 2016) showed that the reaction between CH_2OO and
12 water dimers (present in the ppmv range in the atmosphere (Shillings et al., 2011)) is faster
13 than the reaction with water vapor, in agreement with the several theoretical studies
14 (Ryzhkov and Ariya, 2004;Chen et al., 2016;Lin et al., 2016) which indicate the reaction with
15 water dimers to be between 400 and 35,000 times faster than the reaction with water vapor
16 depending on the conformers. Another important reaction of SCI that depends on the SCI
17 conformation is their unimolecular decomposition. The decomposition rate and product
18 formed depend on the SCI conformer structure. *Anti*-SCI are likely to isomerise via the ester
19 channel forming an ester or an acid as final product while *syn*-SCI will form a vinyl
20 hydroperoxide (VHP) which promptly decomposes forming hydroxyl radicals (OH) and a
21 vinoxy radical (Paulson et al., 1999;Johnson and Marston, 2008;Drozd and Donahue,
22 2011;Vereecken and Francisco, 2012;Kidwell et al., 2016). Larger and more complex
23 conformers such as hetero-substituted or cyclic structures are subject to additional
24 unimolecular rearrangements (Vereecken and Francisco, 2012). On the unimolecular

1 decomposition rates and products few experimental data are available (Horie et al.,
2 1997;Horie et al., 1999;Fenske et al., 2000a;Novelli et al., 2014b;Kidwell et al., 2016;Fang et
3 al., 2016a;Smith et al., 2016), but more is available from theoretical studies explicitly
4 focusing on the path followed by different conformers (Anglada et al., 1996;Aplincourt and
5 Ruiz-López, 2000;Kroll et al., 2001;Zhang and Zhang, 2002;Nguyen et al., 2009b;Kuwata et
6 al., 2010).

7 Most of the experimental and theoretical information described above refers to the smaller
8 conformers. These compounds are likely to be formed relatively efficiently in the atmosphere
9 as they can originate from any unsaturated compound with a terminal double bond, but they
10 do not represent the entire Criegee intermediate population.

11 As SCI were found to react quickly with many trace gases, various model studies were
12 performed on the impact SCI have as oxidants in the atmosphere (Vereecken et al., 2012;Boy
13 et al., 2013;Percival et al., 2013;Pierce et al., 2013;Sarwar et al., 2013;Sarwar et al.,
14 2014;Novelli et al., 2014b;Vereecken et al., 2014). Some of these studies focused in
15 particular on the possible impact that SCI might have on the formation of sulfuric acid
16 (H_2SO_4) in the gas phase, following Mauldin III et al. (2012) who suggested that Criegee
17 intermediates are the missing SO_2 oxidant needed to close the sulfuric acid budget over a
18 boreal forest. This is supported by theoretical and laboratory studies that have determined a
19 rate coefficient between SCI and sulfur dioxide (SO_2) of the order of $10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
20 (Aplincourt and Ruiz-López, 2000;Jiang et al., 2010;Kurtén et al., 2011;Vereecken et al.,
21 2012;Welz et al., 2012;Taatjes et al., 2013;Liu et al., 2014b;Sheps et al., 2014;Stone et al.,
22 2014). As the main atmospherically relevant oxidiser of SO_2 in the gas phase is the OH
23 radical with a rather slow rate coefficient at ambient temperature and pressure of 2×10^{-12}
24 $\text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson et al., 2004), the high rate coefficient for SO_2 oxidation would

1 allow SCI to have a significant impact on the H₂SO₄ formation even if present in small
2 concentrations. The model studies have shown that, depending on the environment, SCI can
3 have a potentially important impact on H₂SO₄ formation. All these studies are affected by
4 large uncertainties and many simplifications used for coping with the paucity of data on the
5 reactions of specific SCI with various trace gas species, on the speciation of SCI, and on the
6 steady state concentration of SCI in the troposphere. Until now no direct or reproducible
7 indirect method was able to determine the steady state concentration of SCI in the lower
8 troposphere.

9 In this paper, we firstly estimate the concentration of SCI in the lower troposphere, based on
10 the data collected during the HUMPPA-COPEC 2010 campaign (Williams et al., 2011) in a
11 Boreal forest in Finland and the HOPE 2012 campaign in rural southern Germany. The
12 budget of SCI is analyzed using four different approaches: 1) based on an unexplained H₂SO₄
13 production rate (Mauldin III et al., 2012); 2) from the measured concentrations of unsaturated
14 volatile organic compounds (VOC); 3) from the observed OH reactivity (Nölscher et al.,
15 2012); and 4) from an unexplained production rate of OH (Hens et al., 2014). Secondly, we
16 present measurements obtained using our inlet pre-injector laser-induced fluorescence assay
17 by gas expansion technique (IPI-LIF-FAGE) (Novelli et al., 2014a) during the HUMPPA-
18 COPEC 2010 and the HOPE 2012 campaigns. A recent laboratory study performed with the
19 same instrumental setup showed that the IPI-LIF-FAGE system is sensitive to the detection
20 of the OH formed from unimolecular decomposition of SCI (Novelli et al., 2014b). Building
21 on this study, the background OH (OH_{bg}) (Novelli et al., 2014a) measured during the two
22 field campaigns is investigated in comparison with many other trace gases in order to assess
23 if the observations in controlled conditions are transferable to the ambient conditions.

24

1 **2 Instrumentation and field sites**

2 **2.1 IPI-LIF-FAGE description**

3 A comprehensive description of the IPI-LIF-FAGE ground-based instrument, HORUS
4 (Hydroxyl Radical Measurement Unit based on fluorescence Spectroscopy), is given by
5 Novelli et al. (2014a) and only some important features of the instrument are highlighted
6 here. The IPI-LIF-FAGE instrument consists of: the inlet pre-injector (IPI), the inlet and
7 detection system, the laser system, the vacuum system and the instrument control and data
8 acquisition unit. The air is drawn through a critical orifice into a low pressure region (~300-
9 500 Pa) where OH molecules are selectively excited by pulsed UV light around 308 nm. The
10 light is generated at a pulse repetition frequency of 3 kHz by a Nd:YAG pumped, pulsed,
11 tunable dye laser system and is directed into a multipass "White cell" making 32 passes
12 through the detection volume (White, 1942). The air sample intersects the laser beam and the
13 fluorescence signal from the excited OH molecules is detected using a gated micro-channel
14 plate (MCP) detector. IPI, situated in front of the instrument inlet, is used to measure a
15 chemical zero to correct for possible internal OH signal generation. An OH scavenger
16 (propene) is added to the sample air 5 cm in front of the inlet pinhole in a concentration that
17 allows a known, high proportion of atmospheric OH to be scavenged (~ 90 %). The OH
18 scavenger is added every two minutes so that the instrument measures a total OH signal
19 (OH_{tot}) when the OH scavenger is not injected and a background OH signal (OH_{bg}) when the
20 OH scavenger is injected. The difference between these two signals yields the atmospheric
21 OH concentration (OH_{atm}). The efficiency of this technique for measuring OH with this
22 particular LIF-FAGE instrument is described together with the IPI characterisation in Novelli
23 et al. (2014a). The OH calibration of the HORUS instrument is obtained via the production of

1 a known amount of OH and hydroperoxyl radicals (HO_2) from the photolysis of water at 185
2 nm using a mercury lamp. A more detailed description of the instrument calibration is
3 reported by Martinez et al. (2010) and Hens et al. (2014). A calibration factor for the
4 background OH signal observed by the HORUS instrument is currently not available.
5 Therefore, this signal will be discussed and plotted in OH fluorescence counts per seconds
6 (cps) measured by the MCP, normalized by the laser power and corrected for quenching and
7 sensitivity changes towards the detection of OH. The sensitivity of the instrument towards the
8 OH radical is affected by: alignment of the white cell, optical transmission of the
9 components, sensitivity of the MCP, water vapor, internal pressure, and internal temperature
10 (Martinez et al., 2010). These factors affect the sensitivity of HORUS towards the
11 background OH in a similar manner as they mainly impact the sensitivity of the instrument to
12 the detection of OH.

13 We hypothesise that the OH_{bg} is formed chemically within the IPI-LIF-FAGE instrument.
14 Laser induced production of OH radicals was thoroughly tested in the laboratory and in the
15 field (Novelli et al., 2014a) showing that this background OH signal is not induced by the
16 laser beam from double pulsing, nor from air stagnating in the detection cell. By changing the
17 laser power, no quadratic dependency of the OH_{bg} was observed even at night time, when the
18 contribution of the OH_{bg} to the OH_{tot} measured by the instrument is highest (Novelli et al.,
19 2014a). In addition, during the HUMPPA-COPEC 2010 and HOPE 2012 campaigns, the
20 correlation coefficient of the OH_{bg} with the laser power was $R = 0.002$ and $R = 0.2$,
21 respectively.

22 In contrast, ozonolysis of alkenes performed during laboratory tests showed that the IPI-LIF-
23 FAGE instrument is sensitive to the OH formed from unimolecular decomposition of SCI
24 within the low pressure section of the instrument (Novelli et al., 2014b).

1 Recently, most of the LIF-FAGE instruments have been augmented with the titration of
2 OH_{atm} in different environments to determine their background (Amédro, 2012;Mao et al.,
3 2012;Griffith et al., 2013;Woodward-Massey et al., 2015;Griffith et al., 2016;Tan et al.,
4 2016). Some of these instruments showed the presence of an unknown interference (Mao et
5 al., 2012;Griffith et al., 2013;Tan et al., 2016) while for others no clear conclusions were
6 drawn (Amédro, 2012;Woodward-Massey et al., 2015). In addition, laboratory studies (Fuchs
7 et al., 2016;Griffith et al., 2016) have shown similarity with what was observed with the IPI-
8 LIF-FAGE during experiments of ozonolysis of alkenes although the origin of the OH signal
9 was not uniquely attributed to a particular mechanism.

10 Our hypothesis is that the OH_{bg} measured in ambient air with the IPI-LIF-FAGE at least
11 partially originates from unimolecular decomposition of SCI. Section 4 describes the
12 observed behaviour of the signal during the campaigns and its relationship to other observed
13 chemical tracers and discusses if this is compatible with our hypothesis.

14

15 **2.2 Measurement site and ancillary instrumentation**

16 We present measurements from two sites, a boreal forest site in Finland and a rural site in
17 Southern Germany. The HUMPPA-COPEC 2010 (Hyytiälä United Measurements of
18 Photochemistry and Particles in Air – Comprehensive Organic Precursor Emission and
19 Concentration study) campaign took place during summer 2010 at the SMEAR II station in
20 Hyytiälä, Finland (61° 51' N, 24°17' E, 181 m a.s.l.) in a boreal forest dominated by Scots
21 Pines (*Pinus Silvestris L.*). The site hosts continuous measurements of several trace gases and
22 meteorological parameters as well as aerosol particles concentrations, size distributions and
23 composition (Junninen et al., 2009). Further details and a more complete description of the

1 site, the instrumentation and the meteorological conditions during the campaign can be found
2 in Williams et al. (2011) and Hens et al. (2014). A brief description of the instruments used in
3 this study is given here. Ozone was measured by a UV photometric gas analyser (Model 49,
4 Thermo Electron Corporation). A gas chromatograph (GC, Agilent Technologies 6890A)
5 coupled to a mass-selective detector (MS, Agilent Technologies MSD 5973 *inert*) was used
6 for the measurements of biogenic volatile organic compounds (BVOC) (Yassaa et al., 2012).
7 The total OH reactivity was measured by the comparative reactivity method (CRM) (Sinha et
8 al., 2008) for two different heights, one within and one above the canopy (18 and 24 m,
9 respectively) (Nölscher et al., 2012). CRM uses an in-situ kinetics experiment to measure the
10 OH reactivity based on the competitive scavenging of OH by a reference gas (pyrrole) and
11 atmospheric OH reactants. The overall uncertainty of the method during deployment was
12 16% with a limit of detection of 3.0 s^{-1} (Hens et al., 2014). Sulfur dioxide (SO_2)
13 concentration was measured with a fluorescence analyzer (Model 43S, Thermo 20
14 Environmental Instruments Inc.). Aerosol number size distributions between 3.0 nm and 950
15 nm were measured with a Differential Mobility Particle Sizer (DMPS) (Aalto et al., 2001).
16 The size distributions were used for calculating the loss rate of gas-phase sulfuric acid via
17 condensation sink (CS) with the method presented by Kulmala et al. (2001). Sulfuric acid
18 (H_2SO_4) and OH radical concentrations were measured on the ground with a chemical
19 ionization mass spectrometer (CIMS; (Petäjä et al., 2009)). Time series of the measured trace
20 gases are available in the study from Nölscher et al. (2012) and Hens et al. (2014). The
21 average concentrations and their 1σ variability are listed in Table 1 and Table SI-2. For the
22 first period of the campaign, between the 27th and the 31st of July, the IPI-LIF-FAGE
23 instrument was run on the ground side-by-side with the CIMS. On the 2nd of August the IPI-
24 LIF-FAGE instrument was moved to the top of the HUMPPA tower above the canopy and

1 measured there for the remainder of the campaign (12th of August). The data are therefore
2 separated into ground and tower periods

3 The HOPE 2012 (Hohenpeißenberg Photochemistry Experiment) campaign was conducted
4 during the summer of 2012 at the Meteorological Observatory in Hohenpeissenberg, Bavaria,
5 Germany (47° 48' N, 11° 2' E). The observatory is a Global Atmosphere Watch (GAW)
6 station operated by the German Meteorological Service (DWD) and is located at an altitude
7 of 985 m a.s.l. and about 300 m above the surrounding terrain, mainly consisting of meadows
8 and coniferous forests. More information about the site can be found in Handisides et al.
9 (2003). Ozone was measured by UV absorption with TEI 49C (Thermo Electron Corporation,
10 Environmental Instruments) (Gilge et al., 2010). Non-methane hydrocarbons (NMHC) were
11 measured with a GC-flame ionization detection (FID) system (series 3600CX, Varian,
12 Walnut Creek, CA, USA) (Plass-Dülmer et al., 2002). BVOC were detected using a GC
13 (Agilent 6890) with a FID running in parallel with a MS (Agilent Technologies MSD 5975
14 *inertXL*) described by Hoerger et al. (2014). Photolysis frequencies ($J(\text{NO}_2)$ and $J(\text{O}^1\text{D})$) were
15 measured next to the IPI-LIF-FAGE with a set of filter radiometers (Handisides et al., 2003).
16 The OH reactivity was measured with two instruments for a short period of time from the 10th
17 until the 18th of July. One method was the CRM and the same instrument was used as during
18 the HUMPPA-COPEC 2010 campaign. The second method was a new application of the
19 DWD CIMS instrument (Berresheim et al., 2000) which also measured H_2SO_4 and OH
20 radicals. As the data will be used only in a qualitative way for the current study, a very short
21 description of this novel technique is given here and details will be presented in a future
22 publication. With the CIMS instrument, OH radicals are measured by converting them into
23 H_2SO_4 after reaction with SO_2 in a chemical reactor and subtraction of a corresponding
24 background after scavenging the OH with propane (Berresheim et al, 2000). A second SO_2

1 titration zone was used 15 cm (or 140 ms) downstream of the first injection to determine the
2 OH decay from OH radicals generated in the UV-calibration zone immediately upstream of
3 the first titration. The difference between these two titration zones in two consecutive 2.5 min
4 intervals allows the determination of the OH decay, after correcting for ambient OH and wall
5 losses. The uncertainty is estimated at $\pm 2.0 \text{ s}^{-1}$ and the limit of detection is 2.0 s^{-1} . SO_2
6 concentration was measured with a fluorescence analyzer and aerosol size distributions were
7 measured and used to calculate the loss rate of gas-phase sulfuric acid due to CS formed by
8 existing aerosol surface via the method presented by (Birmili et al., 2003). Time series of the
9 measured trace gases are available in Figure SI-1. The average concentrations and their 1σ
10 variability are listed in Table 1 and Table SI-2

11

12 **3 SCI concentrations during HUMPPA-COPEC 2010 and HOPE 2012**

13 **3.1 Missing H_2SO_4 oxidant**

14 The study by Mauldin III et al. (2012) in a boreal forest during the HUMPPA-COPEC 2010
15 campaign showed a consistent discrepancy between the measured H_2SO_4 and the calculated
16 gas phase H_2SO_4 concentration when considering oxidation of SO_2 from OH radical and the
17 condensation onto pre-existing aerosol particles (CS, condensation sink) as the sole
18 production and loss processes, respectively (Eq. 1).

$$19 \quad [H_2SO_4] = \frac{k_{OH+SO_2} \times [OH] \times [SO_2]}{CS} \quad (1)$$

20 The H_2SO_4 concentration is assumed to be in near-steady state: the lifetime of H_2SO_4 in the
21 gas phase is of the order of minutes, i.e. spanning a similar time period compared to the
22 variability in the production and loss pathways, ensuring fast response of the H_2SO_4

1 concentration to varying conditions. Minor deviations from steady state are not critical for the
2 analysis performed in this study, given the uncertainties induced by other parameters.

3 On average the sulfuric acid in the gas phase calculated using Eq. 1 was only half of the total
4 H₂SO₄ observed in the field and lied outside the uncertainties associated with the calculation
5 of the formation channel and the condensation sink (Mauldin III et al., 2012). Although no
6 unambiguous evidence links SCI to the missing oxidant, laboratory tests performed with a
7 similar instrument (Berndt et al., 2012; Berndt et al., 2014a; Sipilä et al., 2014) confirmed the
8 role that SCI could have in the oxidation of SO₂ and formation of H₂SO₄. Assuming that SCI
9 are the only other species in addition to OH that oxidize SO₂ in the gas phase and knowing
10 the rate coefficient of SCI and OH with SO₂, it is possible to calculate the steady state
11 concentration of SCI in that environment:

$$12 \quad [H_2SO_4] = \frac{(k_{OH+SO_2} \times [OH] + k_{SCI+SO_2} \times [SCI]) \times [SO_2]}{CS} \quad (2)$$

13 The rate coefficient between OH and SO₂ at standard pressure is $(2.0 \pm 0.1) \times$
14 $10^{-12} (T/300)^{-0.27} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson et al., 2004). The rate coefficient of SCI with
15 SO₂ was determined by several groups at $(3.3 \pm 2.0) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, (Welz et al.,
16 2012; Taatjes et al., 2013; Liu et al., 2014b; Sheps et al., 2014; Stone et al., 2014; Chhantyal-Pun
17 et al., 2015; Newland et al., 2015a; Newland et al., 2015b; Foreman et al., 2016; Zhu et al.,
18 2016). An earlier, lower value of $\sim 5.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Mauldin III et al. (2012);
19 Berndt et al. (2012)) appears to be hard to reconcile with the remaining literature, as
20 extensively discussed in the supporting information.

21 Equation 2 allows for the calculation of a time series of SCI (Fig. SI-2) yielding an average
22 $[SCI] = (2.3 \pm 2.0) \times 10^4 \text{ molecules cm}^{-3}$. A similar estimate of the SCI time series was
23 derived for the HOPE 2012 campaign (Fig. SI-3). **These time series are discussed in more**

1 details in the supporting information; for the estimation of atmospheric SCI here we focus
2 mostly on the overall concentration.

3 The H₂SO₄ concentration during this campaign can be mainly explained by the reaction
4 between OH and SO₂. Figure 1 shows the correlation between the total production rate of
5 H₂SO₄ (P(H₂SO₄)_{tot}) calculated from the product of measured H₂SO₄ and the condensation
6 sink, as well as the production rate of H₂SO₄ from the reaction of OH and SO₂. The linear
7 regression following the method of York et al. (2004) yields a slope of 0.9 ± 0.02 with a
8 negligible intercept (57 ± 7.0 molecules cm⁻³ s⁻¹). It should be noted that the H₂SO₄ budget
9 for the HOPE 2012 campaign is nearly closed, such that the moderate fluctuations on the
10 source data (CS, [OH], etc.) lead to very large relative uncertainties of the small missing
11 H₂SO₄ production term, and concomitantly the time series for the SCI concentration (Fig. SI-
12 3) shows extreme variability reflecting this noise on the source data. On average, the [SCI]
13 obtained is low, (2.0 ± 3.0) × 10⁴ molecules cm⁻³, with no values in the time series exceeding
14 10⁵ molecule cm⁻³.

15 Repeating the above analysis using the low k_{SCI+SO₂} value of Mauldin III et al. and Berndt et
16 al. yields concentrations of (1.6 ± 2.0) × 10⁶ and (1.0 ± 3.0) × 10⁶ molecule cm⁻³ for the
17 HUMPPA-COPEC and HOPE campaigns, respectively. It is interesting to notice that both
18 values estimated with the fast and low k_{SCI+SO₂} rate coefficient are in agreement with the
19 concentrations calculated from measured VOC and O₃ for polluted and pristine environments,
20 1.9 × 10⁶ molecules cm⁻³ and 4.5 × 10⁴ molecules cm⁻³ respectively, from a previous study
21 (Welz et al., 2012).

22

1 3.2 Measured unsaturated VOC

2 Another method to estimate the SCI concentration is based on their production and loss
3 processes. In a forest SCI are expected to be formed from the ozonolysis of unsaturated
4 BVOC. It is possible to calculate an average steady state concentration for SCI using the
5 following equation

$$6 \quad [SCI] = \sum_i \left(\frac{k_{VOC_i+O_3} \times [VOC_i] \times Y_{SCI}}{L_{SCI, syn}} \right) \times [O_3] \quad (3)$$

7 Where $k_{VOC_i+O_3}$ is the rate coefficient between the VOC_i and ozone (Table SI-2), Y_{SCI} is the
8 yield of SCI in the ozonolysis reaction, and $L_{SCI, syn}$ is the total loss of *syn*-SCI. We assume
9 $[SCI] \approx [SCI_{syn}]$ following the model described by Novelli et al. (2014b), which accounts for
10 many possible losses of SCI including the reaction with water dimers and unimolecular
11 decomposition. The latter study suggests that *anti*-acetaldehyde oxide and formaldehyde
12 oxide react quickly with water and water dimers and that their contributions can be neglected.
13 A yield of SCI formation (Y_{SCI}) of 0.4 was estimated based on the data by Hasson et al.
14 (2001). The steady state concentration of SCI for the HUMPPA-COPEC 2010 campaign was
15 calculated using the measured data for $[O_3]$ and $[VOC_i]$ and an average value of 40 s^{-1}
16 (Novelli et al., 2014b) for $L_{SCI, syn}$ as this value was found to be rather constant and mainly
17 dependent on the unimolecular decomposition rate of the SCI. Equation 3 allows for the
18 calculation of a time series of SCI (Fig. SI-4) yielding an average $[SCI]$ of $\sim (5.0 \pm 4.0) \times 10^3$
19 molecules cm^{-3} . **These time series are discussed in more details in the supporting information;**
20 **for the estimation of atmospheric SCI here we focus mostly on the overall concentration**
21 During the HOPE 2012 campaign a larger number of unsaturated organic trace gases, both
22 anthropogenic and biogenic, were measured (Table SI-1). For Y_{SCI} the same value of 0.4 was

1 used while for $L_{SCI_{syn}}$ the value of 32 s^{-1} , obtained from the model described by Novelli et al.
2 (2014b) for the rural European environment, was used. Using these values in Eq. 3 results in
3 $[SCI] = (7.0 \pm 6.0) \times 10^3 \text{ molecules cm}^{-3}$, obtained as an average of the SCI time series (Fig.
4 SI-5). It should be noted that recent work on the unimolecular decomposition (Fang et al.,
5 2016b; Long et al., 2016; Smith et al., 2016) yields loss rates significantly faster than used
6 here; this implies that the $[SCI]$ obtained here could be an overestimate.

7

8 **3.3 OH reactivity**

9 During HUMPPA-COPEC 2010, between 27th July and 12th August, an average OH
10 reactivity, $R = 9.0 \pm 7.6 \text{ s}^{-1}$, was measured. On average, the majority of the measured OH
11 reactivity ($R_{unex} = 7.4 \pm 7.4 \text{ s}^{-1}$, i.e. 80 %) was not accounted for by the measured organic and
12 inorganic trace gases (Fig. SI-6). Biogenic emissions comprised up to ~ 10 % of the total
13 measured OH reactivity and up to half of the calculated OH reactivity (Fig. SI-6). As the
14 measurement site was located in a pristine forest environment, affected only little by
15 anthropogenic emissions (Williams et al., 2011), it is likely that a large fraction of the
16 unexplained OH reactivity was formed by unmeasured primary emissions by the vegetation
17 and secondary products of oxidation. By assuming that the unmeasured VOC are unsaturated,
18 and by using a lumped rate coefficient, k_{VOC+OH} , between OH and the fraction of unspciated
19 VOC of $7.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, typical for an OH addition to a carbon-carbon double
20 bond (Atkinson et al., 2004; Peeters et al., 2007), it is possible to estimate the concentration
21 $[VOC_{unknown}]$ of VOC that would be necessary to close the OH reactivity budget (Eq. 4).

$$22 \quad R_{unex} = k_{VOC+OH} \times [VOC_{unknown}] \quad (4)$$

1 Using Eq. 4, a time series for $[VOC_{unknown}]$ with an average of $(1.0 \pm 1.0) \times 10^{11}$ molecules
2 cm^{-3} is obtained. These values are substituted into Eq. 3 and a lumped rate coefficient k of 7.0
3 $\times 10^{-17}$ molecules cm^{-3} is used for reaction of $[VOC_{unknown}]_t$ with $[O_3]_t$ at time t . This k value
4 is based on the rate coefficient of the measured VOC with O_3 weighted with their abundance
5 (Table SI-1). The same Y_{SCI} and L_{SCIsyn} , of 0.4 and 40 s^{-1} , respectively, were used as described
6 in section 3.2. With these values, a time series of SCI (Fig. SI-7) with an average of $\sim (1.0 \pm$
7 $1.0) \times 10^5$ molecules cm^{-3} is obtained. To this SCI concentration estimate, we add the SCI
8 formed from the measured unsaturated VOC, $[SCI] = (5.0 \pm 4.0) \times 10^3$ molecules cm^{-3} , to
9 obtain the total SCI across all VOC. As this estimate requires assumptions for the rate
10 coefficient between $[VOC_{unknown}]$ and OH and O_3 , a sensitivity study probing the upper and
11 lower bounds of this estimate is described in the supplementary information. **The time series**
12 **are discussed in more details in the supporting information; for the estimation of atmospheric**
13 **SCI here we focus mostly on the overall concentration.**

14 During the HOPE 2012 campaign the total OH reactivity was on average $3.5 \pm 3.0 \text{ s}^{-1}$. Using
15 the measured trace gas concentrations it is possible to calculate the expected OH reactivity
16 (Fig. SI-8). Table SI-2 lists all the species included in the calculation of the OH reactivity
17 with their rate coefficient with OH. An average value of $2.7 \pm 0.7 \text{ s}^{-1}$ was calculated. Figure
18 SI-8 shows that half of the measured OH reactivity can be explained by methane, carbonyl
19 compounds (mainly acetaldehyde and propanal) and inorganic compounds which were
20 present in higher concentrations compared to the HUMPPA-COPEC 2010 campaign (Table
21 SI-2). On average, 24 % of the measured OH reactivity remains unexplained by the measured
22 trace gases. In contrast to the HUMPPA-COPEC 2010 campaign, in HOPE 2012 a more
23 complete speciation of VOC was measured (Table SI-1) and the site was influenced by
24 relatively fresh anthropogenic emissions. With the extensive VOC speciation available, the

1 reactivity budget can virtually be closed, but any remaining unexplained OH reactivity could
2 still be due to unmeasured VOC. The time series for this unexplained OH reactivity, typically
3 about $\sim 1 \text{ s}^{-1}$, shows very large variability as it reflects the statistical noise of the small
4 difference between measured and calculated OH reactivities, both of which are associated
5 with variability. The resulting [SCI] time series (Fig. SI-9) is also highly variable, and yields
6 a low average SCI concentration of $(2.0 \pm 1.5) \times 10^4 \text{ molecules cm}^{-3}$, with no values
7 exceeding $6.0 \times 10^4 \text{ molecule cm}^{-3}$.

8 The total SCI is then obtained by summing the SCI predicted from the measured VOC and
9 from the unexplained OH reactivity, leading to a total SCI concentration of $(7.0 \pm 6.0) \times 10^3$
10 molecules cm^{-3} .

11

12 **3.4 Unexplained OH production rate**

13 During the HUMPPA-COPEC 2010 campaign, the comprehensive measurements (Williams
14 et al., 2011) allowed the calculation of a detailed OH budget (Hens et al., 2014). Most of the
15 OH production during daytime is due to photolysis of O_3 and recycling of HO_2 back to OH
16 via reactions with NO and O_3 . This result holds for both high ($R > 15 \text{ s}^{-1}$) and low ($R \leq 15 \text{ s}^{-1}$)
17 OH reactivity episodes during the campaign. While the OH budget can be closed during
18 daytime ($J(\text{O}^1\text{D}) > 3.0 \times 10^{-6} \text{ s}^{-1}$) for low OH reactivity periods, during periods with high OH
19 reactivity there was a large unexplained production rate of OH, $P_{\text{OH}}^{\text{unexplained}} = (2.0 \pm 0.7) \times 10^7$
20 molecule $\text{cm}^{-3} \text{ s}^{-1}$, which can thus be surmised to originate from VOC chemistry. In addition,
21 for both periods, during night time ($J(\text{O}^1\text{D}) \leq 3.0 \times 10^{-6} \text{ s}^{-1}$), the IPI-LIF-FAGE and the CIMS
22 instruments both measured non-negligible OH concentrations (Hens et al., 2014) where most

1 of the OH production was from unknown sources ($P_{OH}^{unexplained} = 1.0 \pm 0.9 \times 10^6$ molecule cm^{-3}
2 s^{-1} (1σ) and $P_{OH}^{unexplained} = 1.7 \pm 0.7 \times 10^7$ molecule $\text{cm}^{-3} \text{s}^{-1}$ (1σ) for low and high reactivity,
3 respectively). Our hypothesis is that ozonolysis of VOC could represent the missing OH
4 source. Indeed, formation of OH from oxidation of unsaturated VOC has been shown to be an
5 important source of OH in winter, indoors and during night time (Paulson and Orlando,
6 1996;Geyer et al., 2003;Ren et al., 2003;Heard et al., 2004;Harrison et al., 2006;Johnson and
7 Marston, 2008;Shallcross et al., 2014). As OH formation from ozonolysis proceeds through
8 Criegee intermediates (Fig. 2), we can attempt to estimate a SCI concentration from the OH
9 budget. First, we estimate from the unexplained OH production $P_{OH}^{unexplained}$ a so-called
10 unexplained O_3 reactivity, $\Sigma(k_{\text{VOC}+\text{O}_3} \times [\text{VOC}_{\text{unidentified}}])$, assuming a certain yield of OH from
11 ozonolysis of unsaturated VOC. Next, we estimate a yield of SCI based on available literature
12 data, and finally we combine both to estimate the SCI concentration required to close the OH
13 budget. In contrast to the previous estimates, an average value is obtained for the SCI, and
14 not a time series, as we start from the average $P_{OH}^{unexplained}$, as reported in Hens et al. (2014).
15 Assuming that all unexplained OH production, $P_{OH}^{unexplained}$, comes from VOC ozonolysis with
16 a certain OH yield Y_{OH} we obtain:

$$17 \quad P_{OH}^{unexplained} = k_{\text{voc}+\text{O}_3} \times [\text{VOC}_{\text{unidentified}}] \times [\text{O}_3] \times Y_{OH} \quad (5)$$

18 where $\text{VOC}_{\text{unidentified}}$ includes the VOC not considered in the OH budget performed by Hens
19 et al. (2014), i.e. the VOC causing the unknown OH reactivity discussed above. The average
20 total OH yield from ozonolysis, Y_{OH} , is estimated at about 0.6 based on observed OH yields
21 from the literature (Atkinson et al., 2006). OH formation from ozonolysis occurs through two
22 channels (Fig. 2): prompt formation by the decomposition of chemically activated CI^* , and

1 delayed OH by formation of SCI followed by their thermal decomposition; there are also
2 product channels not yielding OH. The prompt yield of OH, $Y_{OH}^{CI^*}$ is estimated at ~ 0.4 from
3 SCI scavenging experiments (Atkinson et al., 2004); the remaining yield Y_{OH}^{SCI} is then formed
4 from SCI, where $Y_{OH} = Y_{OH}^{CI^*} + Y_{OH}^{SCI}$ and hence $Y_{OH}^{SCI} \approx 0.2$.

5 We adopt a value for Y_{SCI} of 0.4, as argued in section 3.2. The SCI formed do not all
6 decompose to OH, e.g. *anti*-CI tend to form esters instead. We label all SCI able to yield OH
7 as SCI_{syn} , without mandating a speciation but following the observation that *syn*-CI usually
8 yield OH through the vinylhydroperoxide channel. The total SCI yield is then divided into a
9 fraction, Y_{syn} , forming SCI_{syn} , and the remainder, Y_{anti} , forming non-OH-generating SCI. Little
10 information is available on the $Y_{syn}:Y_{anti}$ ratio, with only a few theoretical calculations on
11 smaller alkenes and a few monoterpenes (Rathman et al., 1999;Fenske et al., 2000b;Kroll et
12 al., 2002;Nguyen et al., 2009b;Nguyen et al., 2009a). For most of these compounds the ratio
13 of *syn*- to *anti*-SCI is between 0.2 and 1.0 (Rickard et al., 1999) where a larger fraction of
14 *syn*- to *anti*-SCI, or vice versa, will depend on the single alkene. As there is no information
15 available for the VOC included in this study, we estimate the ratio of Y_{syn} to Y_{anti} as 1:1. This
16 number avoids overestimating the impact of SCI in the OH production and, using the *syn* to
17 *anti* range indicated above, would cause a variation in the final [SCI] estimate of maximum
18 20 %, (see eq. 7 and Figure 3) well below the total uncertainty of the result.

19 The production of OH from SCI_{syn} formed from VOC not included in the OH budget is then
20 $k_{OH} \times [SCI_{syn}]$, where we estimate $k_{OH} \approx 20 \text{ s}^{-1}$ as measured by Novelli et al. (2014b) for *syn*-
21 CH_3CHOO , and where the steady state concentration of the SCI_{syn} , $[SCI_{syn}]$, is determined by
22 the ratio of the formation processes and the sum $L_{SCI_{syn}}$ of the loss processes already defined
23 above:

$$1 \quad [SCI_{syn}] = \frac{k_{voc+O_3} \times [VOC_{unidentified}] \times [O_3] \times Y_{SCI} \times Y_{syn}}{L_{SCI_{syn}}} \quad (6)$$

2 Merging the above equations, expressing the measured OH production from unknown
 3 sources as the sum of direct OH production from CI^* and indirect from SCI_{syn} , we obtain:

$$4 \quad P_{OH}^{unexplained} = k_{voc+O_3} \times [VOC_{unidentified}] \times [O_3] \times \left(Y_{OH}^{CI^*} + Y_{SCI} \times Y_{syn} \times \frac{k_{OH}}{L_{SCI_{syn}}} \right) \quad (7)$$

5 The measured $P_{OH}^{unexplained}$ and $[O_3]$, and the estimates of the other parameters allow us to
 6 calculate the factor $k_{voc+O_3} \times [VOC_{unidentified}]$. Substituting this factor into Eq. 6 yields an
 7 estimate of the steady state concentration of SCI_{syn} . With a value for $P_{OH}^{unexplained}$ of 1.0×10^6
 8 molecules $cm^{-3} s^{-1}$ as observed for low reactivity episodes and at night during HUMPPA, a
 9 steady state concentration of SCI_{syn} of $(2.0 \pm 2.0) \times 10^4$ molecules cm^{-3} is calculated. For high
 10 reactivity episodes during HUMPPA-COPEC 2010, the missing $P_{OH}^{unexplained}$ of 2.0×10^7
 11 molecules $cm^{-3} s^{-1}$ results in a SCI concentration of $(4.0 \pm 4.0) \times 10^5$ molecules cm^{-3} . To
 12 obtain the total SCI concentration, we then need to add the non-OH-producing SCI. Here we
 13 assume that these are mostly *anti*-SCI or H_2COO , both of which react rather quickly with
 14 H_2O or $(H_2O)_2$ (Taatjes et al., 2013;Chao et al., 2015;Lewis et al., 2015), and that their
 15 contribution can be neglected. We thus obtain that $[SCI] \approx [SCI_{syn}]$. To this we add the SCI
 16 concentration calculated from the measured unsaturated VOC (section 3.2), $(5.0 \pm 4.0) \times 10^3$
 17 molecules cm^{-3} , to obtain the SCI formed from all VOC.

18 For HOPE 2012 it is difficult to accurately derive an OH budget due to the lack of
 19 information on the HONO concentration, which can represent an important primary source of
 20 OH. A detailed analysis of the OH production and loss during the campaign thus requires a

1 detailed model study to derive HONO concentrations, which is outside the scope of this
2 paper. Hence, an estimate on the SCI from a possible missing OH production rate during the
3 HOPE 2012 campaign is not included here.

4 Equation 7, for a given set of yields, unimolecular decomposition rates and SCI losses, allows
5 the estimate of the relative contribution of SCI and Cl^* to the total production rate of OH
6 from the ozonolysis of VOC. With the yields considered in this study and for a unimolecular
7 decomposition rate of SCI into OH of 20 s^{-1} , the SCI would contribute up to 12 % to the total
8 formation of OH from ozonolysis of VOC in both environments. This indicates that the SCI
9 do not have a large impact in the production of OH radicals and at the same time emphasizes
10 how important a realistic estimate of VOC concentration is for modeling the OH radical as
11 already underlined by (Hens et al., 2014).

12 **3.5 Robustness of the [SCI] estimates**

13 Figure 3 summarises the steady state concentration of SCI calculated on the basis of the
14 H_2SO_4 budget, the measured unsaturated VOC concentration and OH reactivity (R), and the
15 OH budget for the HUMPPA-COPEC 2010 and HOPE 2012 campaigns. By considering the
16 lower and the highest values estimated from the measured VOC and from the missing H_2SO_4
17 oxidant for both campaigns, respectively, the steady state concentration of SCI is calculated
18 to be between 5.0×10^3 and 2.0×10^6 molecules cm^{-3} for the boreal forest environment during
19 the HUMPPA-COPEC 2010 campaign and between 7.0×10^3 and 1.0×10^6 molecules cm^{-3}
20 for rural Germany during the HOPE 2012 campaign (Table 2). The SCI concentrations
21 calculated using these approaches represent a best-effort estimate made for the environments
22 studied here based on the available data; due to the many uncertainties related to the
23 chemistry of SCI both in production and loss processes these estimates span about two orders
24 of magnitude.

1 The estimate of the SCI concentration from the sulfuric acid budgets relies on the rate of
2 oxidation of SO₂ to H₂SO₄. As indicated in section 3.1, two significantly different rate
3 coefficients for the reaction of SCI with SO₂ are currently available. One coefficient is high, ~
4 $3.3 \pm 2.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, while the other is several orders of magnitude lower, 5.0
5 $\times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Justifications of the differences in the values due to the diverse
6 procedures, i.e. direct detection of SCI + SO₂ for the high rate coefficient and detection of
7 H₂SO₄ for the lower one, are difficult, while recent measurements tend to agree with the
8 highest value. This casts doubts on the highest obtained SCI concentrations of $\sim 10^6$
9 molecules cm⁻³. In addition, the remaining three estimates strongly depend on the yield of
10 SCI, $k_{\text{voc}+o}$ and $L_{\text{SCI}_{\text{syn}}}$. Among these, the parameter with the highest uncertainty is the loss
11 rate of *syn*-SCI, $L_{\text{SCI}_{\text{syn}}}$, as it is based on relatively few studies, which report large differences
12 between the observations. In this study, a value of 40 s^{-1} and of 32 s^{-1} , based on previous
13 model analysis (Novelli et al., 2014b), for the HUMPPA-COPEC 2010 and HOPE 2012
14 campaigns respectively, were used. Recent work (Smith et al., 2016; Fang et al., 2016a; Long
15 et al., 2016) suggests a faster unimolecular decomposition rate for the acetone oxide Criegee
16 intermediate, exceeding 10^2 s^{-1} in ambient conditions. It is currently not clear whether this
17 rate applies to more substituted SCI as formed from monoterpenes but the use of these higher
18 decomposition rate in the model by (Novelli et al., 2014b) would result in a total $L_{\text{SCI}_{\text{syn}}}$ of ~
19 110 s^{-1} . This loss rate would decrease the estimated SCI concentration by almost a factor of 3,
20 closer to the lower estimates not exceeding $10^5 \text{ molecule cm}^{-3}$; this also casts doubt on the
21 highest estimates given in Figure 3. Therefore, an average estimated SCI concentration of
22 about $5 \times 10^4 \text{ molecules cm}^{-3}$, with an order of magnitude uncertainty, is considered more
23 appropriate for both campaigns.

24

1 **4 The source of the OH background signal**

2 In this section we examine the background OH signal, OH_{bg} (Novelli et al., 2014b) measured
3 during the two field campaigns discussed in the previous sections. In particular, we examine
4 if this signal is consistent with the SCI chemistry and concentrations indicated above.

5 **4.1 Correlation of OH_{bg} with temperature**

6 The time series of the background OH signal measured during the HUMPPA-COPEC 2010
7 and HOPE 2012 campaigns are shown together with temperature and $J(\text{O}^1\text{D})$ values in Fig. 4.
8 Increases and decreases in the OH_{bg} signal follow the temperature changes. During the
9 HUMPPA-COPEC 2010 campaign the OH_{bg} shows a strong correlation with temperature
10 (Fig. 5) with a correlation coefficient $R = 0.8$ for the exponential fit. The exponential
11 dependency with temperature is in agreement with data shown by Di Carlo et al. (2004) for
12 the unexplained OH reactivity and indicates that the species responsible for the OH_{bg} strongly
13 correlate with emission of biogenic VOC (BVOC) such as monoterpenes and sesquiterpenes,
14 which have been shown to also exponentially depend on temperature (Guenther et al.,
15 1993;Duhl et al., 2008;Hakola et al., 2003). This suggests that OH_{bg} is directly related to
16 BVOC chemistry. The relationship between OH_{bg} and temperature during the HOPE 2012
17 campaign is less obvious. It is possible to observe a weakly exponential correlation between
18 the two ($R = 0.51$, Fig. SI-10) but there is very large scatter in the data. It is worthwhile to
19 underline the differences between the two environments. The forest in Finland is essentially
20 pristine and BVOC dominated while in southern Germany a large fraction of non-biogenic
21 VOC was observed. The lack of a clear exponential correlation between OH_{bg} and
22 temperature during the HOPE 2012 campaign could suggest different precursors or a
23 different origin for the OH_{bg} within the two environments.

1 During both campaigns a negligible correlation, $R = 0.2$, was observed between background
2 OH and $J(O^1D)$. This suggests that the OH_{bg} does not primarily originate from photolabile
3 species.

4 **4.2 Correlation of OH_{bg} with unexplained OH reactivity**

5 As described in section 3.3, during the HUMPPA-COPEC 2010 campaign high average OH
6 reactivity was observed ($\sim 9 \text{ s}^{-1}$), of which between 60 % and 90 % cannot be explained by
7 the loss processes calculated from the measured species (Nölscher et al., 2012). A large
8 unexplained fraction of the reactivity has often been observed, especially in forested
9 environments (Di Carlo et al., 2004; Sinha et al., 2008; Edwards et al., 2013) indicating a large
10 fraction of undetected BVOC and/or secondary oxidation products. The OH_{bg} shows some
11 correlation with the measured unexplained OH reactivity at 18 m, for the period on the
12 ground ($R = 0.4$), and the measured unexplained OH reactivity at 24 m, for the period on the
13 tower ($R = 0.4$) (Fig. 6). If we consider only night time data, i.e. $J(O^1D) \leq 3.0 \times 10^{-6} \text{ s}^{-1}$
14 (Hens et al., 2014), we obtain better agreement between the two datasets for both ground and
15 tower periods. During the night a large fraction of observed OH production (section 3.4)
16 could not be explained, which can tentatively be attributed to formation of OH from
17 ozonolysis of BVOC, suggesting that the background OH could be related to such a process.
18 Correlation between the OH_{bg} and the OH reactivity was also observed in a study by Mao et
19 al. (2012) in a Ponderosa pine plantation (California, Sierra Nevada Mountains) dominated
20 by isoprene where even higher OH reactivity was observed ($\sim 20 \text{ s}^{-1}$).

21 During the HOPE 2012 campaign such a correlation with the unexplained OH reactivity was
22 not observed ($R = 0.1$). The OH reactivity was, on average, 3 times less than during the
23 campaign in Finland and, as shown in section 3.3, 50 % can be explained by reaction of OH
24 with methane, formaldehyde, acetaldehyde, inorganic compounds (NO_x , SO_2 , CO) and

1 anthropogenic VOC. On average only 17 % of the OH reactivity is caused by reaction of OH
2 with BVOC in this environment (Fig SI-8), dropping to 10 % during the night. The
3 unexplained OH reactivity is not influenced by distinguishing between day and night time
4 data suggesting a small contribution of non-measured BVOC. As this site is more strongly
5 affected by anthropogenic emissions (Table SI-2) compared to the site in Finland, assuming
6 that the OH_{bg} originates from BVOC driven chemistry, a lack of correlation between OH_{bg}
7 and OH reactivity can be expected.

8

9 **4.3 Correlation of OH_{bg} with ozonolysis chemistry**

10 During the HUMMPA-COPEC 2010 campaign a high correlation with O_3 , $R = 0.7$ (Fig. SI-
11 11), indicates that background OH likely originates from ozonolysis processes. A comparison
12 of background OH with the product of ozone concentration, measured unsaturated VOC
13 concentration and their ozonolysis rate coefficient does not show the same relationship. No
14 correlation ($R = 0.05$) is found by using the measured BVOC concentrations (Table SI-1). As
15 most of the OH reactivity remains unexplained, with measured BVOC comprising less than
16 10 % of the measured OH reactivity (Fig SI-6, Table SI-2), the lack of correlation could
17 suggest that the VOC responsible for the formation of SCI detected by the HORUS
18 instrument are likely part of the large fraction of unmeasured species to which a correlation
19 was reported in the previous section.

20 During HOPE 2012 a weak correlation was observed between background OH and ozone (R
21 $= 0.5$, fig. SI-12).

22 This campaign, from July 10th to August 19th 2012, encompasses a time period, from 1st to 3rd
23 of August 2012, which was characterized by tree cutting in the vicinity of the measurement

1 site. During this period a significantly larger fraction of unexplained OH reactivity, up to 40
2 % (Fig. SI-13), was observed. The relative contribution of measured BVOC and inorganic
3 compounds did not change, while the presence of unidentified BVOC emitted from the trees
4 as a result of the stress induced on the plants from the cutting activity, caused the larger
5 fraction of unexplained reactivity. Figure 7 shows the correlation between OH_{bg} and the
6 product $k_{\text{O}_3}[\text{VOC}][\text{O}_3]$ of measured unsaturated VOC concentration (Table SI-1), $[\text{O}_3]$ and
7 the relevant ozonolysis rate coefficients. In red are depicted the data points belonging to the
8 tree cutting period, which naturally correspond to a larger OH_{bg} concentration for similar
9 concentrations of measured VOC during the rest of the campaign, as the additional
10 contribution from the non-identified BVOC is neglected. The overall correlation appears to
11 be pretty poor in particular due to the few points scattering in the lower right corner. These
12 points all belong to three consecutive days, from 26th to 28th of July, which were
13 characterised by high temperature and large concentrations of BVOC (Table SI-3). As
14 noticeable in Figure 4, during those three days the OH_{bg} strongly deviates from the
15 temperature trends and reaches lower values. At present, the reason for such a low
16 concentration of OH_{bg} , during a period which should favour its formation if it originates from
17 SCI, is unclear. The instrument was left unattended at the site and the drop in the quality of
18 the signals required its shutdown on the evening of the 28th of July. However, as no evidence
19 was found to suggest an error in the data the points have not been omitted. Excluding that
20 period yields a correlation factor of $R = 0.65$. The correlation line intercept could arise for a
21 number of reasons. Unmeasured components of the OH reactivity (i.e. unspicated VOCs)
22 are not accounted for in the calculation, and doing so would shift the data to higher $[\text{VOC}]$,
23 decreasing the positive intercept. This is also consistent with a higher intercept for the cutting
24 tree period where a larger unexplained OH reactivity was observed. It is also conceivable that

1 the intercept is in part due to an additional, non-ozonolysis source of background OH. One
2 candidate for the night time periods could be NO₃ as found in the work by Fuchs et al. (2016).
3 Unfortunately, there was no measurement of the NO₃ radical during the HOPE 2012
4 campaign, but based on previous studies at the site (Handisides et al., 2003), a concentration
5 up to 14 pptv of NO₃ could be present and could have a detectable impact.

6 Apart from the possible partial origin of OH_{bg} from NO₃ or other interferences, there are also
7 indications that the background OH could originate from ozonolysis of unsaturated biogenic
8 compounds. The correlation analysis requires that all VOCs are accounted for, and omitting
9 large contributions from unspiciated VOCs, as evidenced e.g. by OH reactivity
10 measurements, can be expected to reduce the correlation as observed in the case of
11 HUMPPA-COPEC 2010. The reason for the lack of correlation during the period from 26th to
12 28th July 2012 during HOPE-2012 characterised by large BVOC emissions remains unclear.

13

14 **4.4 Correlation of OH_{bg} with P(H₂SO₄)_{unex}**

15 During both campaigns, measurements of H₂SO₄, SO₂, OH and CS (condensation sink) were
16 performed allowing the calculation of the sulfuric acid budget in the gas phase. As shown by
17 Mauldin III et al. (2012), during the HUMPPA-COPEC 2010 campaign the well-known SO₂
18 oxidation process by OH (Wayne, 2000) (Eq. 1) was not sufficient to explain the measured
19 concentration of H₂SO₄. As shown in section 3.1, half of the production rate of H₂SO₄, ~ 1 x
20 10⁴ molecules cm⁻³ s⁻¹, cannot be explained by reaction with OH radicals (Fig. 8). The
21 missing oxidant is assumed to be SCI, as discussed in section 3.1, because of their fast
22 reaction rate with SO₂. As our hypothesis about the origin of the OH_{bg} supports this
23 assumption, we compared the [H₂SO₄]_{unex} observed during the HUMPPA-COPEC 2010

1 campaign with the OH_{bg} multiplied by SO_2 for the ground-based period when the instruments
2 (HORUS and CIMS) measured side-by-side (Fig. 9). The two datasets indicate a correlation
3 coefficient of $R = 0.6$ suggesting that whichever species is responsible for the oxidation of
4 SO_2 is related to the formation of OH within the HORUS instrument.
5 Note that for the HOPE 2012 campaign the same budget calculation shows only a small
6 fraction (10 %) of unexplained H_2SO_4 production rate (Fig. 1).
7 Assuming SCI to be the unknown SO_2 oxidant, the results observed in both campaigns are in
8 agreement with the modeling study by Boy et al. (2013), who analyzed measurements at the
9 same sites described in this study. Similar to our result, they found a larger contribution of
10 SCI in the formation of H_2SO_4 for the boreal forest compared to rural Germany. As the OH
11 concentration differs by, on average, less than 50 % between the two environments, a similar
12 concentration of SCI in HOPE to that calculated for HUMPPA-COPEC 2010 would
13 contribute up to 30 % in the formation of H_2SO_4 . However, the H_2SO_4 budget during this
14 campaign can approximately be closed by only considering the measured OH concentrations,
15 suggesting that the concentration of SCI in this environment is smaller than that during the
16 HUMPPA-COPEC 2010 campaign. This is consistent with the calculation in section 3 based
17 on the smaller reactivity and hence smaller VOC concentration in this environment

18 **4.5 Scavenging experiments**

19 A series of scavenging tests of the OH_{bg} was performed during the HOPE 2012 campaign to
20 help identify the interfering species. SO_2 was chosen as scavenger for the species causing the
21 OH_{bg} , as it has been shown in several laboratory studies to react quickly with SCI ($k \sim 3.3 \times$
22 $10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) mostly independently of their structure (Taatjes et al., 2014). The
23 injection of SO_2 was performed through the IPI system (Novelli et al., 2014a) together with
24 an OH scavenger. First the OH scavenger propane was injected within IPI to remove the

1 atmospheric OH; subsequently, SO₂ was injected in addition to the OH scavenger (Fig. 10).
2 A set of experiments were performed at the end of the campaign resulting in the depletion of
3 the OH_{bg} signal as shown in Figure 10. The concentration of SO₂ is small enough not to
4 scavenge SCI inside the low pressure section of the instrument, nor is it additionally
5 removing atmospheric OH within the IPI system as the lifetime of OH by reaction with SO₂
6 is 200 times that of propane. With the addition of SO₂ (1 x 10¹³ molecules cm⁻³ in the sampled
7 air) it is possible to suppress the OH_{bg} signal from the instrument to within the zero noise,
8 indicating that the OH_{bg} signal originates from an SCI-like species that reacts with SO₂ and
9 decomposes unimolecularly to OH. Similar results were obtained in later field campaigns;
10 this will be discussed in the pertaining upcoming publications. Note that it is not possible to
11 link the signal strength directly to an OH or precursor concentration, as analysed in the
12 following section.

13

14 **4.6 SCI as a source of background OH**

15 During the HUMPPA-COPEC 2010 campaign the background OH showed a strong
16 exponential relationship with temperature (R = 0.8) and it correlates with unexplained OH
17 reactivity (R = 0.5), which suggests correlation with BVOC, with ozone (R = 0.7), and also
18 with the P(H₂SO₄)_{unex} (R = 0.6). During the HOPE 2012 campaign a weak exponential
19 correlation with temperature was recognized (R = 0.5) but no correlation was observed with
20 OH reactivity. The OH_{bg} correlated with the product of ozone and unsaturated VOC for most
21 of the campaign (R = 0.6) although not for a period of three days at the end of July with
22 partly higher BVOC-O₃ turnover. In addition, during HOPE 2012 the OH_{bg} signal was
23 scavenged by the addition of SO₂.

1 All evidence presented indicates that substantial parts of the OH_{bg} originate from a species
2 formed during the ozonolysis of unsaturated VOC that decomposes into OH, is removable by
3 SO_2 and, if present in a significant concentration, increases the H_2SO_4 production. We are
4 currently not aware of any chemical species, other than SCI, known to oxidise SO_2 at a fast
5 enough rate and also decompose into OH. In addition, HORUS was shown to be sensitive to
6 the OH formed after unimolecular decomposition of SCI in the low-pressure region of the
7 instrument (residence time 2 ms) in controlled laboratory studies (Novelli et al., 2014b).
8 During the HUMPPA-COPEC 2010 campaign, the correlation with OH reactivity improved
9 when considering only data during night time, the period during which a higher fraction of
10 the production rate of OH could not be accounted for (Hens et al., 2014). Indeed, during the
11 night recycling via HO_2+NO is low due to the negligible NO concentration, therefore a
12 different path of formation of OH is expected. One likely path could be the formation of OH
13 from excited and stabilised CI formed from ozonolysis of unsaturated compounds.

14 The considerations above are all consistent with the hypothesis that OH_{bg} largely originates
15 from unimolecular decomposition of SCI in the field as well as in the laboratory.

16 Attempts to analyse the absolute concentration of SCI based on our OH_{bg} , however, indicates
17 that this hypothesis is not without difficulties. A particular problem is that to date no method
18 is available to produce and quantify a known concentration of a specific SCI conformer,
19 which precludes the absolute calibration of SCI-generated OH. *A priori*, it seems unlikely
20 that the IPI-LIF-FAGE instrument calibration factor for ambient OH, i.e. sampled from
21 outside the instrument through the nozzle, is identical to the sensitivity for OH generated
22 inside. The transmission factor through our nozzle pinhole is currently not known for OH
23 radicals; the calibration factor used for ambient OH accounts for this transmission as well as
24 for e.g. OH losses on the walls, alignment of the white cell, transmission optics, and response

1 of the MCP. These last three factors should affect the OH generated from any interfering
2 species similarly, while wall losses and transmission through the pinhole are different and
3 possibly also differ between SCI conformers. Additionally, different SCI vary in their
4 unimolecular decomposition rates and hence affect calibration by a different time-specific
5 OH yield. For example, theoretical studies (Vereecken and Francisco, 2012) and laboratory
6 experiments (Smith et al., 2016) indicate that acetone oxide will decompose faster than *syn*-
7 acetaldehyde oxide causing the formation of a different amount of OH, which in turn will
8 also be affected by different loss rates in the low pressure segment of the instrument. Thus, it
9 is not possible to convert the internal OH to an absolute SCI concentration since the mixture
10 of SCI is not known. At best one could obtain an "average" sensitivity factor, if one knew the
11 OH_{bg} formed from a series of reference SCI conformers, and if the ambient SCI speciation is
12 known and not too strongly dependent on reaction conditions. To further illustrate the need of
13 a SCI-specific calibration, we try to simply calculate the external [SCI] from the internal
14 OH_{bg} signal strength, calibrated based on the combined experimental and modelling study by
15 Novelli et al. (2014b). For a SCI mixture that behaves identical to *syn*- CH_3CHOO , the OH_{bg}
16 from the HUMPPA-COPEC 2010 campaign would then indicate an external [SCI] $\geq 2 \times 10^7$
17 molecules cm^{-3} , well above the estimates presented in section 3. Moreover, the observed
18 OH_{bg} signal interpreted in this way would imply an ambient OH production exceeding $4 \times$
19 10^8 molecules $\text{cm}^{-3} \text{ s}^{-1}$, clearly in disagreement with known chemistry, and also inconsistent
20 with our estimates (Table 2). If we assume a faster decomposition rate for the SCI of 200 s^{-1} ,
21 a higher fraction of the SCI decomposes in the low-pressure region, i.e. 80 % compared to 25
22 % for $k_{\text{uni}} = 20 \text{ s}^{-1}$. This leads to a higher OH signal per SCI, and from this a [SCI] of $4.0 \times$
23 10^6 molecules cm^{-3} , though the implied ambient OH production would remain significantly
24 too high. Thus, the conversion of the OH signal to an absolute concentration of ambient SCI

1 is not unambiguous without full SCI speciation and knowledge of their chemical kinetics.
2 Note furthermore that these [SCI] estimates would represent a lower limit as we only observe
3 SCI that decompose to OH, whereas e.g. *anti*-SCI convert to acids/esters.

4 In an effort to work towards SCI-specific calibration, we probed the transmission of OH and
5 *syn*-CH₃CHOO through the nozzles and the low-pressure region in the instrument, with
6 explorative laboratory tests using a traditional nozzle and a molecular beam skimmer nozzle,
7 where the latter has much thinner sidewalls and a significantly narrower gas expansion,
8 strongly reducing wall contact. The laboratory test showed that the OH radical has a 23 %
9 higher transmission through the molecular beam nozzle compared to the traditional nozzle.
10 The *syn*-acetaldehyde oxide did not show any statistical difference in the transmission
11 between the two nozzles. This indicates that (a) SCI and OH have a different transmission
12 efficiency and most likely different wall losses, underlining that the OH calibration factor is
13 not applicable to SCI for ambient measurements, and (b) that the calibration factor for OH
14 obtained for ambient OH alone does not allow the quantification of the absolute OH
15 concentration in the low-pressure section of the FAGE instrument. This is the fundamental
16 reason why the earlier simple estimate of [SCI] and OH production leads to strong over-
17 estimations.

18 In addition to the above effects, one should also consider that OH-production from SCI in the
19 low-pressure section might be catalysed to proceed at rates beyond their ambient counterpart,
20 biasing our interpretation of their ambient fate. The catalysis might involve wall-induced
21 isomerisation of the higher-energy *anti*-SCI to the more stable, OH-producing *syn*-SCI,
22 which would artificially increase the *syn:anti* ratio. Another possibility is the evaporation of
23 clusters stabilizing the SCI, as it is known that SCI efficiently form complexes with many
24 compounds, including water, acids, alcohols, hydroperoxides, HO_x radicals, etc. (Vereecken

1 and Francisco, 2012). Redissociation of secondary ozonides (SOZ) seems less important,
2 except perhaps the SOZ formed with CO₂ (Aplincourt and Ruiz-López, 2000), which has no
3 alternative accessible unimolecular channels. At present, insufficient (if any) information is
4 available to assess the impact of such catalysis.

5 Taking into account the factors considered above, and assuming that the estimates for the SCI
6 concentration in both environments are correct, it appears unlikely that SCI are responsible
7 for such a large OH_{bg} signal as observed by the HORUS instrument. If SCI were to be solely
8 responsible for the OH_{bg} signal, the HORUS instrument would need to be far more sensitive
9 to the detection of SCI than to the detection of OH radicals by, for example, pinhole losses
10 that are 100 times smaller for SCI than for OH radicals. The evident discrepancy between the
11 qualitative evidence in support of the SCI hypothesis and the current quantitative difficulty in
12 reconciling the OH_{bg} signal with the estimated ambient concentration of SCI does not allow
13 an unequivocal identification of the origin of the OH_{bg} within our system. It cannot be
14 excluded that multiple species are contributing to the OH_{bg} signal. NO₃ chemistry during
15 night time has been identified as a possible source of OH_{bg} in the LIF-FAGE instrument of
16 the FZ-Jülich (Fuchs et al., 2016). However, in the case of the large observed night time OH_{bg}
17 concentrations during HUMPPA-COPEC 2010, the measured night time NO₃ concentrations
18 were below 1 ppt and therefore too small to explain the observed OH_{bg}.

19

20 **5 Conclusions**

21 We estimated a steady state concentration of SCI for the HUMPPA-COPEC 2010 and the
22 HOPE 2012 campaigns based on a large dataset. Starting from four different approaches, i.e.
23 based on unaccounted (i.e. non-OH) H₂SO₄ oxidant, measured VOC concentrations,

1 unexplained OH reactivity or unexplained production rates of OH, we estimated the
2 concentration of SCI to be between $\sim 10^3$ and $\sim 10^6$ molecules cm^{-3} . The highest values in
3 this range are linked to an assumed low rate coefficient for SCI + SO₂ of 5.0×10^{-13} cm³
4 molecule⁻¹ s⁻¹ (see section 3.1), which is at odds with a larger body of more direct
5 measurements on this rate coefficient. Hence, higher SCI values appear to be relatively less
6 likely. We thus obtain an average SCI concentration of about 5.0×10^4 molecules cm^{-3} , with
7 an order of magnitude uncertainty, for both campaigns. At such concentrations, SCI are
8 expected to have a significant impact on H₂SO₄ chemistry during the HUMPPA-COPEC
9 2010 campaign while during the HOPE 2012 campaign their impact is much smaller and
10 possibly negligible. Additionally, it was shown that, based on the yields and unimolecular
11 decomposition rate applied in this study, SCI do not have a large impact on the OH
12 production compared to the direct OH generation from ozonolysis of unsaturated VOC.
13 During both campaigns, the IPI-LIF-FAGE instrument detected an OH background signal
14 that originates from decomposition of one or more species inside the low pressure region of
15 the instrument. The source compound of the OH_{bg} was shown to be unreactive towards
16 propane but to be removed by SO₂, and a relationship was found with the unaccounted H₂SO₄
17 production rate. It correlates with temperature in the same way as the emission of terpenes
18 and, in most but not all measurements periods, with the product of unsaturated VOC and
19 ozone as well as with the OH reactivity. While it is not possible at the moment to
20 unequivocally state that OH_{bg} originates from stabilised Criegee intermediates, the
21 observations are consistent with known SCI chemistry. The contribution of SCI to the
22 observed OH_{bg} cannot be quantified until a calibration scheme for SCI in the IPI-FAGE
23 system has been developed.

1 The predicted SCI concentrations derived in this study are low, likely not exceeding 10^5
2 molecule cm^{-3} , therefore, the presence of SCI is unlikely to have a large impact on
3 atmospheric chemistry; the main exception appears to be H_2SO_4 production in selected
4 environments.

5

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1

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1 Table 1. Average concentration (molecule cm⁻³), with 1σ variability, of trace gases relevant for this
 2 study.

Compound	HUMPPA-COPEC 2010	HOPE 2012
SO₂^a	(1.4 ± 1.7) x 10 ¹⁰	(2.2 ± 2.3) x 10 ⁹
H₂SO₄^a	(2.0 ± 2.0) x 10 ⁶	(8.5 ± 8.5) x 10 ⁵
OH^a	(7.0 ± 8.0) x 10 ⁵	(1.6 ± 1.6) x 10 ⁶
O₃^a	(1.1 ± 0.2) x 10 ¹²	(1.1 ± 0.3) x 10 ¹²
Σ[VOC]^{a,b}	(7.3 ± 7.1) x 10 ⁹	(9.8 ± 9.0) x 10 ⁹
OH Reactivity^c	9.0 ± 7.6	3.5 ± 3.0
Condensation sink (CS)^c	(10 ± 4.0) x 10 ⁻³	(7.0 ± 3.0) x 10 ⁻³

3 a, Units: molecules cm⁻³.

4 b, HUMPPA COPEC 2010: isoprene, (-)/(+) α-pinene, (-)/(+) β-pinene, 3-carene, and
 5 myrcene.

6 HOPE 2012: isoprene, α-pinene, β-pinene, 3-carene, myrcene, limonene, 2-
 7 methylpropene, but-1-ene, sabinene, γ-terpinene, propene, cis-2-butene and ethene.

8 c, Units: s⁻¹.

9 1 ppbv = 2.5 x 10¹⁰ molecules cm⁻³ at 295K and 1013 hPa.

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1 Table 2. SCI estimates for the HUMPPA-COPEC 2010 and HOPE 2012 campaigns. Average
 2 concentration (molecule cm⁻³), with 1σ variability.

Approach	HUMPPA-COPEC 2010	HOPE 2012
Missing H₂SO₄	(2.3 ± 2.0) x 10 ⁴ ^a	(2.0 ± 3.0) x 10 ⁴ ^a
	(1.6 ± 2.0) x 10 ⁶ ^b	(1.0 ± 3.0) x 10 ⁶ ^b
Measured unsaturated VOC	(5.0 ± 4.0) x 10 ³	(7.0 ± 6.0) x 10 ³
Unexplained OH reactivity	(1.0 ± 1.0) x 10 ⁵	(2.0 ± 1.5) x 10 ⁴
Unexplained OH production	(2.0 ± 2.0) x 10 ⁴ ^c	n. a.
	(4.0 ± 4.0) x 10 ⁵ ^d	n. a.

3 a, $k_{\text{SCI}+\text{SO}_2} = 3.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

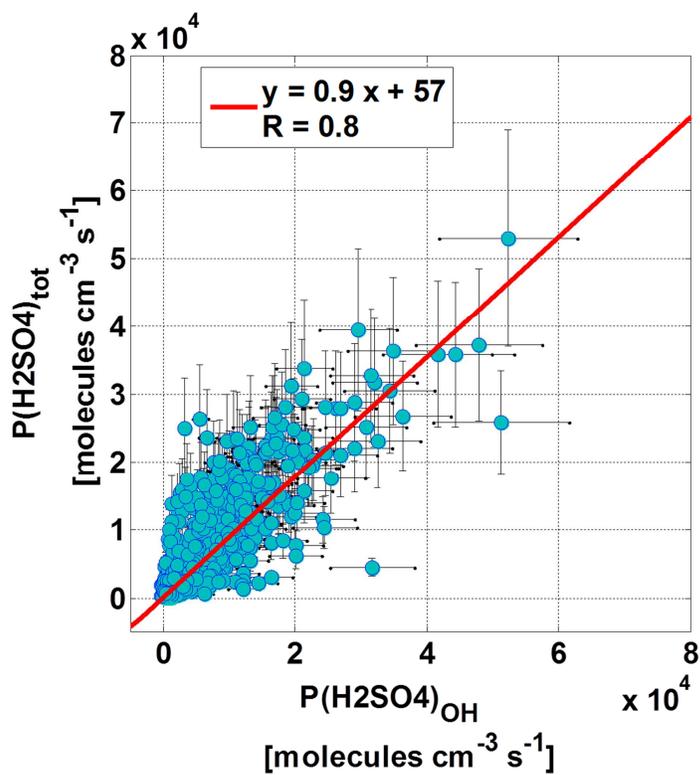
4 b, $k_{\text{SCI}+\text{SO}_2} = 5.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

5 c, $P_{\text{OH}}^{\text{unexplained}} = 1.0 \times 10^6 \text{ molecule cm}^{-3} \text{ s}^{-1}$

6 d, $P_{\text{OH}}^{\text{unexplained}} = 2.0 \times 10^7 \text{ molecule cm}^{-3} \text{ s}^{-1}$

7 1 ppbv = $2.5 \times 10^{10} \text{ molecules cm}^{-3}$ at 295K and 1013 hPa.

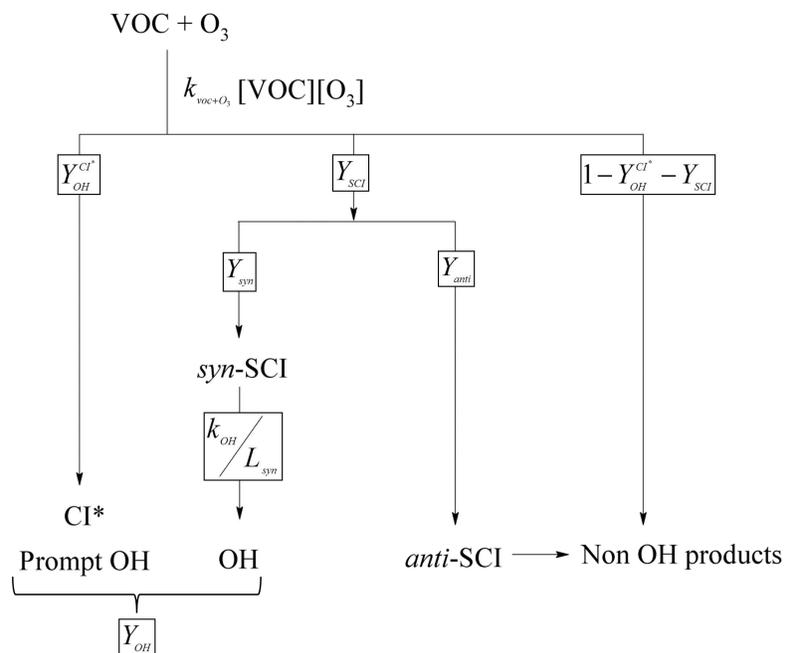
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2 Figure 1. Total production rate of H_2SO_4 ($P(\text{H}_2\text{SO}_4)_{\text{tot}}$) as a function of the production rate of
 3 H_2SO_4 from the reaction between OH and SO_2 during the HOPE 2012 campaign. The linear
 4 regression, following the method of York et al. (2004), yields a slope of 0.9 ± 0.02 and a
 5 intercept of 57 ± 7 .

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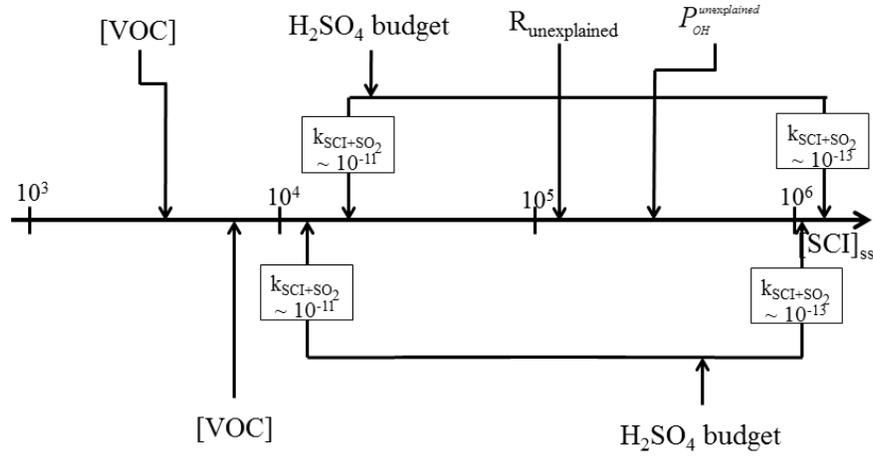
2 Figure 2. Schematic representation of the formation of OH from the ozonolysis of unsaturated
 3 VOC.

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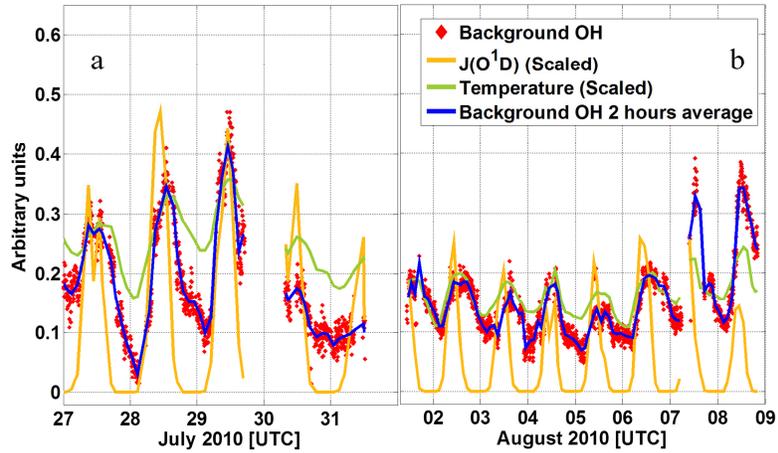
Boreal Forest (HUMPPA-COPEC 2010)



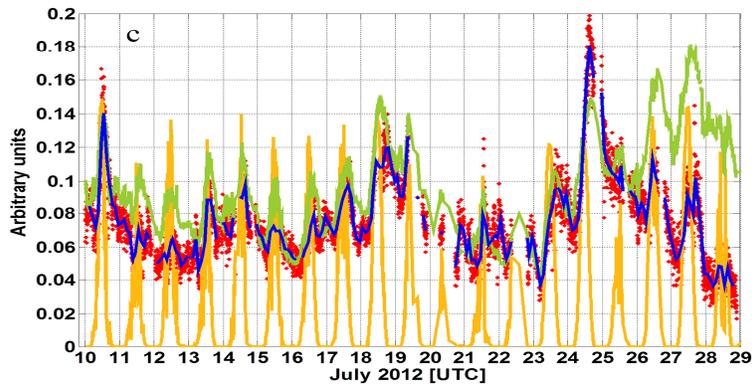
(Rural Europe)HOPE 2012

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 2 Figure 3. Schematic overview of the estimated steady state concentration of SCI ($[SCI]_{ss}$,
 3 molecules cm^{-3}) observed during the HUMPPA-COPEC 2010 and HOPE 2012 campaigns.
 4 For both campaigns the SCI estimate is based on the unsaturated VOC concentration
 5 measured, $[VOC]$, and the H_2SO_4 budget using different SCI+ SO_2 rate coefficients (k_{SCI+SO_2}
 6 in $cm^3 \text{ molecule}^{-1} \text{ s}^{-1}$). In addition, during the HUMPPA-COPEC campaign SCI can be
 7 calculated from the unexplained OH reactivity, $R_{unexplained}$, and unexplained OH production,
 8 $P_{unexplained}^{OH}$. See main text for more details (Section 3).

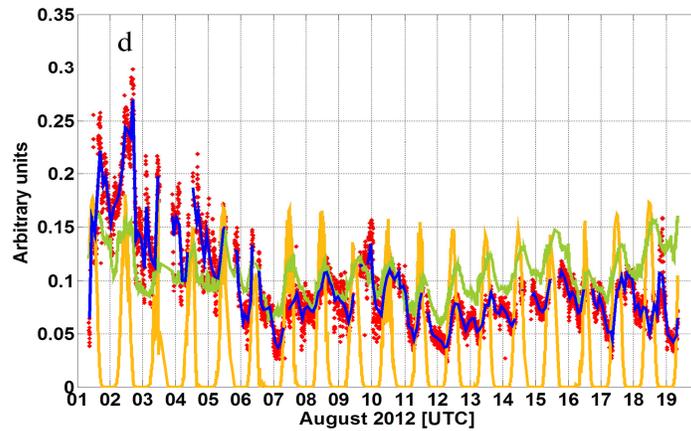
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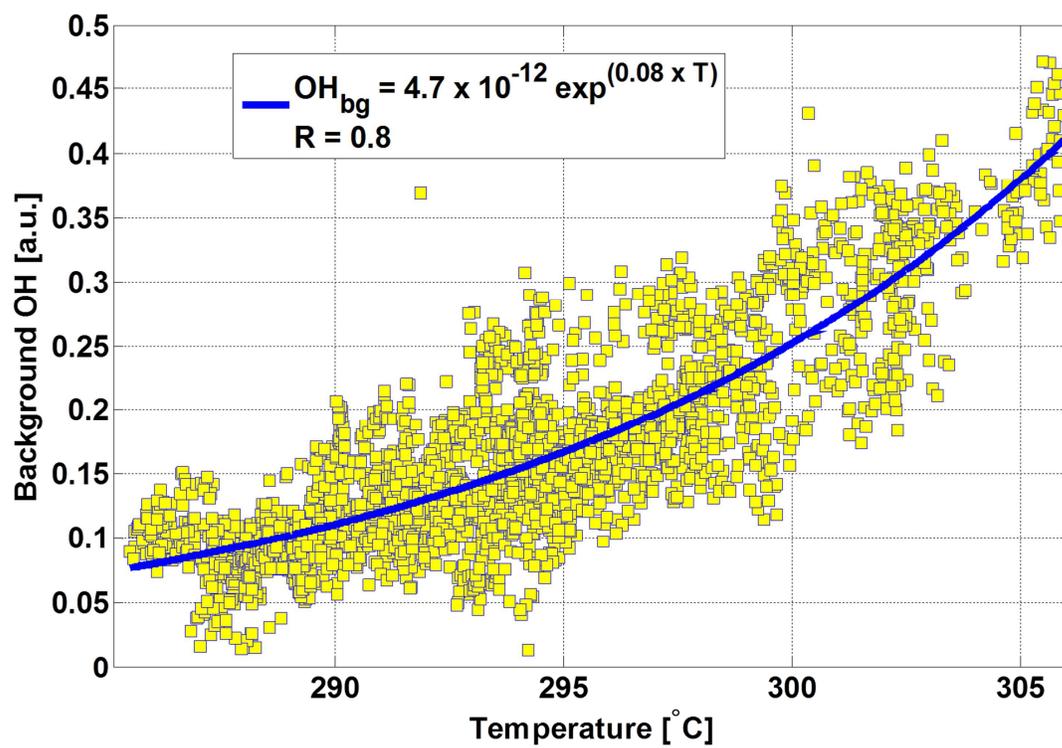


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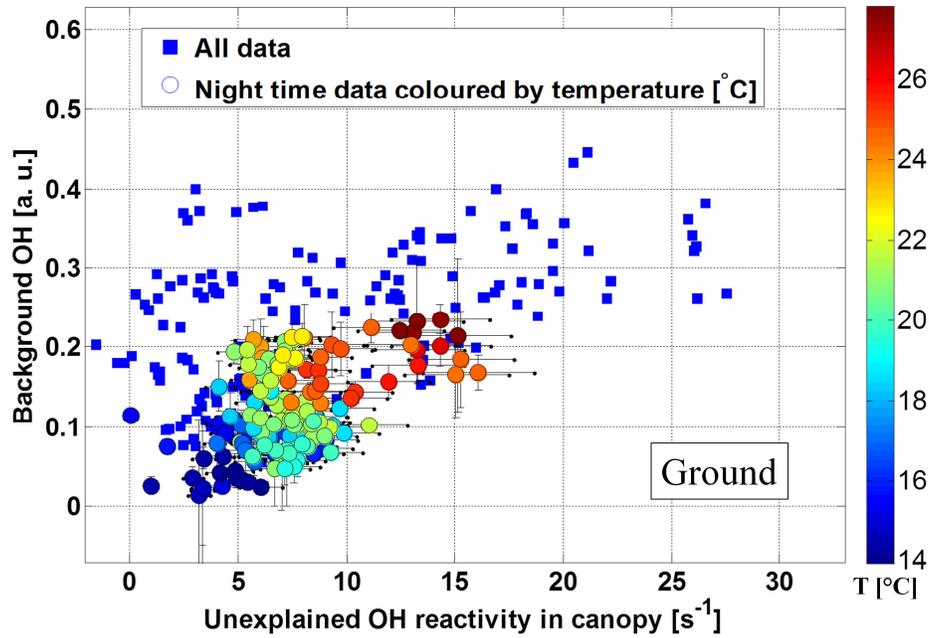
4 Figure 4. Background OH (red diamonds) measured during the HUMPPA-COPEC 2010 (a,
 5 ground and b, tower) and the HOPE 2012 (c, July and d, August) campaigns together with
 6 scaled $J(O^1D)$, multiplied by 4.0×10^4 and 4.0×10^3 for HUMPPA-COPEC 2010 and HOPE
 7 2012, respectively (orange), and scaled temperature divided by 90 and 160 K for HUMPPA-
 8 COPEC 2010 and HOPE 2012, respectively (green).



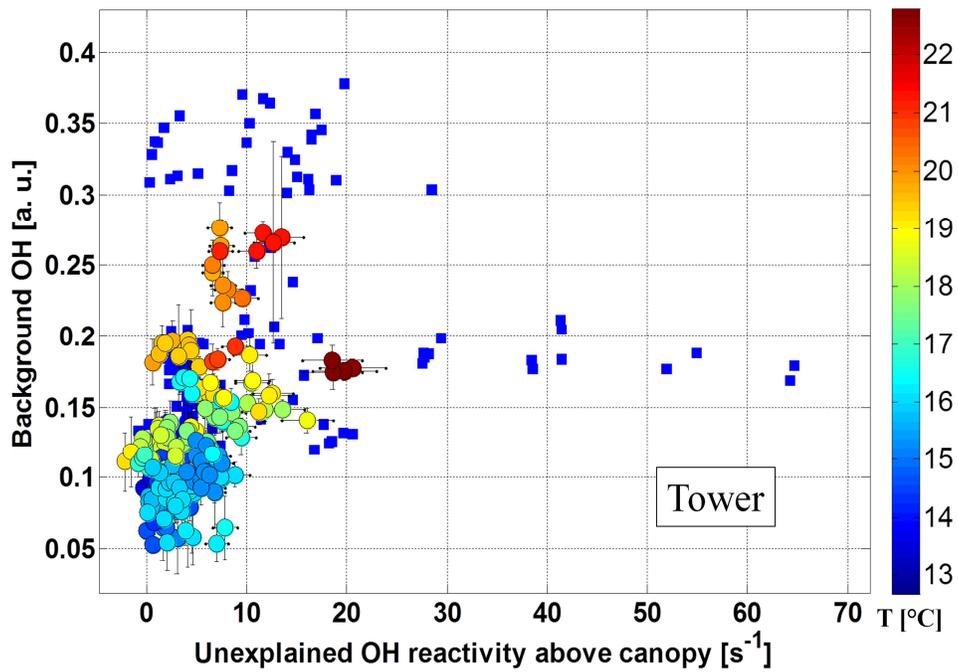
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2 Figure 5. Background OH as a function of the temperature during the HUMPPA-COPEC
3 2010 campaign.

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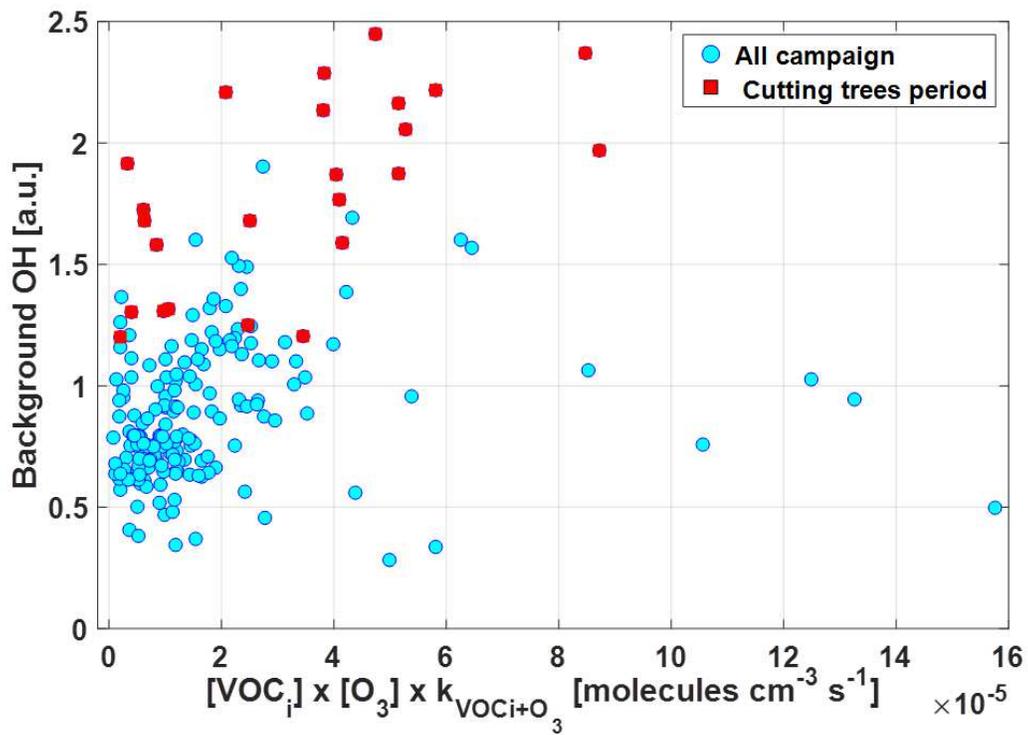
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3 Figure 6. Background OH as a function of unexplained OH reactivity for ground and tower
 4 period measurements during the HUMPPA-COPEC 2010 campaign. Squares represent the
 5 daytime data, bullets represent night time data and are coloured accordingly to temperature
 6 (right legend).

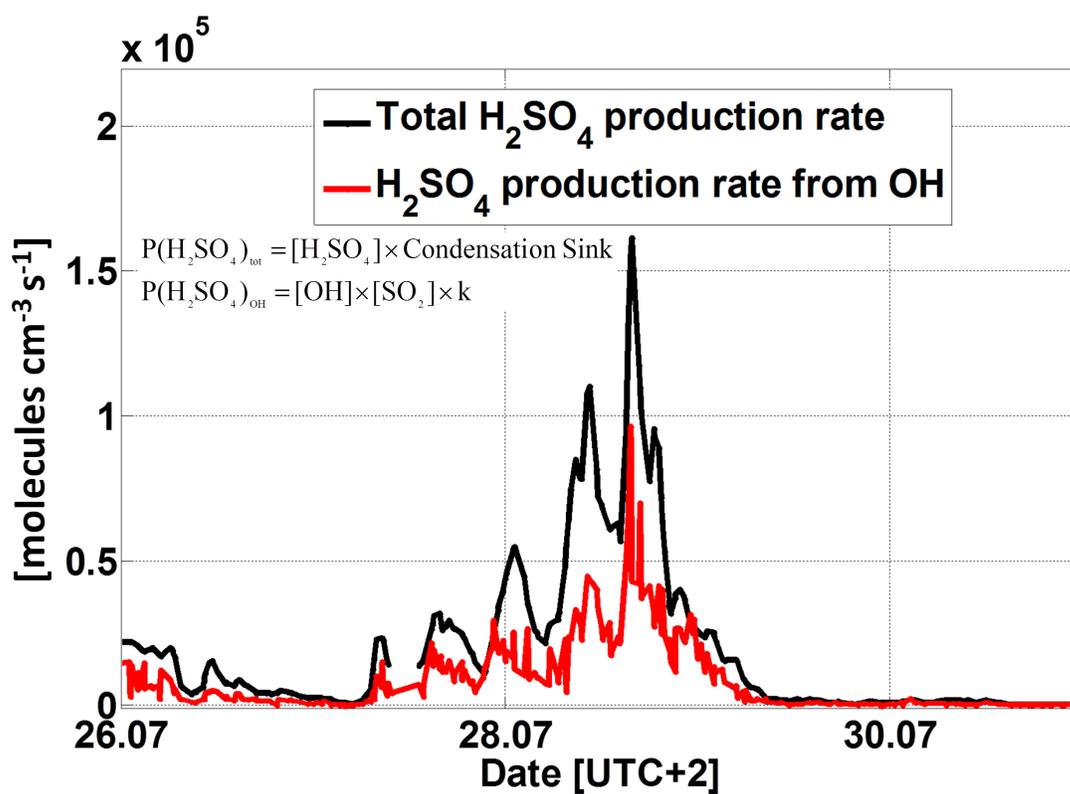
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2 Figure 7. Background OH as a function of the sum of the product of the measured
 3 unsaturated VOC-ozone turn-over (Table SI-1), during the HOPE 2012 campaign. The blue
 4 points refer to the entire field campaign excluding tree cutting, which occurred between 1st
 5 and 3rd of August 2012, described by the red squares.

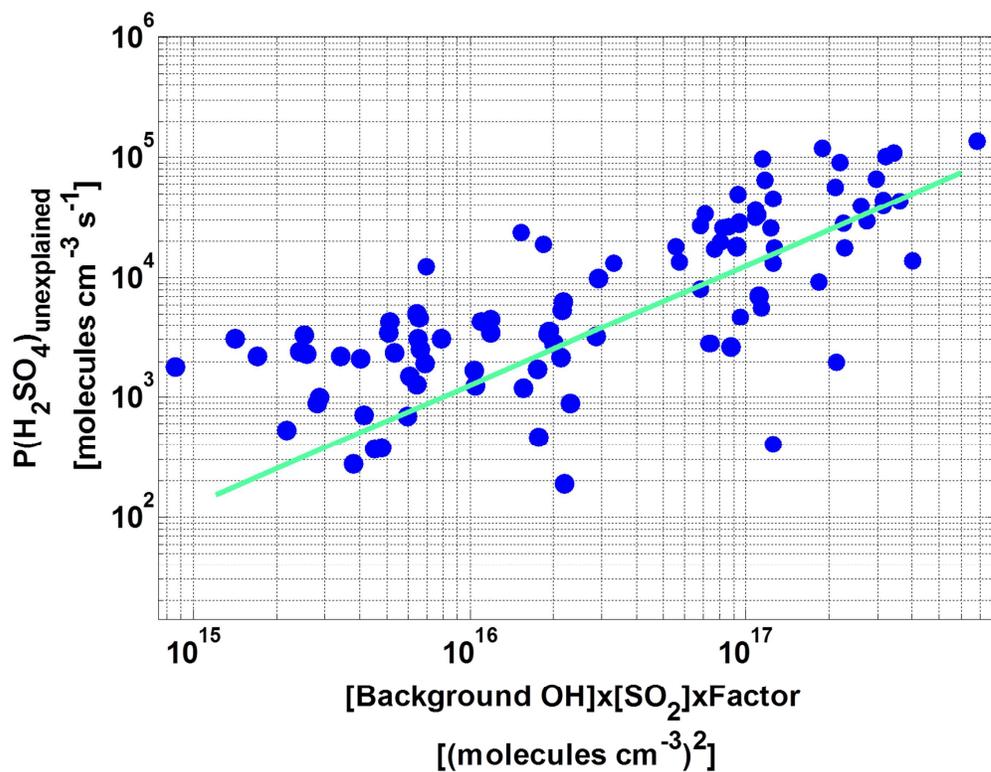
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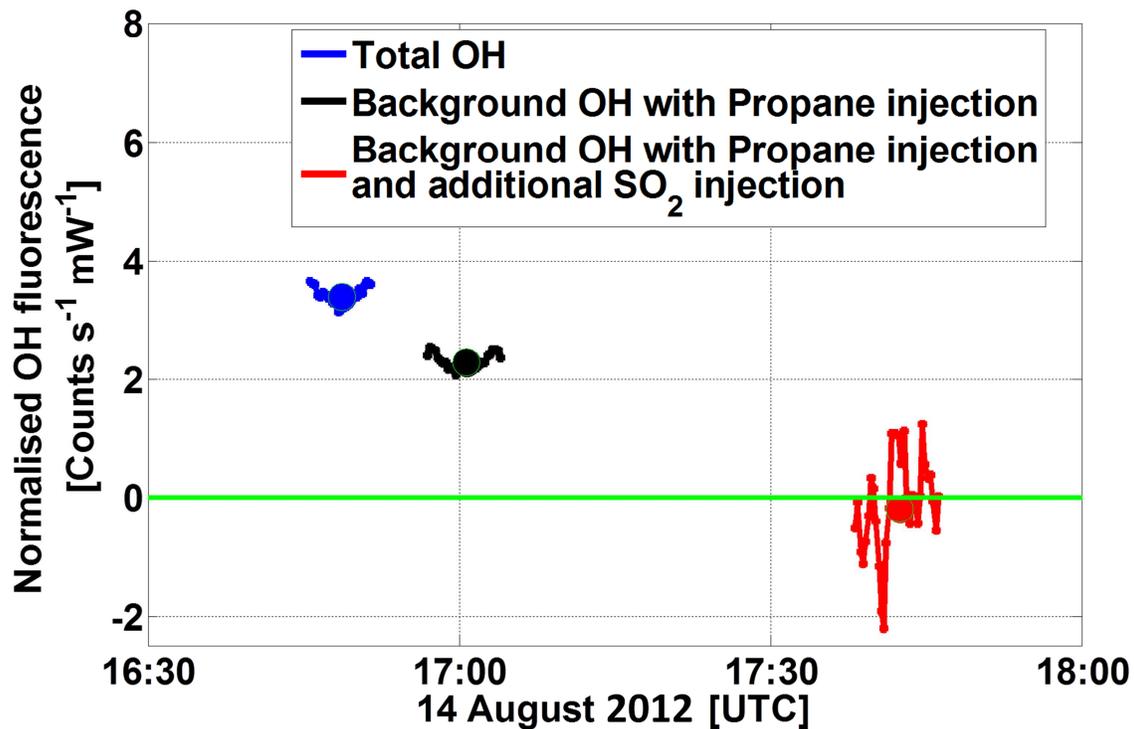
2 Figure 8. Comparison of the total H_2SO_4 production rate (black line), calculated from the
 3 measured H_2SO_4 , and the production rate of H_2SO_4 (red line) involving only the oxidation
 4 process of SO_2 by OH for the ground measurements during the HUMPPA-COPEC 2010
 5 campaign.

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Figure 9. The production rate of H₂SO₄ unaccounted for by the oxidation of SO₂ by OH as a function of the OH_{bg} multiplied by SO₂ concentration during the ground measurements of the HUMPPA-COPEC 2010 campaign. OH_{bg} is expressed in molecules cm⁻³ equivalents of OH.



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2 Figure 10. SO₂ injection test within IPI during the HOPE 2012 campaign. The blue data
 3 points represent the total OH measured when no injection is performed. The black data points
 4 represent the background OH measured while injecting propane (2.5×10^{15} molecules cm⁻³)
 5 scavenging > 90 % of ambient OH. The red signal is the background OH observed when SO₂
 6 (1.0×10^{13} molecules cm⁻³) is injected in addition to propane.

7

1 **Supplementary information**

2 **Estimating the atmospheric concentration of Criegee** 3 **intermediates and their possible interference in a FAGE-LIF** 4 **instrument**

5 Anna Novelli, Korbinian Hens, Cheryl Tatum Ernest, Monica Martinez, Anke C. Nölscher,
6 Vinayak Sinha, Pauli Paasonen, Tuukka Petäjä, Mikko Sipilä, Thomas Elste, Christian Plass-
7 Dülmer, Gavin J. Phillips, Dagmar Kubistin, Jonathan Williams, Luc Vereecken, Jos
8 Lelieveld and Hartwig Harder

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11 **Assessment of the available rate coefficients for the SCI + SO₂ reaction**

12 The disagreement between the rate coefficient for the SCI + SO₂ reaction obtained by
13 Mauldin III et al. (2012) and Berndt et al. (2012), $5.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, and the one
14 obtained by a number of other groups (Welz et al., 2012; Taatjes et al., 2013; Liu et al.,
15 2014b; Sheps et al., 2014; Stone et al., 2014; Chhantyal-Pun et al., 2015; Newland et al.,
16 2015a; Newland et al., 2015b; Foreman et al., 2016; Zhu et al., 2016), $3.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1}$
17 s^{-1} , is not straightforward to explain.

18 A first factor is that Mauldin III et al. (2012) and Berndt et al. (2012) measure the rate of
19 formation of H₂SO₄ rather than the loss of SCI by SO₂. Theoretical and experimental results
20 (Carlsson et al., 2012; Ahrens et al., 2014) indicate that SO₃ is the main product of the SCI +
21 SO₂ reaction, with a yield near 100% at all reaction conditions considered. Barring secondary
22 chemistry removing SO₃ prior to its reaction with H₂O to form H₂SO₄, which seems unlikely
23 under their reaction conditions, the H₂O₄ yield should match the SCI loss. Earlier theoretical
24 work by Vereecken et al. (2012) suggested that the secondary ozonide (SOZ) formed as an

1 intermediate from the reaction between larger SCI and SO₂ could stabilize and undergo
2 bimolecular reaction without formation of SO₃; the loss of SOZ would then reduce SO₃
3 formation, explaining the difference in the rate coefficients for the different experiments.
4 However, more recent theoretical work (Kuwata et al., 2015) found additional low-lying
5 pathways that make collisional stabilization of the SOZ unlikely. Experiments by Carlsson et
6 al. (2012) and Ahrens et al. (2014) observed high yields of SO₃ close to unity suggesting that
7 the SOZ is not lost under the conditions used, i.e. in chambers with high concentrations of
8 reactants and in the absence of water.

9 A second factor is that the reaction conditions used by Mauldin III et al. (2012) and Berndt et
10 al. (2014) differ from the other studies, i.e. they were performed either at ambient air
11 conditions or with lower concentrations of reagents and in the presence of water, while the
12 remaining experiments were typically performed under lower pressures, without efficient
13 colliders present. The mechanism of the SCI+SO₂ reaction as obtained by several authors
14 (Vereecken et al., 2012;Kuwata et al., 2015;Jiang et al., 2010;Kurtén et al., 2011) all indicate
15 a barrierless formation of a pre-reactive complex or cycloadduct. This type of reactions
16 typically show faster rate coefficients at higher pressures due to lower redissociation of the
17 adduct; this is corroborated by the theoretical study on the pressure dependence by Kuwata et
18 al. (2015) who finds no pressure dependence up to 10132.5 hPa and an increase in the
19 effective rate coefficient for higher pressures. Experimental studies of the pressure
20 dependence (Liu et al., 2014b;Huang et al., 2015;Chhantyal-Pun et al., 2016) do not show
21 extensive pressure dependence up to 300 Torr, and all show a positive pressure dependence,
22 in line with the currently accepted reaction mechanism. The Carlsson et al. (2012)
23 experiments at 1013.51 hPa likewise can be fitted using a faster CI + SO₂ rate coefficient of 1
24 $\times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. This suggests that the reaction conditions used by Mauldin III et al.
25 and Berndt et al. would likely lead to faster rate coefficients, especially for larger SCI as used

1 in Mauldin III et al. due to the lower redissociation rate and hence higher thermalization yield
2 of the intermediates.

3 A third factor is that the Mauldin III et al. examine SCI formed from larger terpenoids, rather
4 than the smaller SCI examined in the remaining studies. A larger SCI should mean a longer
5 lifetime for the SOZ intermediate, especially as this longer lifetime makes collisional
6 thermalization more efficient. Hence the large SOZ might indeed live long enough to react in
7 bimolecular reactions prior to dissociation to SO_3 , contrary to smaller SOZ. Unfortunately,
8 SOZ chemistry has not been studied in detail; for the current case the reaction with e.g. H_2O
9 could be a potential loss process. A prerequisite for this scavenging to be effective is that no
10 H_2SO_4 precursor should be formed. This scavenging of the SOZ intermediate would however
11 not apply to the experiments of Berndt et al., which examined CH_3CHOO and $(\text{CH}_3)_2\text{COO}$
12 Criegee intermediates, similar in size to those used in the studies yielding higher rate
13 coefficients. For SCI of this size, the RRKM master equation analysis of (Kuwata et al., 2015)
14 predicts very fast SOZ decomposition.

15 Finally, an alternative explanation could be based on analysis of the studies by Mauldin III et
16 al. (2012) and Berndt et al. (2012). In their experiments, the rate of the $\text{SCI} + \text{SO}_2$ reaction is
17 derived relative to the total loss rate of SCI, L_{SCI} , as it governs the steady-state concentration
18 of SCI with negligible SO_2 present. This L_{SCI} has a value on the order of ~ 3 to 5 s^{-1} in both
19 experiments. Since these studies, a large body of experimental and theoretical data has
20 become available, regarding the reactivity of SCI towards many coreactants present in the
21 reaction mixture (Taatjes et al., 2013; Ouyang et al., 2013; Ahrens et al., 2014; Buras et al.,
22 2014; Liu et al., 2014a; Stone et al., 2014; Sheps et al., 2014; Welz et al., 2014; Lewis et al.,
23 2015). From this new data, we should consider that a total loss rate of about 4 s^{-1} is an
24 underestimate. In a previous study by Novelli et al. (2014) a value of $L_{\text{SCI}} = 40 \text{ s}^{-1}$ under
25 atmospheric conditions was proposed. A re-analysis of the study by Mauldin III et al. (2012)

1 using $L_{\text{SCI}} = 40 \text{ s}^{-1}$ and the measured yield of SCI for α -pinene of 0.1 (Donahue et al., 2011),
2 results in a rate coefficient for the α -pinene-derived SCI + SO₂ reaction of $2.6 \times 10^{-11} \text{ cm}^3$
3 $\text{molecule}^{-1} \text{ s}^{-1}$. Likewise, for the other compounds examined in the two studies (Berndt et al.,
4 2012;Mauldin III et al., 2012), the derived rate of SCI+SO₂ would shift significantly towards
5 the higher values obtained in the other studies (Welz et al., 2012;Taatjes et al., 2013;Liu et al.,
6 2014b;Sheps et al., 2014;Stone et al., 2014). One must consider, though, that the study by
7 Berndt et al. (2012) included a measurement of k_{loss} , based on the observed H₂SO₄ formation
8 from the steady state SCI in the absence of SO₂. Hence, this second explanation is only viable
9 if another source of H₂SO₄ exists in the system; this has already been suggested by Newland
10 et al. (2015a) based on their SO₂ oxidation experiments.

11 Still, as these considerations for the lower values by Mauldin III et al. (2012) and Berndt et al.
12 (2012) are merely speculative, we will consider both $3.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $5 \times 10^{-}$
13 $^{13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ as possible rate coefficients for the SCI + SO₂ reaction in the current
14 budget analysis.

15

16 **SCI time series**

17 Time series of SCI were derived for two field campaigns, HUMPPA-COPEC 2010 and HOPE
18 2012, obtained based on different source data, i.e. the sulfuric acid budget, the speciated VOC
19 concentrations measured, and the unexplained OH reactivity.

20 The time series for the HUMPPA-COPEC 2010 campaign (Figures SI-2, SI-4, and SI-7) are
21 fairly well defined, at least in view of intrinsic uncertainty of the underlying data; as detailed
22 in the main text, this is the campaign with the highest expected SCI concentrations. Fig SI-2,
23 using the H₂SO₄ budget as data source, shows a less pronounced diurnal cycle, but figure SI-4
24 and SI-7 both show a clear diurnal cycle of the predicted SCI concentration, as well as some

1 daily differences. These plots both link [SCI] to VOC concentrations, and the SCI
2 concentration follows the diel variation of these VOCs, as expected from the ozonolysis
3 chemistry as a source of SCI. Our analysis is not able to account for different yields or
4 lifetimes of SCI as a function of VOC speciation differences from day to night, due to lack of
5 data. In principle this could superimpose an additional SCI concentration diel variation, but
6 we anticipate this to be minor considering that the VOC speciation does not change drastically
7 between day and night. Both plots also show clear daily differences.

8 The [SCI] time series for the HOPE 2012 campaign are characterized mostly by their
9 statistical noise. As discussed in the main paper, the SCI concentration during this campaign
10 was expected to be low, and the SCI concentration estimates are typically derived from a
11 small difference between large numbers, each with their own statistical noise, leading to
12 highly variable data with very large relative uncertainties even when the absolute numbers
13 remain small. Under these conditions, neither diurnal cycles, day-to-day variations, nor even
14 minimum and peak values carry strong significance, and no meaningful in-depth analysis can
15 be done beyond stating that the concentrations are predicted to be low indeed.

16 Across all SCI time series, we find that the minimum and maximum values of the predicted
17 SCI concentration remains within a relatively modest factor of the median and the average
18 [SCI], only exceeding a factor of 5 for a handful of data points. Considering the uncertainties
19 already incurred through the analysis methodology itself, and the variability and uncertainties
20 on the source data underlying these studies, secondary effects such as day-to-day variability,
21 diurnal cycles, or multi-day variations have only a moderate to small impact on the overall
22 uncertainty of the CI estimates proposed in the main paper, where we indicate uncertainties
23 that exceed an order of magnitude.

24

1 **Sensitivity study on the unexplained OH reactivity SCI estimate**

2 The estimate of SCI from the unexplained OH reactivity data contains larger uncertainties
3 compared to the previous estimates as the rate coefficient for ozonolysis of unsaturated
4 compounds varies by up to three orders of magnitude. In addition, the rate coefficient between
5 OH and unsaturated compounds, depending on whether these are unsaturated NMHC or
6 OVOC, primary emissions, or secondary oxidation products, varies by an order of magnitude.
7 A sensitivity study was done on the SCI estimates from the unexplained OH reactivity to
8 attempt to account for this uncertainty in rate coefficients. It is possible to calculate a lower
9 limit for the SCI concentration by using the highest rate coefficient between OH and
10 unsaturated compounds, $1.0 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson et al., 2006) combined with a
11 slow rate coefficient for the unsaturated compounds and ozone, $1.0 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
12 (Atkinson et al., 2006), leading to a $[\text{SCI}] = (8.7 \pm 8.0) \times 10^3 \text{ molecules cm}^{-3}$. For the upper
13 limit, a slower rate coefficient for OH and unsaturated OVOC, $\sim 3.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
14 (Atkinson et al., 2006; Teruel et al., 2006) together with a higher rate coefficient with O_3 , $1.0 \times$
15 $10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson et al., 2006) results in a concentration of $[\text{SCI}] = (3.0 \pm 3.0)$
16 $\times 10^5 \text{ molecules cm}^{-3}$. These are the values obtained for the HUMPPA-COPEC 2010
17 campaign. For the HOPE 2012 campaign, the same assumptions would yield a lower and an
18 upper limit of $(1.0 \pm 0.2) \times 10^3 \text{ molecules cm}^{-3}$ and $(2.9 \pm 0.7) \times 10^4 \text{ molecules cm}^{-3}$,
19 respectively.

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1 Table SI-1. Average concentrations with 1σ standard deviation of measured unsaturated VOC
 2 during the HUMPPA-COPEC 2010 and HOPE 2012 campaigns, together with the rate
 3 coefficients of the reaction with ozone (IUPAC recommended values) (Atkinson et al., 2006).

Compound	[molecule cm ⁻³]		Rate coefficient with O ₃ [cm ³ molecule ⁻¹ s ⁻¹]
	HUMPPA- COPEC 2010	HOPE 2012	
isoprene	(1.8 ± 1.8) x 10 ⁹	(2.2 ± 2.2) x 10 ⁹	1.0 x 10 ⁻¹⁴ exp(-1995/T)
α-pinene	(2.7 ± 3.0) x 10 ⁹	(1.5 ± 1.5) x 10 ⁹	8.1 x 10 ⁻¹⁶ exp(-640/T)
β-pinene	(1.9 ± 6.6) x 10 ⁸	(9.0 ± 9.0) x 10 ⁸	1.4 x 10 ⁻¹⁵ exp(-1270/T)
3-carene	(1.7 ± 2.0) x 10 ⁹	(5.6 ± 4.7) x 10 ⁸	4.8 x 10 ^{-17, b}
myrcene	(2.6 ± 2.7) x 10 ⁸	(2.2 ± 1.6) x 10 ⁸	2.7 x 10 ⁻¹⁵ exp(-520/T)
limonene	n.a.	(2.9 ± 2.1) x 10 ⁸	2.8 x 10 ⁻¹⁵ exp(-770/T)
sabinene	n.a.	(9.2 ± 9.6) x 10 ⁸	8.2 x 10 ^{-17, b}
γ-terpinene	n.a.	(1.0 ± 1.0) x 10 ⁸	1.5 x 10 ^{-16, b}
2-methylpropene	n.a.	(4.2 ± 2.5) x 10 ⁸	2.7 x 10 ⁻¹⁵ exp(-1630/T)
but-1-ene	n.a.	(1.4 ± 4.2) x 10 ⁸	1.2 x 10 ^{-17, a, b}
propene	n.a.	(4.7 ± 3.7) x 10 ⁸	5.5 x 10 ⁻¹⁵ exp(-1880/T)
cis-2-butene	n.a.	(6.1 ± 3.0) x 10 ⁷	3.2 x 10 ⁻¹⁵ exp(-965/T)
ethene	n.a.	(7.3 ± 9.0) x 10 ⁹	9.1 x 10 ⁻¹⁵ exp(-2580/T)

4 a, rate coefficient from Adeniji et al. (1981).

5 b, at 298 K

6 1 ppbv = 2.46 x 10¹⁰ molecules cm⁻³ at 295K and 1013 hPa.

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1 Table SI-2. Average concentrations with 1σ standard deviation of measured trace gas during
 2 the HUMPPA-COPEC 2010 and HOPE 2012 campaigns, with the rate coefficients of the
 3 reaction with OH (IUPAC recommended values) (Atkinson et al., 2006; Atkinson et al., 2004)

Compound	[molecule cm ⁻³]		Rate coefficient with OH [cm ³ molecule ⁻¹ s ⁻¹]
	HUMPPA- COPEC 2010	HOPE 2012	
isoprene	$(1.8 \pm 1.8) \times 10^9$	$(2.2 \pm 2.0) \times 10^9$	$2.7 \times 10^{-11} \exp(390/T)$
α-pinene	$(2.7 \pm 3.0) \times 10^9$	$(1.5 \pm 1.5) \times 10^9$	$1.2 \times 10^{-11} \exp(440/T)$
β-pinene	$(1.9 \pm 6.6) \times 10^8$	$(9.0 \pm 9.0) \times 10^8$	$7.4 \times 10^{-11, a, b}$
3-carene	$(1.7 \pm 2.0) \times 10^9$	$(5.6 \pm 4.7) \times 10^8$	$8.8 \times 10^{-11, a, b}$
myrcene	$(2.6 \pm 2.7) \times 10^8$	$(2.2 \pm 1.6) \times 10^8$	$3.3 \times 10^{-10, b, c}$
limonene	n.a.	$(2.9 \pm 2.1) \times 10^8$	$3 \times 10^{-11} \exp(515/T)^d$
sabinene	n.a.	$(9.2 \pm 9.6) \times 10^8$	$1.2 \times 10^{-10, a, b}$
γ-terpinene	n.a.	$(1.0 \pm 1.0) \times 10^8$	$1.7 \times 10^{-10, b}$
MACR	$(1.0 \pm 0.9) \times 10^{10}$	$(1.4 \pm 0.9) \times 10^9$	$8 \times 10^{-12} \exp(380/T)$
ethanol	$(3.6 \pm 2.2) \times 10^{10}$	$(1.8 \pm 1.1) \times 10^{10}$	$3.2 \times 10^{-12} \exp(20/T)$
methanol	$(1.0 \pm 1.4) \times 10^{11}$	$(9.0 \pm 3.4) \times 10^{10}$	$9.0 \times 10^{-13, b}$
ozone	$(1.1 \pm 0.2) \times 10^{12}$	$(1.1 \pm 0.3) \times 10^{12}$	$1.7 \times 10^{-12} \exp(-940/T)$
SO₂	$(1.4 \pm 1.7) \times 10^{10}$	$(2.3 \pm 2.2) \times 10^9$	$2.0 \times 10^{-12, b}$
H₂O₂	$(1.1 \pm 1.0) \times 10^{10}$	n.a.	$1.7 \times 10^{-12, b}$
HO₂	$(9.0 \pm 9.5) \times 10^8$	$(1.4 \pm 8.6) \times 10^8$	$4.8 \times 10^{-11} \exp(250/T)$
NO	$(6.5 \pm 7.0) \times 10^8$	$(3.8 \pm 5.0) \times 10^9$	$1.3 \times 10^{-11, b}$
NO₂	$(9.5 \pm 5.0) \times 10^9$	$(3.8 \pm 2.4) \times 10^{10}$	$1.1 \times 10^{-11, b}$
CO	$(3.0 \pm 1.2) \times 10^{12}$	$(2.8 \pm 0.4) \times 10^{12}$	$2.1 \times 10^{-13, b}$
HONO	$(3.4 \pm 3.1) \times 10^9$	n.a.	$6.0 \times 10^{-12, b}$
propanal	n.a.	$(5.8 \pm 3.0) \times 10^9$	$4.9 \times 10^{-12} \exp(405/T)$

acetaldehyde	$(1.8 \pm 1.0) \times 10^{10}$	$(2.9 \pm 1.4) \times 10^{10}$	$1.5 \times 10^{-11, b}$
formaldehyde	$(1.4 \pm 1.6) \times 10^{10}$	$(2.1 \pm 0.4) \times 10^{10}$	$8.5 \times 10^{-12, b}$
acetone	$(8.2 \pm 3.8) \times 10^{10}$	$(6.0 \pm 2.2) \times 10^{10}$	$1.8 \times 10^{-13, b}$
CH₄	$(4.4 \pm 0.07) \times 10^{13}$	$(4.3 \pm 0.1) \times 10^{13}$	$6.4 \times 10^{-15, b}$
2-methylpropene	n.a.	$(4.2 \pm 2.5) \times 10^8$	$6.1 \times 10^{-11, a, b}$
but-1-ene	n.a.	$(1.4 \pm 4.2) \times 10^8$	$3.1 \times 10^{-11, a, b}$
propene	n.a.	$(4.7 \pm 3.7) \times 10^8$	$2.9 \times 10^{-11, b}$
cis-2-butene	n.a.	$(6.1 \pm 3.0) \times 10^7$	$6.4 \times 10^{-11, b}$
ethene	n.a.	$(7.3 \pm 9.0) \times 10^9$	$7.8 \times 10^{-12, b}$
p-xylene	n.a.	$(7.2 \pm 5.2) \times 10^8$	$2.0 \times 10^{-11, a, b}$
benzene	$(2.1 \pm 1.9) \times 10^9$	$(8.0 \pm 4.0) \times 10^8$	$1.2 \times 10^{-12, a, b}$
ethylbenzene	n.a.	$(2.3 \pm 2.1) \times 10^8$	$7.0 \times 10^{-12, a, b}$
Toluene	$(6.1 \pm 3.0) \times 10^9$	$(1.2 \pm 0.7) \times 10^9$	$5.6 \times 10^{-12, a, b}$
ethane	n.a.	$(1.8 \pm 0.3) \times 10^{10}$	$4.8 \times 10^{-11} \exp(250/T),^a$
propane	n.a.	$(5.6 \pm 3.6) \times 10^9$	$1.1 \times 10^{-12, a, b}$
methylpropane	$(1.8 \pm 2.3) \times 10^9$	$(1.4 \pm 0.9) \times 10^9$	$2.1 \times 10^{-12, a, b}$
butane	$(1.8 \pm 1.6) \times 10^9$	$(2.0 \pm 1.2) \times 10^9$	$2.3 \times 10^{-12, a, b}$
2-methylbutane	$(1.6 \pm 1.2) \times 10^9$	n.a.	$3.6 \times 10^{-12, a, b}$
n-pentane	$(1.0 \pm 0.9) \times 10^9$	$(5.6 \pm 5.0) \times 10^9$	$3.8 \times 10^{-12, a, b}$

1 a, rate coefficient from (Atkinson and Arey, 2003).

2 b, at 298 K.

3 c, rate coefficient from (Hites and Turner, 2009)

4 d, rate coefficient from (Braure et al., 2014)

5 1 ppbv = 2.46×10^{10} molecules cm^{-3} at 295K and 1013 hPa.

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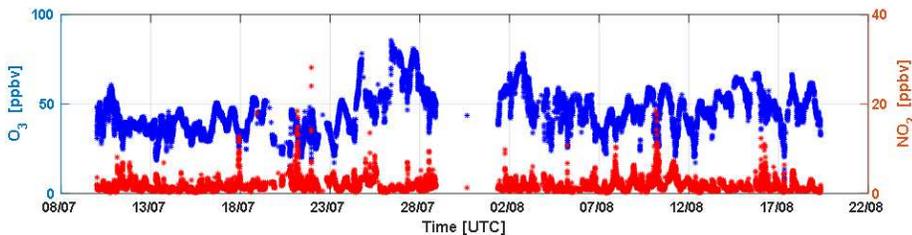
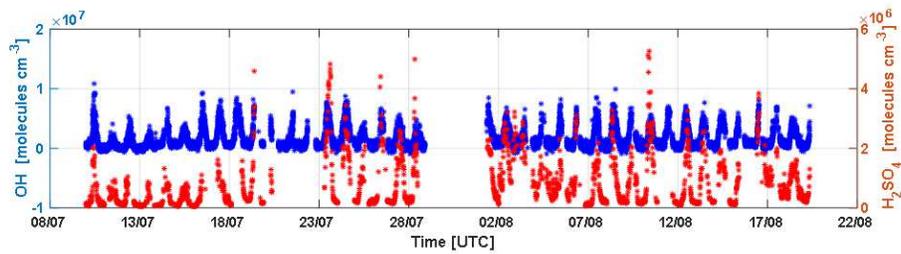
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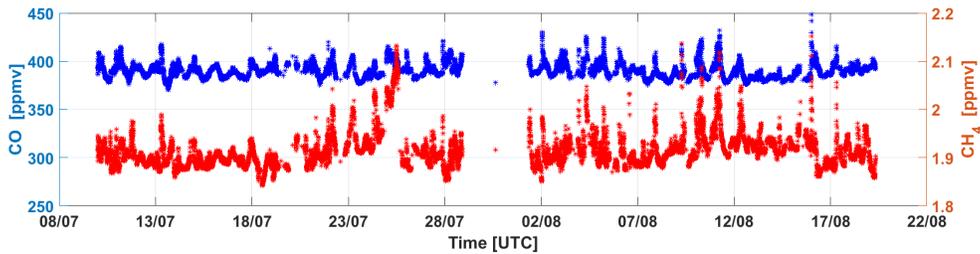
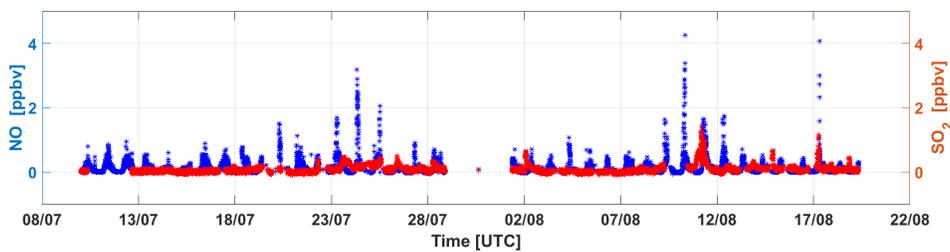
1 Table SI-3. Average sum of concentrations with 1σ standard deviation of BVOC (isoprene, α -
2 pinene, β -pinene, 3-carene, myrcene, limonene, sabinene, γ -terpinene) and temperature for the
3 entire HOPE 2012 field campaign excluding the period between 26th to 28th of July 2012.

	$\Sigma[\text{VOC}] [\text{molecules cm}^{-3}]$	Temperature [$^{\circ}\text{C}$]
HOPE 2012 campaign	$(5.0 \pm 4.0) \times 10^9$	16 ± 3.0
26 th to 28 th of July 2012	$(1.3 \pm 0.9) \times 10^{10}$	22 ± 3.0

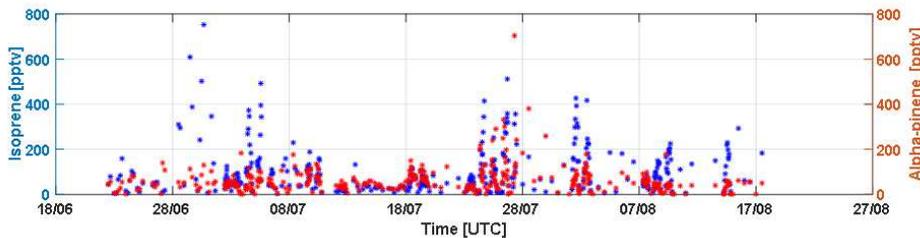
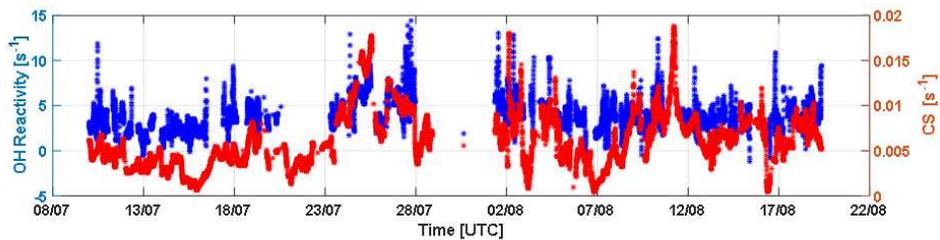
4 1 ppbv = 2.46×10^{10} molecules cm^{-3} at 295K and 1013 hPa.
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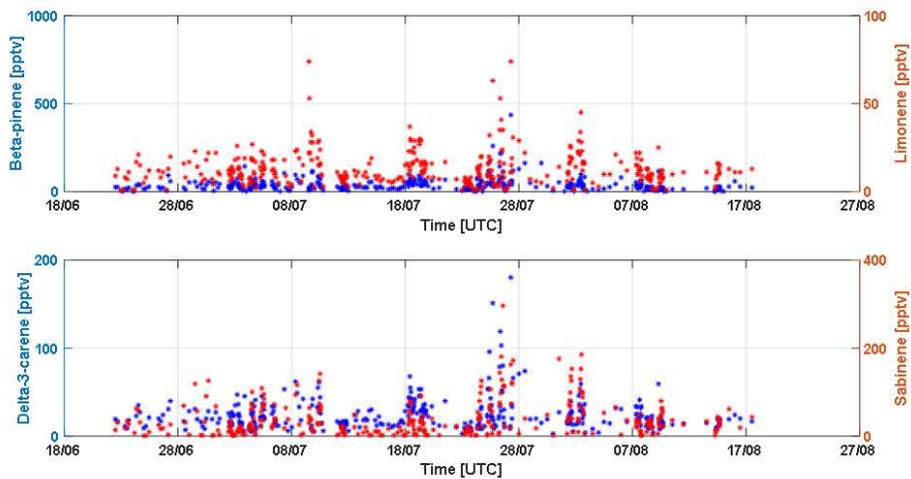
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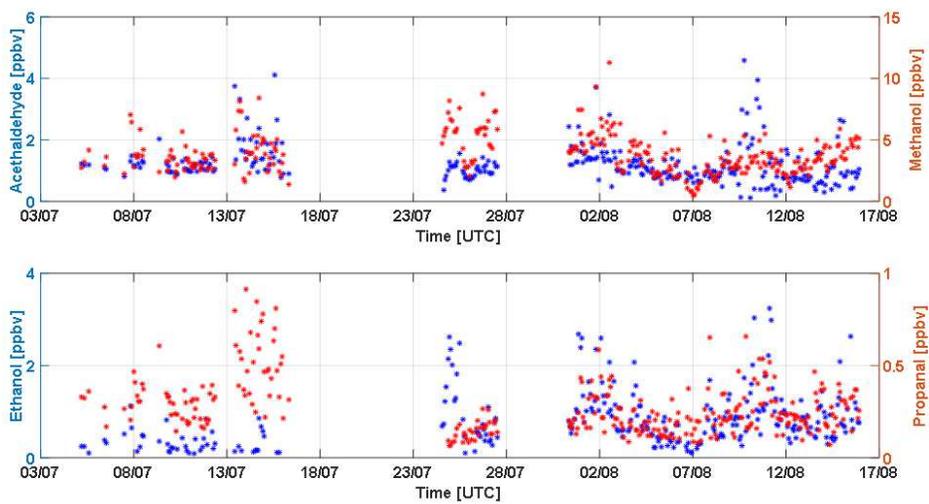
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4 Figure SI-1. Time series of trace gases measured during the HOPE 2012 campaign.

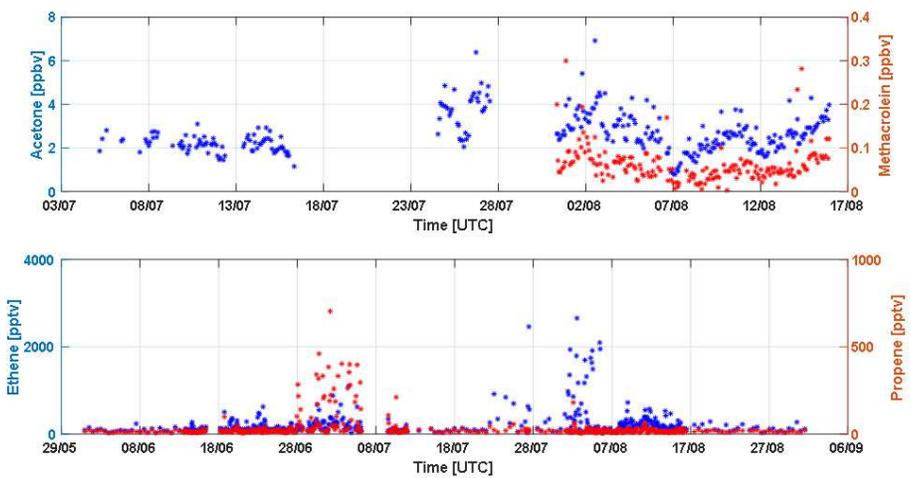
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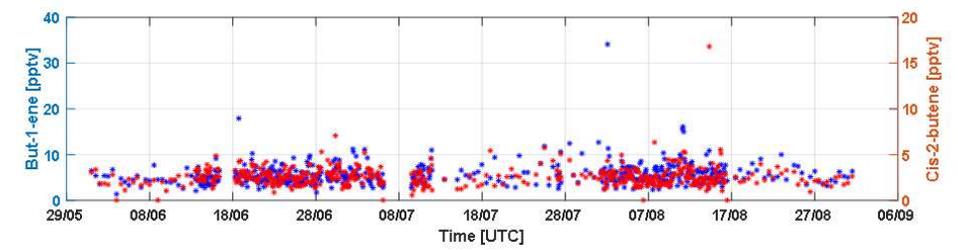


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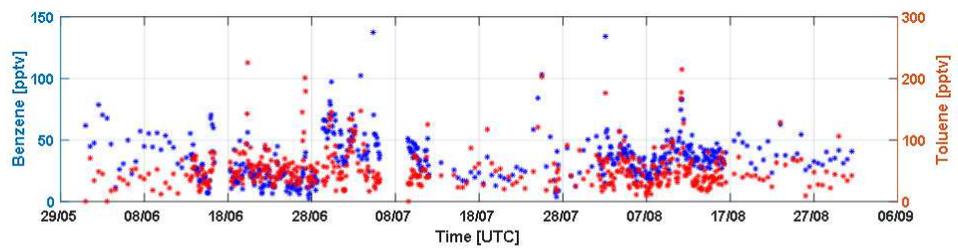
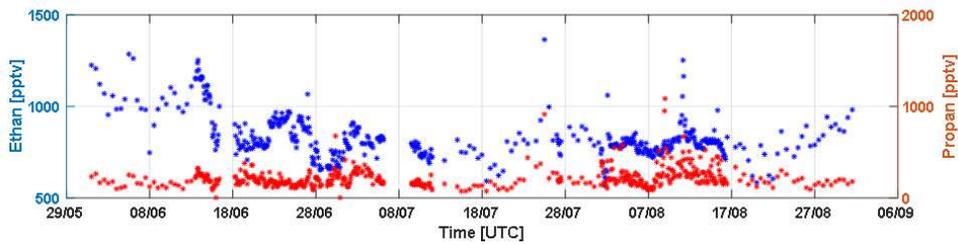


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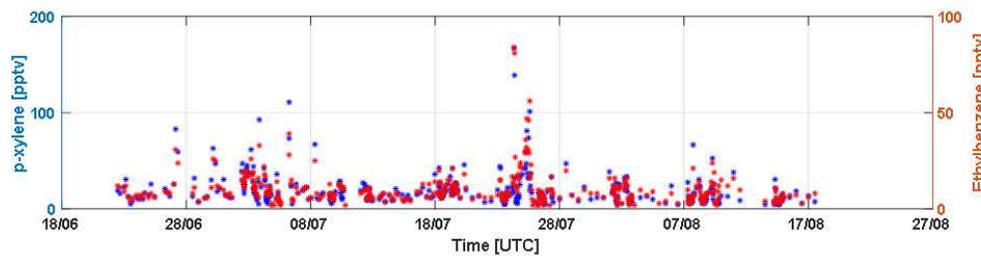
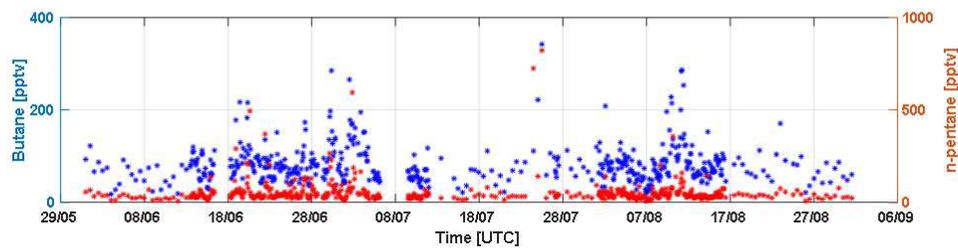
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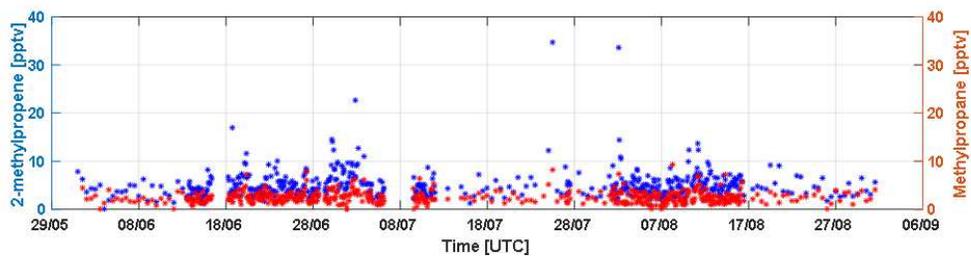
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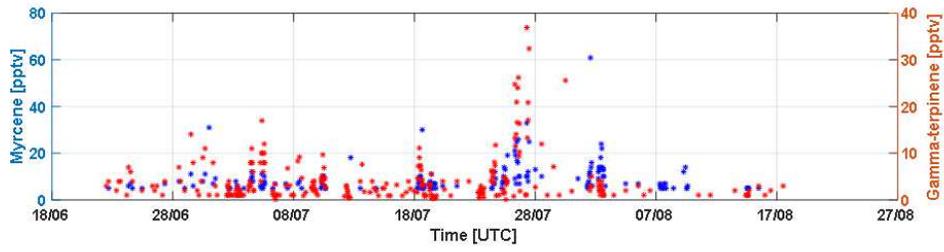
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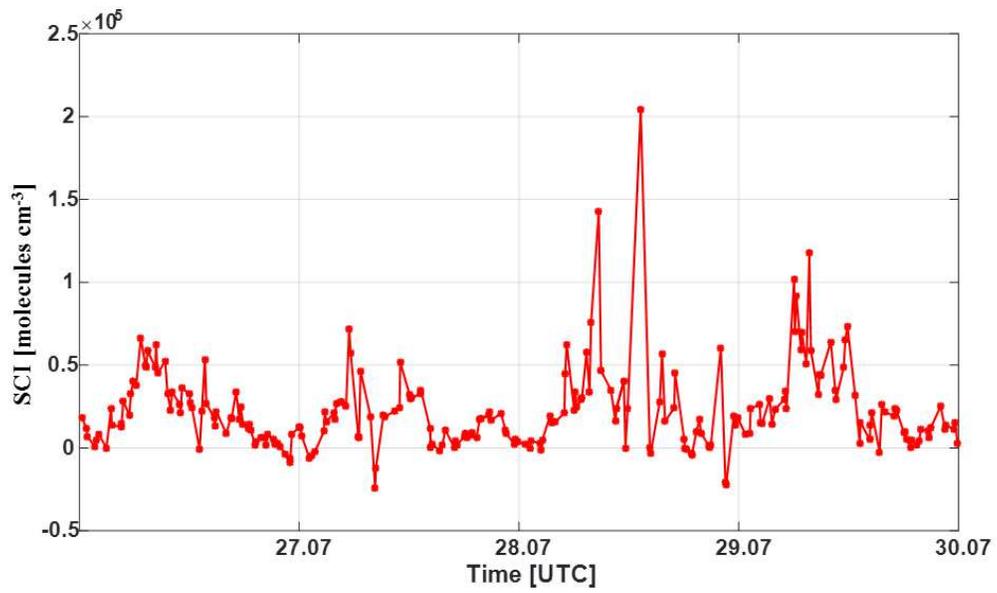


4 Figure SI-1, continued



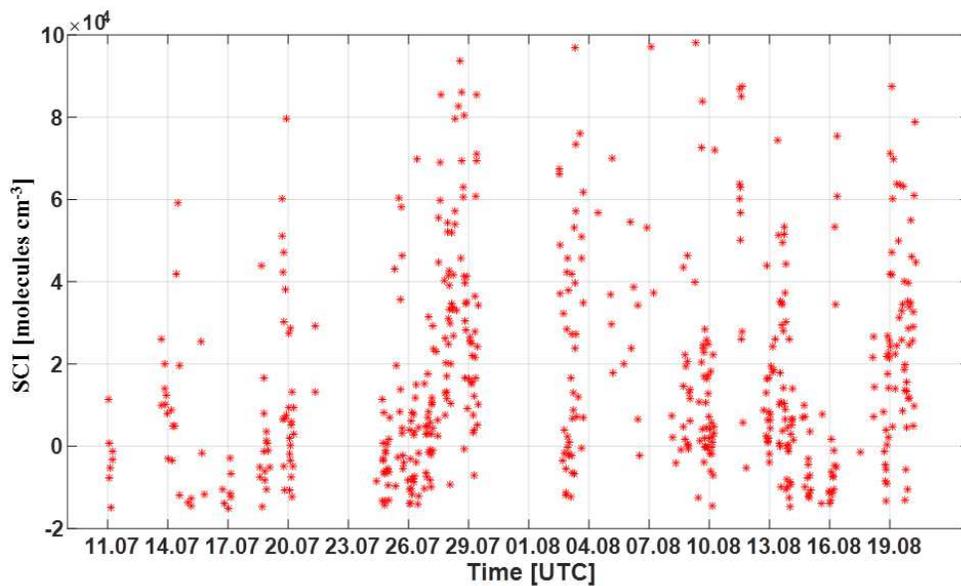
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Figure SI-1, continued



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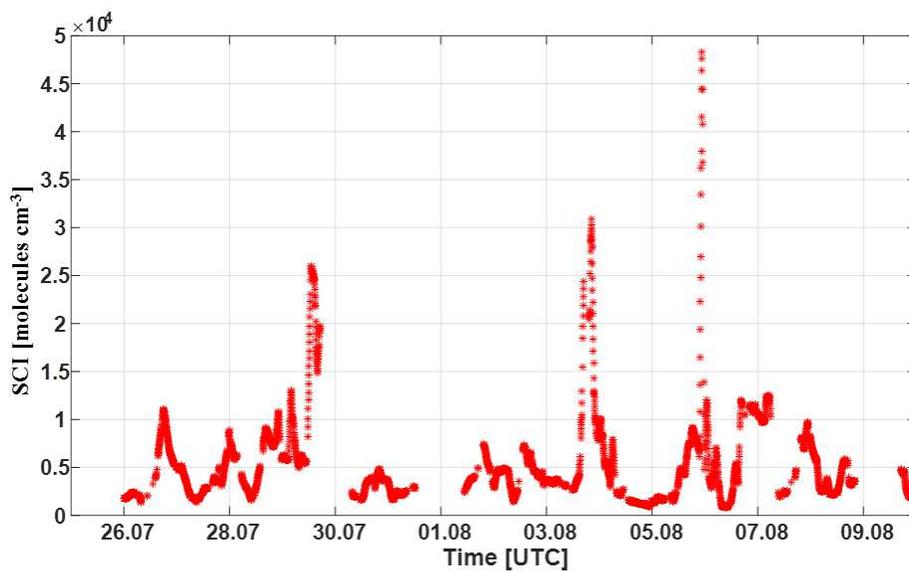
Figure SI-2. SCI time series as calculated from the sulfuric acid budget during the HUMPPA-COPEC 2010 campaign.



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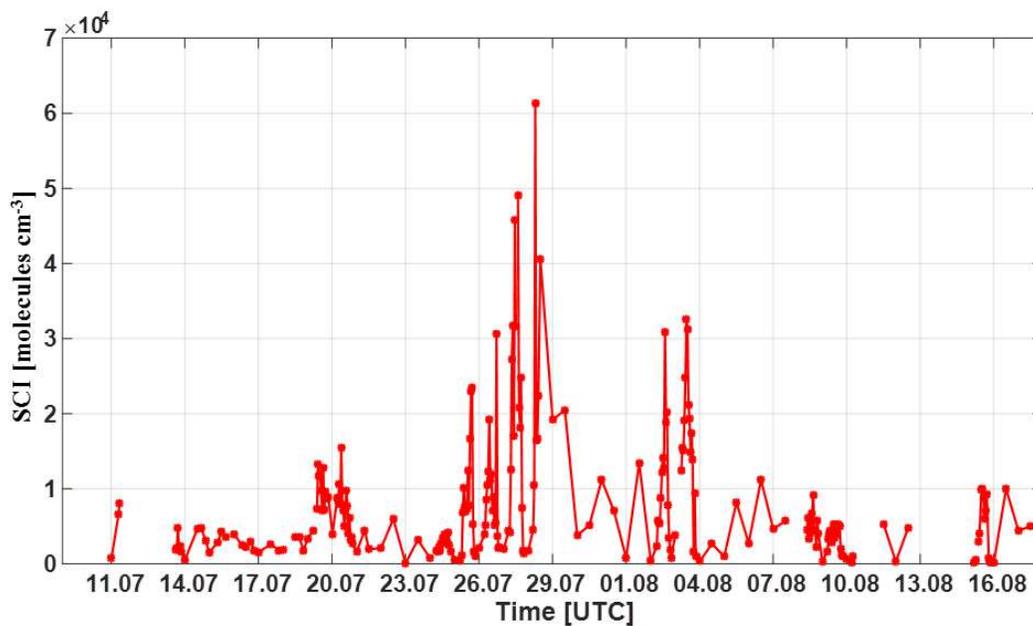
2 Figure SI-3. SCI time series as calculated from the sulfuric acid budget during the HOPE
 3 2012 campaign.

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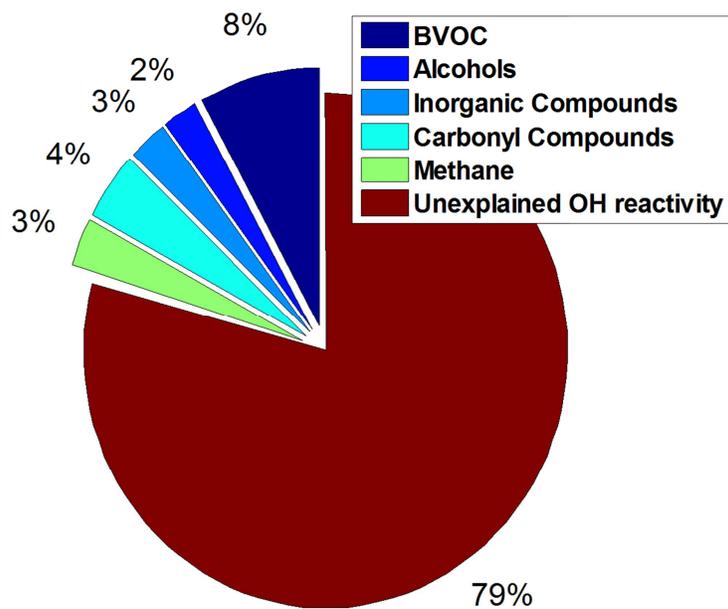
6 Figure SI-4. SCI time series as calculated from the measured unsaturated VOC during the
 7 HUMPPA-COPEC 2010 campaign.



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2 Figure SI-5. SCI time series as calculated from the measured unsaturated VOC during the
 3 HOPE 2012 campaign.

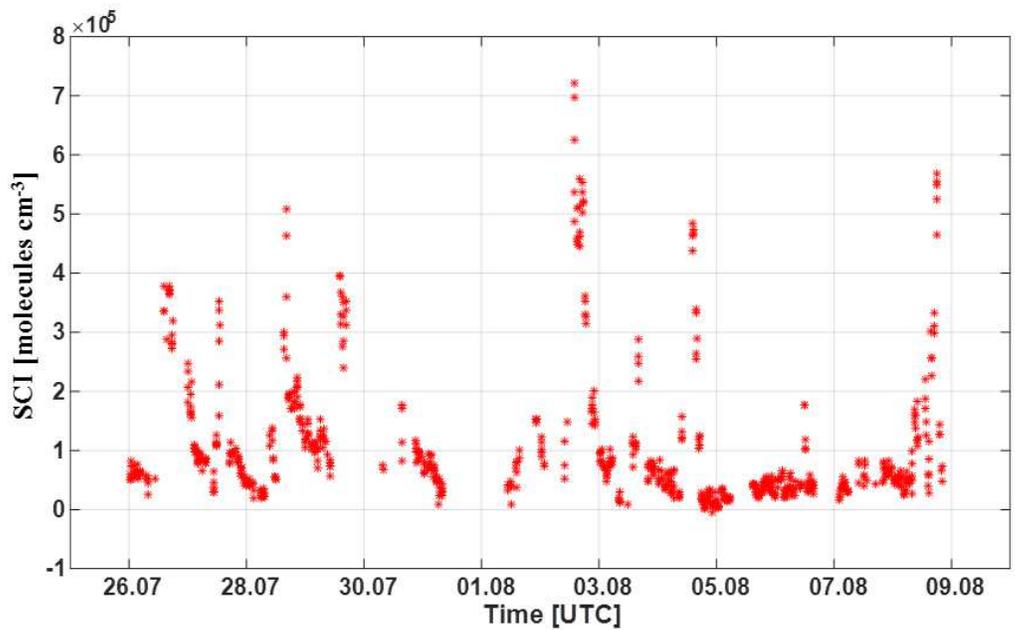
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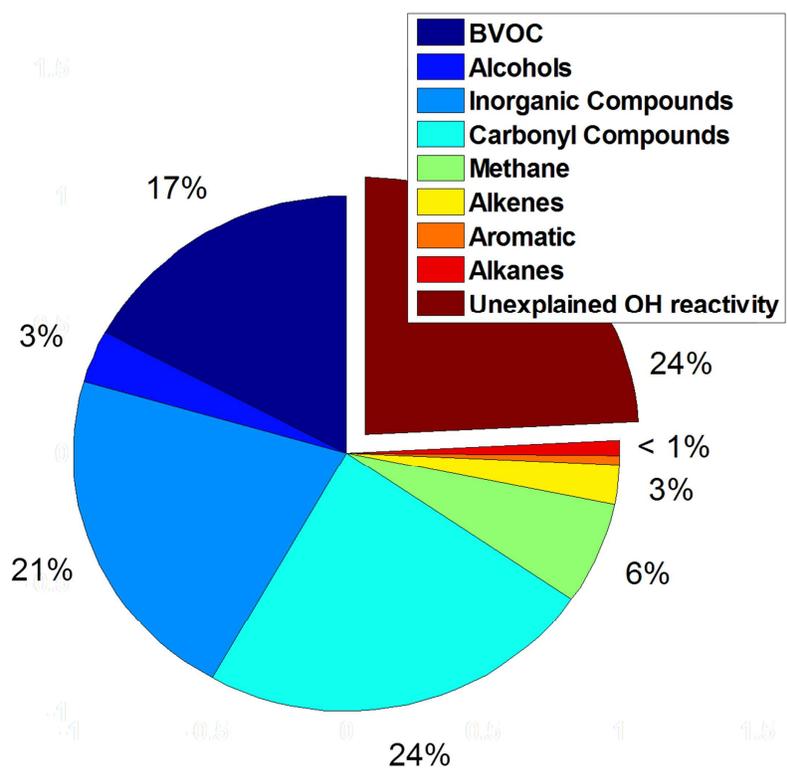
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6 Figure SI-6. Contributions of measured trace gases to the measured OH reactivity during the
 7 HUMPPA-COPEC 2010.

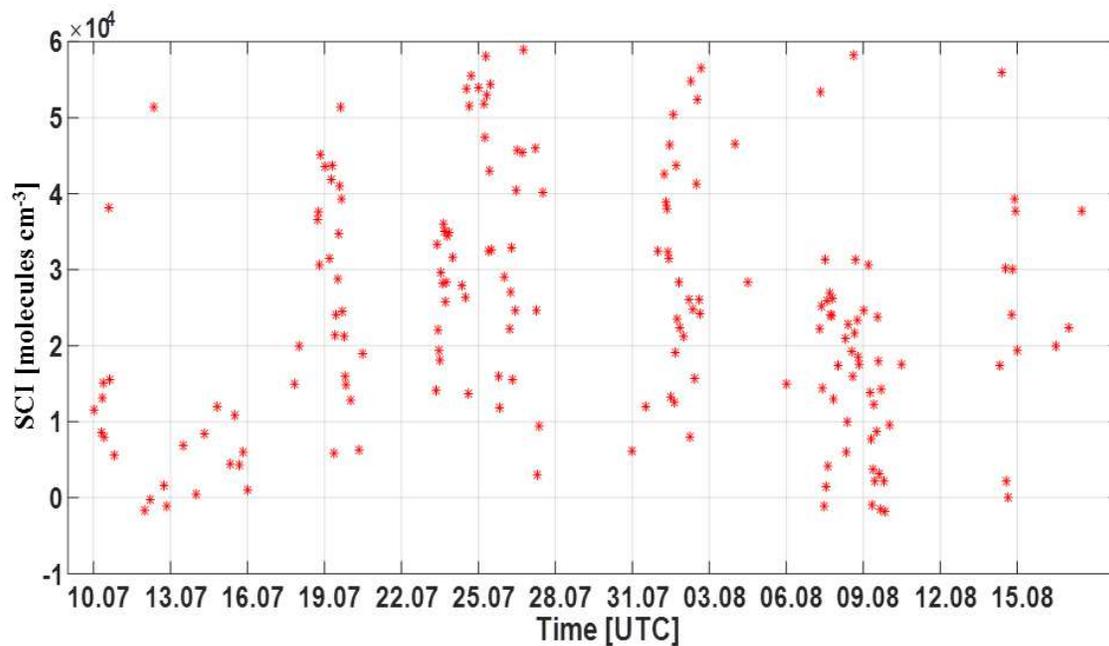
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 2 Figure SI-7. SCI time series as calculated from the unexplained OH reactivity during the
 3 HUMPPA-COPEC 2010 campaign.

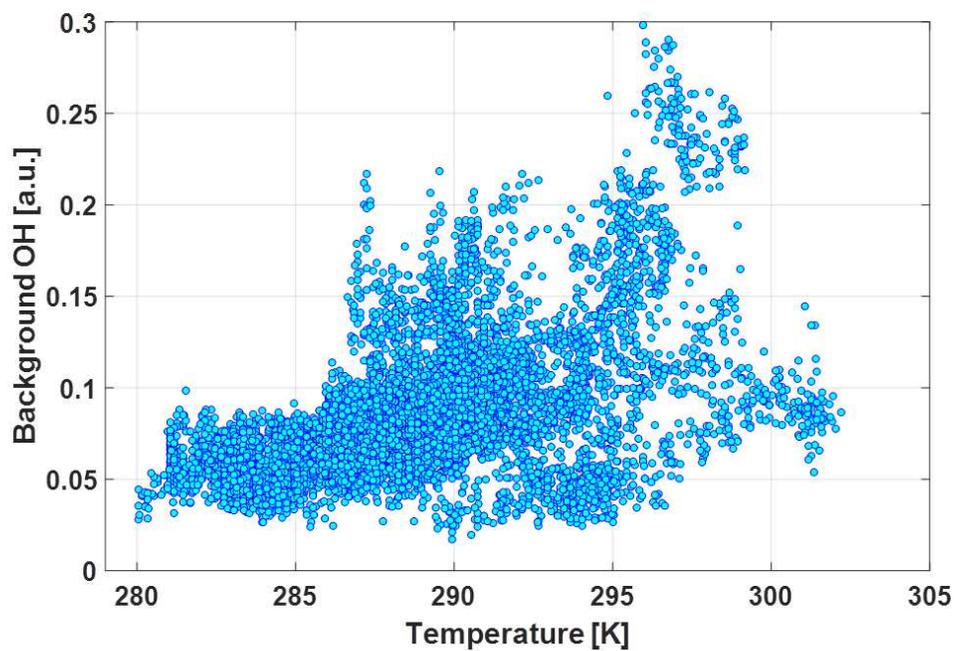


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 5 Figure SI-8. Contributions of measured trace gases to the measured OH reactivity during the
 6 HOPE 2012.



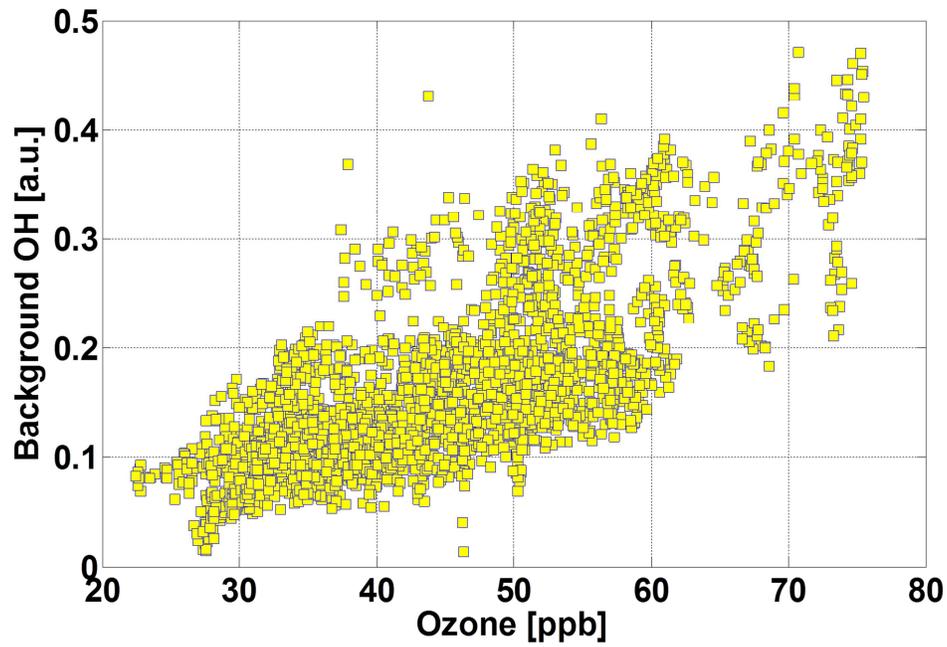
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2 Figure SI-9. SCI time series as calculated from the unexplained OH reactivity during the
 3 HOPE 2012 campaign.



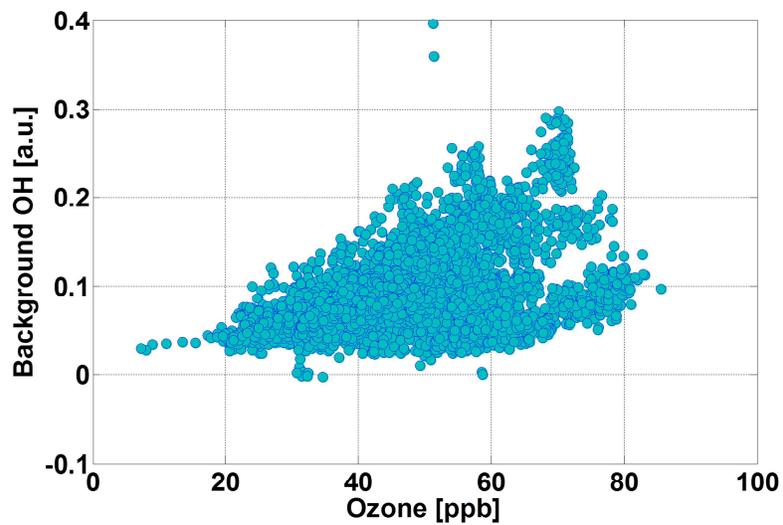
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5 Figure SI-10. Background OH as a function of temperature during the HOPE 2012 campaign.



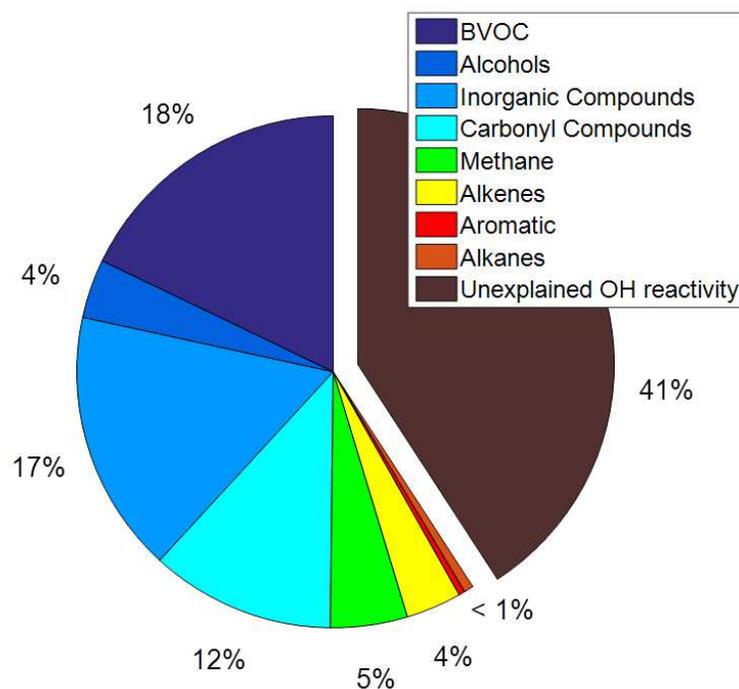
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2 Figure SI-11. Background OH as a function of the ozone concentration during the HUMPPA-
3 COPEC 2010 campaign.



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5 Figure SI-12. Background OH signal as a function of ozone concentration during the HOPE
6 2012 campaign.



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2 Figure SI-13. Contribution of measured trace gases to the measured OH reactivity during
3 HOPE 2012 between the 1st and 3rd of August 2012.

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