We thank the anonymous referees 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.

Anonymous Referee #1

This paper focuses on the analysis of data from two field measurement campaigns, and combines results from laboratory experiments to assess relationships between inferred amounts of stabilized Criegee intermediates (SCI) in the atmosphere, and their possible contribution to the background signals in the measurement of hydroxyl radicals (OH) by a particular laser induced fluorescence (LIF)-based instrument.
The physical chemistry of SCI is currently a subject of great interest, as is improved understanding of the components of the background in LIF-based OH instrumentation. Analysis of data collected during comprehensive ambient field campaigns is a sensible way to attack this problem. The authors have done a good job of precisely describing their assumptions and the potential pitfalls of various approaches. They have used various statistical parameters (e.g. correlation coefficients) to allow the reader to understand the robustness of the relationship under discussion. The literature is well-cited, and indeed the reference list serves as a useful list of recent Criegee intermediate-related papers.

General comments.
1) This reviewer finds the discussion of the average concentration of SCI over an entire field campaign not very useful. It would be much better to work with an entire time series of SCI, followed by development of average diurnal cycles, and dependence of the derived concentrations on various parameters such as ozone, NOx, OH reactivity, reactivity from all BVOC, reactivity from all alkenes, and so on. This would give the reader a better feel as to what to expect from SCI behavior in various atmospheric environments.

The authors understand the reviewers' concern, and a clarification is needed. The average value for the SCI concentrations from the different approaches in the two different environments is obtained from a time series of SCI. The time series are now shown in the supplementary information. Average diurnal cycles of the OH background signals from both campaigns discussed in this paper have been previously published by Novelli et al. (2014). The only exception is represented by the SCI estimate from the unexplained production rate of OH where the average value is used instead as it is directly taken from Hens et al. (2014). This is now better explained in the revised version of the manuscript. The authors do not support the suggestion of showing the dependence of the SCI concentration on various parameters; this is beyond the scope of this manuscript as its goal is to try and provide the boundary concentration of SCI in two environments rather than targeting the behavior of the SCI in general. The title of the manuscript has been changed in the revised version to better reflect this focus.

2) Regarding the rate coefficient for SCI with SO_2, this reviewer suggests going with the larger value obtained by several groups, and simply mentioning in the discussion that if the Mauldin et al., 2012 value is correct, then the concentrations of SCI increase by a factor of 66 (3.3E-11 / 5E-13). As the current discussion implies, the values derived with the Mauldin et al. value seem high when various constraints are imposed.

The authors would still prefer to keep the lower rate coefficient in the calculation of the SCI concentration from the sulfuric acid budget as this value is published and no different

measurement from the same group showing a different value is available yet. We have moved all of the discussion on possible causes of the difference in the rate coefficients to the supporting information (following the suggestion of reviewer #2) where we now also discuss a much broader range of possible sources of differences.

3) The data for both studies is lacking measurements of important species. For example, HUMPPACOPEC 2010 is missing some terpenes, mono-alkenes, small alkanes, and aromatic compounds. HOPE 2012 is more complete, but is missing hydrogen peroxide, HONO, and a pentane isomer. Both studies are light on oxygenated species (5 compounds). Other measurements such as NO_y, alkyl and peroxy nitrates, nitric acid, and HO_x radicals would help to put the measurements in an overall context of pollutant level and oxidizing capacity. It should be possible to use other studies in the region to estimate concentrations of these other species, using perhaps, ratios to CO or some other approach.

The authors agree with the reviewer about the incompleteness of the data set for the HUMPPA-COPEC 2010 campaign, though we feel that the data set from HOPE 2012 is very extensive and covers a sufficient suite of trace gases. It seems unlikely, especially given the large uncertainties related directly to SCI yields, unimolecular decomposition rates and rate coefficients with other trace gases, that the addition of other trace gases would improve the estimates. Also, several of the compounds measured (alkanes, aromatics, HONO, H_2O_2) are not sources of SCI. As discussed in the answer to the first comment, the aim of the paper is to give boundaries for the SCI concentration, not to assess their role in the atmosphere.

4) The presentation of data in a table with average values give the reader only one dimension of their behavior with time, radiation, temperature, and other species. Time series plots of all the species in the Supplemental Information would be preferred, but in their place, additional information in the table would be helpful. Suggest including with the average (mean) values, include median, and standard deviation of the mean. For species with significant diurnal variations, average diurnal plots would be useful. Also, values in mixing ratio units (e.g. ppbv and pptv) should be used rather than molecular units. Plots of average ozone, OH, and HO2 versus NO or NOx would help the reader understand the chemical regime of the air masses measured. Such plots may help the authors decide how to divide the data into various measurement regimes (e.g. background, polluted, mixed, anthropogenic, biogenic).

For the time series of all the species from the HUMPPA-COPEC 2010 campaign we now refer directly to Hens et al. (2014) and Nölscher et al. (2012) which contain such data. For the HOPE 2012 campaign time series of the species listed in the tables have been added to the supplementary information. The authors did look into the possible division of the data into various chemical regimes but this did not produce any particular additional insight.

5) In several places, the sum of the VOC concentration is given. This reviewer is not convinced that this is a very useful parameter, since the various VOCs measured have very different reactivities with OH, ozone, and NO_3. It might be better to use the sum of the OH reactivity due to the VOCs to describe the varying composition of air masses (e.g. when discussing the tree cutting event).

We agree with the reviewer about the different reactivities VOCs have towards oxidants. Within this study we tried several times to underline this issue. For example, for the unexplained OH reactivity estimate of the SCI concentration (Chapter 3.3), we perform a sensitivity study (now moved to the supplementary information following the suggestion of reviewer #2) to account for the

different reactivity VOCs have towards OH and O_3. In the case of the estimate of the SCI concentration from the unexplained OH production (Chapter 3.4) we actually estimate the VOC ozone reactivity exactly to avoid the use of the sum of VOCs. This is better explained in the revised version of the manuscript. The delineation between the tree cutting period and the rest of the "normal" campaign is based on the differences in the measured and unexplained OH reactivity due to the VOCs.

6) With a more complete set of species measured and estimated, it makes sense to perform model runs with the Master Chemical Mechanism (or other mechanism) modified as needed based on the latest information on SCI reactions and photolysis. These runs will aid in the budget analysis of individual SCI and their sum, as well as budgets of other species (e.g. OH, sulfuric acid).

The authors agree that modelling with the MCM can be beneficial, but for this particular paper we consider it to be out of scope, as it is very long already. Currently, the model would not bring any additional meaningful information on the budget beyond what has been already done in the manuscript, given the uncertainties associated with the chemistry of SCI. Moreover, we currently do not have the necessary information to speciate the SCI (we have rate coefficients for only a handful of them) and a model study would not provide this.

7) Some species and parameters are so important to the analyses described in this paper as to deserve further discussion on their validity (e.g. OH reactivity). Have the methods been compared in the laboratory and/or the field with other techniques? Do the values behave as expected and as seen in other studies as functions of time of day, NO_x, OH reactivity, etc? While everyone in such campaigns submits their data in the best possible state that has been carefully quality assured and quality controlled, mistakes can be made. Detailed data examinations can sometimes reveal such problems.

The authors understand and share the concerns of the reviewer regarding the quality and validity of the data used in this or any study. We have no reason to doubt the data provided by our fellow colleagues, who have checked their validity. Furthermore, most of the data has been already published in other manuscripts and was critically evaluated at that time. For other parameters we have included extensive discussions as to the expected uncertainties (e.g. k(T) of SCI + SO_2, condensation H_2SO_4 sink,...).

8) This reviewer is not convinced that the current title describes the content of the paper. Suggest changing the title to more accurately reflect the paper contents and conclusions.

The authors agree with the reviewer and, also in response to the comments of reviewer#2, changed the paper title into: "Estimating the atmospheric concentration of Criegee intermediates and their possible interference in a FAGE-LIF instrument".

Specific comments.
Page 2, line 11. Suggest "…through the addition to sulphur dioxide."

The sentence was rephrased.

Page 2, line.11. The term "central value" is used here and elsewhere in the paper. Does this refer to the mean or median value or something else? Suggest using standard statistical terms.

The term central value was replaced with the term average.

Page 4, line 6. Suggest "…while lower limits have been determined…"

Changed accordingly.

Page 5, line 23. In giving an OH value, is this meant to be globally, daily maximum, or campaign average.
This value seems a bit high for the daily maximum remote locations, and perhaps a bit low for polluted situations. Suggest adding a bit more text to describe what is mean by this value.

The value of OH was meant to give an idea of the order of magnitude of the OH concentration globally, but as it was misleading it was removed from the manuscript.

Page 6, line 1. Suggest another word in place of "relevant", perhaps "significant".

Changed accordingly.

Page 7, line 15. An OH scavenger is mentioned, but its identify is not revealed. Suggest saying specifically what compound is used.

Changed accordingly.

Page 9, line 1. Suggest "…titration of OH_{atm} is performed…" and "…to determine their backgrounds in different environments."

The sentence was unclear and was rephrased.

Page 9, line 5. The description of "better operation" is vague. Suggest a bit more information or rewording.

Changed accordingly.

Page 9, line 20. Suggest "…Scots Pines…"

Changed accordingly.

Page 9, line 22. Suggest "…aerosol particle concentrations, size distributions…"

Changed accordingly.

Page 10, line 6. Check to make sure BVOC is defined earlier in the paper.

The definition of BVOC has been added.

Page 10, line 6-8. Given the importance of the OH reactivity measurements, suggest adding more information including the estimated uncertainties.

A short description of the technique together with the uncertainty on the measurement was added.

Page 11, line 22-25. The discussion of this method of OH reactivity has a bit more information. Suggest making the discussion similar for both methods. Discussion of a comparison of these two techniques would be beneficial, if it has been done.

There is no peer-reviewed information available comprising an intercomparison between these two techniques.

Page 12, line 14. This equation arises out of the steady state assumption for sulfuric acid. Suggest adding a bit of discussion of the assumptions that why steady state should be expected.

A discussion on the validity of the assumption of steady state for sulfuric acid was added.

Page 13, line 1. Suggest "…the rate coefficients of SCI…"

Changed accordingly.

Page 13, line 2. It is stated that the steady state concentration of SCI can be calculated, but equation (2) is that assuming steady state for sulfuric acid. One can calculate the SCI value, but it is not the steady state value. As discussed earlier, suggest doing this calculation for every data point for which all the data needed are available. Then perform statistics and comparison with the full time series.

Please refer to the answer given to the first general comment.

Page 15, line 9-11. It is not clear what the steady state concentration (although it is not the steady state concentration, as discussed earlier) remains in agreement with. Suggest a bit more text to clarify this. Also, suggest "…based on the measured concentrations of VOC…"

The sentence has been rephrased.

Page 15, line 14. It appears to this reader that the calculation yields total sulfuric acid loss (rather than production). Of course, in steady state, production and loss are equal.

While we agree with the reviewer, as discussed in the comments above, we think that the assumption of steady state is reasonable within the uncertainty of our study and therefore production and loss rate are equal.

Page 16, equation 3. This equation yields values of individual SCI using the assumption of steady state. In addition to loss of SCI from unimolecular decomposition, It appears that reaction with water, and other reactions should be included. Also the equation should be clearer as to which terms are being summed. This reviewer believes that the summation should be over k, [VOC], Y_{SCI}, and the loss terms. Ozone is the only parameter that should be outside the summation. Suggest constructing a full time series for this estimate of SCI.

The loss of SCI of 40 s^{-1} already includes reaction with water, water dimers and several trace gases as described in the text as this value is obtained from a previous work. (Novelli et al., 2014b). The formula has been changed as requested. Due to the limited information available, our analysis uses the same Y_{SCI} and loss processes as an average value for all SCI, such that they can be factored out of the summation, which is what we did in the original version.

Page 16, line 8. Suggest "We assume…"

Changed accordingly.

Page 16, line 13. Doesn't Y_{SCI} depend on the VOC that reacts? If so, then the value should be different for each one.

See answer to previous comment.

Page 17, line 12. Suggest "…in a pristine forest environment…"

Changed accordingly.

Page 18, line 24. Should the statement "…half of the measured OH…" actually be "…one-third of the measured OH…"?

The sentence was unclear and has been rephrased.

Page 19, line 22. The phenomenon of unexplained OH production when OH reactivity is high is interesting.
It makes sense to this reviewer that this observation could be due, at least in part, to errors in the measurement of OH reactivity. It also could show up when NOx is high, if NOx correlates with OH reactivity. If so, could it be to errors in measuring HONO or errors in the estimate of J(HONO)? The point is that it is not necessarily related to VOC levels or chemistry. Does the need for unexplained OH production disappear when the OH reactivity calculated from individual measured species is used rather than the directly measured OH reactivity?

In the Hens et al. (2014) study from which the unexplained OH production is taken there is a detailed analysis that takes into account how the uncertainty on individual data would impact the OH budget. The conclusion was that an unexplained OH production would still appear for large OH reactivity. The OH reactivity calculated from only the measured species gives a value of 2 ± 2 s^{-1} for the entire duration of the campaign. If such a value is used for the OH budget, the production rate would exceed the loss rate by a factor of 4 for any conditions. Therefore, we believe that the measured total OH reactivity better represents the chemistry in the forest.

Page 20, line 1. Suggest "…during low sun…" since a positive value for J(O1D), even though small, is not night time.

The authors would prefer to keep the text as is as the distinction between the two different ranges of $J(O^1D)$ was taken from Hens et al. (2014) where it was necessary to choose a value of $J(O^1D)$ to separate between daylight conditions (photolysis of trace gases) and night conditions. We agree with the reviewer that a small positive value of $J(O^1D)$ indicates presence of light but we find the simplification of defining such low values for night-time periods suitable for the paper and easier to follow for the reader.

Page 20, line 15. The statement that only certain VOC are considered is confusing, because those VOC causing the unknown OH reactivity are themselves unknown. Suggest rewording this discussion.

The discussion was reworded.

Page 21, line 11. It is not clear exactly what is meant that the ratio of syn- to anti-SCI is within a factor of 5. Does that mean the ratio can go from 0.2 to 5? Or is anti-SCI always greater than or equal to syn-SCI? A bit more discussion would be helpful.

The paragraph was edited for clarity.

Page 22, line 18. Suggest "…which can represent an important primary source…" since whether HONO photolysis is important depends on conditions.

Changed accordingly.

Page 23, line 1-2. You could assume a range of HONO levels and do the calculations with those to see what the impact is.

The authors think that the SCI estimate that would be obtained by assuming a certain concentration of HONO would carry such a large uncertainty that the resulting SCI concentration would be meaningless.

Page 23, section 3.5. While Figure 3 is a clever and useful way to show all the estimates of SCI concentrations, it might also be helpful to put the values into a table. Estimates of uncertainties for each value should also be given.

A table of the estimated SCI concentrations was added.

Page 24. Perhaps calculations with a range of unimolecular decomposition and other reactions would be instructive. Estimates on individual SCI species would be preferred. A discussion of the atmospheric impacts (e.g. oxidation of SO_2, oxidation of VOCs) of SCI over the range of values calculated would be welcome.

The authors agree with the reviewer about the importance of estimates of individual SCI species and the benefit of discussing the atmospheric impact SCI would have in the two specific environments. Unfortunately, the current data available does not allow for a SCI specific estimate. For example, there is little to no information on the unimolecular decomposition rate for speciated SCI. An estimate of a minor impact that SCI would have, for example towards SO_2, is discussed. We consider a more in depth analysis of the SCI impact on several trace gases not within the scope of this study.

Page 25. While the sensitivity of the LIF instrument to OH cannot be used to calculate SCI concentrations from the OH background, this reviewer believes that the OH backgrounds should be normalized by the instrument sensitivity to account for internal instrument changes (e.g. laser power, white cell alignment) when discussing the OH background dependence on temperature and other parameters.

The sensitivity to OH is normalized by a calibration procedure described in the instrumental description (Chapter 2.1); the OH background is normalized to the laser power, possible change in the alignment of the white cell and quenching due to water vapor, all factors which would affect both atmospheric OH and background OH concentrations.

Page 25, line 10. Suggest saying that there is a strong correlation except for the 26-28 July (which are discussed later).

The authors think that there may be some confusion. The specific period of 26-28 July discussed later refers to the HOPE 2012 campaign while the reviewer points at page 25, line 10 when the

discussion is about the HUMPPA-COPEC 2010 campaign where we have no solid reasons to exclude the 26-28 July period.

Page 25, line 21. This reviewer does not see how southern Germany has a larger fraction of non-biogenic VOC than Finland, based on the values in table SI-2. Suggest checking this statement for accuracy.

The statement was misleading and it has been rephrased.

Page 29, line 11. Suggest "The reason for the lack of correlation…"

Changed accordingly.

Page 31. In order to understand the possible impact of SCI on the instrument background, some information on residence times in various parts of the instrument would be helpful.

Information about the residence time of the sampled air between the pinhole and the area where the OH is detected which is relevant for the decomposition of SCI in the LIF instrument was added.

Page 32, line 6-8. Since OH produced by ozonolysis reactions quickly reacts, a mechanism for conversion of peroxy radicals to OH is critical. One possibility is $HO_2 + O_3$, and while not very fast, could be important.

The reactions suggested by the reviewer were already included in the model study performed in Hens et al. (2014) and did not improve the agreement between measured and calculated OH radicals.

Page 36, line 4. Suggest "Hence, higher SCI values appear to be less likely."

Changed accordingly.

Page 38-48. Some of the references are not in alphabetical order.

Checked.

Table 1. See earlier comments about Table SI-1 and 2. The "a" footnote is missing. Suggest adding more species (e.g. NOx, CO, etc.) to this table.

Changed accordingly.

Figure 3. It appears the box for $k_{SCI+SO2}$~10^{-11} for HOPE 2012 should be moved to the left.

Changed accordingly.

Figure 11. The flow lines for the skimmer do not seem reasonable. They should move toward the wall at least somewhat.

The schematic shown is very simplified. We agree with the reviewer, but the main purpose of the figure is to underline the large difference in how the air evolves in the low pressure region of the instrument depending on the typology of nozzle, not to reproduce the air pattern rigorously.

Nevertheless as the figure is not critical, and possibly misleading, it was removed from the manuscript.

Anonymous Referee #2

This paper summaries steady-state calculations of the expected concentration of stabilized Criegee intermediates (SCIs) during two field campaigns (HUMPPA-COPEC 2010 and HOPE 2012). Several methods are used to estimate the concentration of SCIs in these environments, including estimates based on the missing H2SO4 oxidant, the ozonolysis of measured unsaturated compounds, unexplained total OH reactivity, and unexplained OH production rates. These different methods result in estimated SCI concentrations between 5 x 103 and 2 x 106 cm−3 in these environments, although given the uncertainty associated with some of the assumptions used in these calculations the authors conclude that a value of 5 x 104 cm−3 with an uncertainty of approximately and order of magnitude is the most appropriate estimate of the SCI concentration in these environments.

The authors then provide empirical evidence that the artifact in their LIF-FAGE measurements during these field campaigns is the result of decomposition of SCIs in their low pressure detection cell. The evidence includes strong correlations of the observe OH background signal with temperature, ozone, and BVOC concentrations. In addition, scavenging experiments where SO2 is added externally also removes the interference. However, the observed background OH signal corresponds to an equivalent concentration that is several orders of magnitude greater than the calculated SCI concentration suggesting that SCIs are not the only contributor to the background signal. Although the authors attempt to provide some possible explanations to account for this discrepancy, including a greater decomposition rate inside their detection cell and a different transmission efficiency of SCIs through their inlet compared to OH, they cannot fully explain the observed discrepancy.

The paper is well written and suitable for publication in ACP after the authors have addressed the following comments:

1) The title of the paper is somewhat misleading, as the paper does not explicitly identify Criegee intermediates given that the background OH signal cannot be solely attributed to SCIs. A more appropriate title might be “Estimating the concentration of Criegee intermediates as potential oxidants in the atmosphere.”

Please refer to the answer to the general comment 7 given to the reviewer #1. We propose “Estimating the atmospheric concentration of Criegee intermediates and their possible interference in a FAGE-LIF instrument”.

2) The description of the different methods used to calculate the steady-state concentration is long and may detract from the overall conclusions of the paper. Moving some of this discussion to the Supplement would help maintain the focus of the paper on the resulting concentration estimates and interference discussion. Did the authors compare their estimations of the concentration of SCIs to that predicted by the Master Chemical Mechanism?

Part of the discussion of the SCI estimates, in particular the discussion about uncertainty in the rate coefficients used in this study, was moved to the supplementary information.

A comparison of the SCI estimates with the MCM was not performed as the current MCM mechanism still lacks the majority of reactions and SCI conformers that would be needed in order to compare the values, i.e. there is little to compare against. In order to use the MCM to calculate the SCI concentration from different monoterpenes a lot of changes to the model would be needed, which is out of the scope of this study, though it is part of an upcoming study.

3) The strongest piece of evidence that the source of the OH background signal is due to SCIs is the SO2 scavenging experiment described on page 30 and Figure 10. However, the paper would benefit from an expanded discussion of these measurements. What are the equivalent OH concentrations corresponding to the signals shown in Figure 10? Do they correspond to the high equivalent OH concentrations discussed on page 33? Did the authors attempt more than one scavenging experiment at different times during the day and/or night? Was the background signal consistently scavenged during multiple experiments? Were there periods when addition of SO2 did not scavenge all of the background signal? Providing more details on these experiments would give additional confidence that SCIs were responsible for the high background OH signal.

The discussion regarding the SO_2 scavenging experiments was somewhat expanded as suggested by the reviewer. In the following, please find some brief answers to the questions raised by the reviewer. The equivalent of the OH concentration corresponding to the signal shown in Figure 10 would be ~ 2×10^6 molecules cm^{-3} and it would match with the values described at page 33. During the HOPE campaign we performed a few experiments at the very end of the campaign during the day and the results were similar to what is shown in figure 10. Since we put forward the hypothesis that the OH background observed in the LIF could be caused by the unimolecular decomposition of SCI, scavenging experiments with SO_2 were performed for every subsequent field campaign. In every environment in which the instrument was deployed, it was possible to scavenge the OH background signal with SO_2. This data will be the subject of future publication.

References

Hens, K., Novelli, A., Martinez, M., Auld, J., Axinte, R., Bohn, B., Fischer, H., Keronen, P., Kubistin, D., Nölscher, A. C., Oswald, R., Paasonen, P., Petäjä, T., Regelin, E., Sander, R., Sinha, V., Sipilä, M., Taraborrelli, D., Tatum Ernest, C., Williams, J., Lelieveld, J., and Harder, H.: Observation and modelling of HOx radicals in a boreal forest, Atmos. Chem. Phys., 14, 8723-8747, 10.5194/acp-14-8723-2014, 2014.

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Relevant changes in the manuscript

- Title of the manuscript was changed to: “Estimating the atmospheric concentration of Criegee intermediates and their possible interference in a FAGE-LIF instrument.
- Time series of the SCI concentrations estimated and of all relevant trace gases for the HOPE 2012 campaign were added in the supplementary information.
- Analysis of uncertainties from the H_2SO_4 (Chapter 3.1) and OH reactivity (Chapter 3.3) estimates were moved to the supplementary information.
- The analysis on the reason for discrepancy in the SCI + SO_2 rate coefficient in the supplementary information was expanded.
- A table with the average values for the SCI concentration estimated was added.
- Figure 11 was removed.
- Several paragraphs were rephrased and modified for clarity.

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

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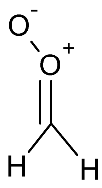
Abstract

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

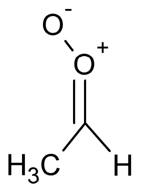
1 Introduction

Criegee intermediates (CI), or carbonyl oxides, are formed during the ozonolysis of unsaturated organic compounds (Criegee, 1975;Johnson and Marston, 2008;Donahue et al., 2011): in the gas phase ozone attaches to a double bond forming a primary ozonide (POZ) that quickly decomposes forming a Criegee intermediate and a carbonyl compound. The CI can exist as thermally stabilised CI (SCI) or as chemically activated CI (Kroll et al., 2001;Drozd et al., 2011), where the chemically activated CI have high energy content and in the atmosphere either undergo unimolecular decomposition, or are stabilised by collisional energy loss forming SCI.

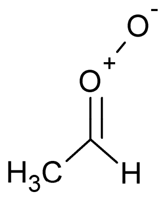
For many decades the chemistry of Criegee intermediates was investigated both with theoretical and indirect experimental studies as reviewed in detail by Johnson and Marston (2008), Vereecken and Francisco (2012), and Vereecken et al. (2015). During the last few years, numerous experimental studies specifically on stabilised Criegee intermediates have been performed following their first detection by Welz et al. (2012). Many laboratories have now detected SCI with various techniques (Berndt et al., 2012;Mauldin III et al., 2012;Ouyang et al., 2013;Taatjes et al., 2013;Ahrens et al., 2014;Buras et al., 2014;Liu et al., 2014a;Sheps et al., 2014;Novelli et al., 2014b;Stone et al., 2014;Chhantyal-Pun et al., 2015;Lee, 2015;Newland et al., 2015a;Fang et al., 2016a;Smith et al., 2016) and have confirmed that they are very reactive towards many atmospheric trace gases. Currently, the most studied Criegee intermediates are formaldehyde oxide, CH_2OO, acetaldehyde oxide, CH_3CHOO (*syn* and *anti,* i.e. with the outer oxygen pointing towards or away from an alkyl group, respectively) and acetone oxide, $(CH_3)_2COO$.



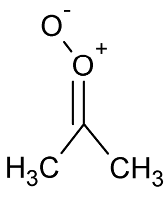
Formaldehyde oxide



Syn-acetaldehyde oxide



Anti-Acetaldehyde oxide



Acetone oxide

The importance of stabilised Criegee intermediates as oxidants in the atmosphere depends on the rate coefficient of their reaction with water vapour as the latter is ubiquitously present in relatively high concentrations in the boundary layer (between 10^{16} to 10^{17} molecules cm^{-3}). The rate of this reaction strongly depends on the CI conformation (Aplincourt and Ruiz-López, 2000;Tobias and Ziemann, 2001;Ryzhkov and Ariya, 2003;Kuwata et al., 2010;Anglada et al., 2011;Anglada and Sole, 2016;Chen et al., 2016;Lin et al., 2016;Long et al., 2016) and until now the rate coefficient has been measured for *anti*-CH_3CHOO (Taatjes et al., 2013;Sheps et al., 2014) while lower limits have been determined for CH_2OO (Stone et al., 2014), *syn*-CH_3CHOO (Taatjes et al., 2013;Sheps et al., 2014) and $(CH_3)_2COO$ (Huang et al., 2015;Newland et al., 2015b). The uncertainties in these rate coefficients make it difficult to estimate the importance of Criegee intermediates and the impact they may have as oxidants in the atmosphere. Additionally, recent studies (Berndt et al., 2014b;Chao et al., 2015;Lewis et al., 2015;Smith et al., 2015;Lin et al., 2016) showed that the reaction between CH_2OO and water dimers (present in the ppmv range in the atmosphere (Shillings et al., 2011)) is faster than the reaction with water vapor, in agreement with the several theoretical studies (Ryzhkov and Ariya, 2004;Chen et al., 2016;Lin et al., 2016) which indicate the reaction with water dimers to be between 400 and 35,000 times faster than the reaction with water vapor depending on the conformers. Another important reaction of SCI that depends on the SCI conformation is their unimolecular decomposition. The decomposition rate and product formed depend on the SCI conformer structure. *Anti*-SCI are likely to isomerise via the ester channel forming an ester or an acid as final product while *syn*-SCI will form a vinyl hydroperoxide (VHP) which promptly decomposes forming hydroxyl radicals (OH) and a vinoxy radical (Paulson et al., 1999;Johnson and Marston, 2008;Drozd and Donahue, 2011;Vereecken and Francisco, 2012;Kidwell et al., 2016). Larger and more complex conformers such as hetero-substituted or cyclic structures are subject to additional unimolecular rearrangements (Vereecken and Francisco, 2012). On the unimolecular decomposition rates and products few experimental data are available (Horie et al., 1997;Horie et al., 1999;Fenske et al., 2000a;Novelli et al., 2014b;Kidwell et al., 2016;Fang et al., 2016a;Smith et al., 2016), but more is available from theoretical studies explicitly focusing on the path followed by different conformers (Anglada et al., 1996;Aplincourt and Ruiz-López, 2000;Kroll et al., 2001;Zhang and Zhang, 2002;Nguyen et al., 2009b;Kuwata et al., 2010).

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

As SCI were found to react quickly with many trace gases, various model studies were performed on the impact SCI have as oxidants in the atmosphere (Vereecken et al., 2012;Boy et al., 2013;Percival et al., 2013;Pierce et al., 2013;Sarwar et al., 2013;Sarwar et al., 2014;Novelli et al., 2014b;Vereecken et al., 2014). Some of these studies focused in particular on the possible impact that SCI might have on the formation of sulfuric acid (H_2SO_4) in the gas phase, following Mauldin III et al. (2012) who suggested that Criegee intermediates are the missing SO_2 oxidant needed to close the sulfuric acid budget over a boreal forest. This is supported by theoretical and laboratory studies that have determined a rate coefficient between SCI and sulfur dioxide (SO_2) of the order of 10^{-11} cm^3 $molecule^{-1}$ s^{-1} (Aplincourt and Ruiz-López, 2000;Jiang et al., 2010;Kurtén et al., 2011;Vereecken et al., 2012;Welz et al., 2012;Taatjes et al., 2013;Liu et al., 2014b;Sheps et al., 2014;Stone et al., 2014). As the main atmospherically relevant oxidiser of SO_2 in the gas phase is the OH radical with a rather slow rate coefficient at ambient temperature and pressure of 2×10^{-12} cm^3 $molecule^{-1}$ s^{-1} (Atkinson et al., 2004), the high rate coefficient for SO_2 oxidation would allow SCI to have a significant impact on the H_2SO_4 formation even if present in small concentrations. The model studies have shown that, depending on the environment, SCI can have a potentially important impact on H_2SO_4 formation. All these studies are affected by large uncertainties and many simplifications used for coping with the paucity of data on the reactions of specific SCI with various trace gas species, on the speciation of SCI, and on the steady state concentration of SCI in the troposphere. Until now no direct or reproducible indirect method was able to determine the steady state concentration of SCI in the lower troposphere.

In this paper, we firstly estimate the concentration of SCI in the lower troposphere, based on the data collected during the HUMPPA-COPEC 2010 campaign (Williams et al., 2011) in a Boreal forest in Finland and the HOPE 2012 campaign in rural southern Germany. The budget of SCI is analyzed using four different approaches: 1) based on an unexplained H_2SO_4 production rate (Mauldin III et al., 2012); 2) from the measured concentrations of unsaturated volatile organic compounds (VOC); 3) from the observed OH reactivity (Nölscher et al., 2012); and 4) from an unexplained production rate of OH (Hens et al., 2014). Secondly, we present measurements obtained using our inlet pre-injector laser-induced fluorescence assay by gas expansion technique (IPI-LIF-FAGE) (Novelli et al., 2014a) during the HUMPPA-COPEC 2010 and the HOPE 2012 campaigns. A recent laboratory study performed with the same instrumental setup showed that the IPI-LIF-FAGE system is sensitive to the detection of the OH formed from unimolecular decomposition of SCI (Novelli et al., 2014b). Building on this study, the background OH (OH_{bg}) (Novelli et al., 2014a) measured during the two field campaigns is investigated in comparison with many other trace gases in order to assess if the observations in controlled conditions are transferable to the ambient conditions.

2 Instrumentation and field sites

2.1 IPI-LIF-FAGE description

A comprehensive description of the IPI-LIF-FAGE ground-based instrument, HORUS (Hydroxyl Radical Measurement Unit based on fluorescence Spectroscopy), is given by Novelli et al. (2014a) and only some important features of the instrument are highlighted here. The IPI-LIF-FAGE instrument consists of: the inlet pre-injector (IPI), the inlet and detection system, the laser system, the vacuum system and the instrument control and data acquisition unit. The air is drawn through a critical orifice into a low pressure region (~300-500 Pa) where OH molecules are selectively excited by pulsed UV light around 308 nm. The light is generated at a pulse repetition frequency of 3 kHz by a Nd:YAG pumped, pulsed, tunable dye laser system and is directed into a multipass ”White cell” making 32 passes through the detection volume (White, 1942). The air sample intersects the laser beam and the fluorescence signal from the excited OH molecules is detected using a gated micro-channel plate (MCP) detector. IPI, situated in front of the instrument inlet, is used to measure a chemical zero to correct for possible internal OH signal generation. An OH scavenger (propene) is added to the sample air 5 cm in front of the inlet pinhole in a concentration that allows a known, high proportion of atmospheric OH to be scavenged (~ 90 %). The OH scavenger is added every two minutes so that the instrument measures a total OH signal (OH_{tot}) when the OH scavenger is not injected and a background OH signal (OH_{bg}) when the OH scavenger is injected. The difference between these two signals yields the atmospheric OH concentration (OH_{atm}). The efficiency of this technique for measuring OH with this particular LIF-FAGE instrument is described together with the IPI characterisation in Novelli et al. (2014a). The OH calibration of the HORUS instrument is obtained via the production of a known amount of OH and hydroperoxyl radicals (HO_2) from the photolysis of water at 185 nm using a mercury lamp. A more detailed description of the instrument calibration is reported by Martinez et al. (2010) and Hens et al. (2014). A calibration factor for the background OH signal observed by the HORUS instrument is currently not available. Therefore, this signal will be discussed and plotted in OH fluorescence counts per seconds (cps) measured by the MCP, normalized by the laser power and corrected for quenching and sensitivity changes towards the detection of OH. The sensitivity of the instrument towards the OH radical is affected by: alignment of the white cell, optical transmission of the components, sensitivity of the MCP, water vapor, internal pressure, and internal temperature (Martinez et al., 2010). These factors affect the sensitivity of HORUS towards the background OH in a similar manner as they mainly impact the sensitivity of the instrument to the detection of OH.

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

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

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

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

2.2 Measurement site and ancillary instrumentation

We present measurements from two sites, a boreal forest site in Finland and a rural site in Southern Germany. The HUMPPA-COPEC 2010 (Hyytiälä United Measurements of Photochemistry and Particles in Air – Comprehensive Organic Precursor Emission and Concentration study) campaign took place during summer 2010 at the SMEAR II station in Hyytiälä, Finland (61° 51’ N, 24°17’ E, 181 m a.s.l.) in a boreal forest dominated by Scots Pines (*Pinus Silvestris L.*). The site hosts continuous measurements of several trace gases and meteorological parameters as well as aerosol particles concentrations, size distributions and composition (Junninen et al., 2009). Further details and a more complete description of the site, the instrumentation and the meteorological conditions during the campaign can be found in Williams et al. (2011) and Hens et al. (2014). A brief description of the instruments used in this study is given here. Ozone was measured by a UV photometric gas analyser (Model 49, Thermo Electron Corporation). A gas chromatograph (GC, Agilent Technologies 6890A) coupled to a mass-selective detector (MS, Agilent Technologies MSD 5973 *inert*) was used for the measurements of biogenic volatile organic compounds (BVOC) (Yassaa et al., 2012). The total OH reactivity was measured by the comparative reactivity method (CRM) (Sinha et al., 2008) for two different heights, one within and one above the canopy (18 and 24 m, respectively) (Nölscher et al., 2012). CRM uses an in-situ kinetics experiment to measure the OH reactivity based on the competitive scavenging of OH by a reference gas (pyrrole) and atmospheric OH reactants. The overall uncertainty of the method during deployment was 16% with a limit of detection of 3 s^{-1} (Hens et al., 2014). Sulfur dioxide (SO_2) concentration was measured with a fluorescence analyzer (Model 43S, Thermo 20 Environmental Instruments Inc.). Aerosol number size distributions between 3 nm and 950 nm were measured with a Differential Mobility Particle Sizer (DMPS) (Aalto et al., 2001). The size distributions were used for calculating the loss rate of gas-phase sulfuric acid via condensation sink (CS) with the method presented by Kulmala et al. (2001). Sulfuric acid (H_2SO_4) and OH radical concentrations were measured on the ground with a chemical ionization mass spectrometer (CIMS; (Petäjä et al., 2009)). Time series of the measured trace gases are available in the study from Nölscher et al. (2012) and Hens et al. (2014). The average concentrations and their 1σ variability are listed in Table 1 and Table SI-2. For the first period of the campaign, between the 27th and the 31st of July, the IPI-LIF-FAGE instrument was run on the ground side-by-side with the CIMS. On the 2nd of August the IPI-LIF-FAGE instrument was moved to the top of the HUMPPA tower above the canopy and measured there for the remainder of the campaign (12th of August). The data are therefore separated into ground and tower periods

The HOPE 2012 (Hohenpeißenberg Photochemistry Experiment) campaign was conducted during the summer of 2012 at the Meteorological Observatory in Hohenpeissenberg, Bavaria, Germany (47° 48' N, 11° 2' E). The observatory is a Global Atmosphere Watch (GAW) station operated by the German Meteorological Service (DWD) and is located at an altitude of 985 m a.s.l. and about 300 m above the surrounding terrain, mainly consisting of meadows and coniferous forests. More information about the site can be found in Handisides et al. (2003). Ozone was measured by UV absorption with TEI 49C (Thermo Electron Corporation, Environmental Instruments) (Gilge et al., 2010). Non-methane hydrocarbons (NMHC) were measured with a GC-flame ionization detection (FID) system (series 3600CX, Varian, Walnut Creek, CA, USA) (Plass-Dülmer et al., 2002). BVOC were detected using a GC (Agilent 6890) with a FID running in parallel with a MS (Agilent Technologies MSD 5975 *inertXL*) described by Hoerger et al. (2014). Photolysis frequencies (J(NO_2) and J(O^1D)) were measured next to the IPI-LIF-FAGE with a set of filter radiometers (Handisides et al., 2003). The OH reactivity was measured with two instruments for a short period of time from the 10th until the 18th of July. One method was the CRM and the same instrument was used as during the HUMPPA-COPEC 2010 campaign. The second method was a new application of the DWD CIMS instrument (Berresheim et al., 2000) which also measured H_2SO_4 and OH radicals. As the data will be used only in a qualitative way for the current study, a very short description of this novel technique is given here and details will be presented in a future publication. With the CIMS instrument, OH radicals are measured by converting them into H_2SO_4 after reaction with SO_2 in a chemical reactor and subtraction of a corresponding background after scavenging the OH with propane (Berresheim et al, 2000). A second SO_2

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

3 SCI concentrations during HUMPPA-COPEC 2010 and HOPE 2012

3.1 Missing H_2SO_4 oxidant

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

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

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

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

On average the sulfuric acid in the gas phase calculated using Eq. 1 was only half of the total H_2SO_4 observed in the field and lied outside the uncertainties associated with the calculation of the formation channel and the condensation sink (Mauldin III et al., 2012). Although no unambiguous evidence links SCI to the missing oxidant, laboratory tests performed with a similar instrument (Berndt et al., 2012;Berndt et al., 2014a;Sipilä et al., 2014) confirmed the role that SCI could have in the oxidation of SO_2 and formation of H_2SO_4. Assuming that SCI are the only other species in addition to OH that oxidize SO_2 in the gas phase and knowing the rate coefficient of SCI and OH with SO_2, it is possible to calculate the steady state concentration of SCI in that environment:

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

The rate coefficient between OH and SO_2 at standard pressure is (2.04 ± 0.10) x 10^{-12} $(T/300)^{-0.27}$ cm^3 $molecule^{-1}$ s^{-1} (Atkinson et al., 2004). The rate coefficient of SCI with SO_2 was determined by several groups at (3.3 ± 2) x 10^{-11} cm^3 $molecule^{-1}$ s^{-1}, (Welz et al., 2012;Taatjes et al., 2013;Liu et al., 2014b;Sheps et al., 2014;Stone et al., 2014;Chhantyal-Pun et al., 2015;Newland et al., 2015a;Newland et al., 2015b;Foreman et al., 2016;Zhu et al., 2016). An earlier, lower value of ~ 5 x 10^{-13} cm^3 $molecule^{-1}$ s^{-1} (Mauldin III et al. (2012); Berndt et al. (2012)) appears to be hard to reconcile with the remaining literature, as extensively discussed in the supporting information.

Equation 2 allows for the calculation of a time series of SCI (Fig. SI-2) yielding an average $[SCI] = (2.3 \pm 2) \times 10^4$ molecules cm^{-3}.

A similar estimate of the SCI time series was derived for the HOPE 2012 campaign (Fig. SI-3). The H_2SO_4 concentration during this campaign can be mainly explained by the reaction between OH and SO_2. Figure 1 shows the correlation between the total production rate of H_2SO_4 ($P(H_2SO_4)_{tot}$) calculated from the product of measured H_2SO_4 and the condensation sink, as well as the production rate of H_2SO_4 from the reaction of OH and SO_2. The linear regression following the method of York et al. (2004) yields a slope of 0.90 ± 0.02 with a negligible intercept (57 ± 7 molecules cm^{-3} s^{-1}). It should be noted that the H_2SO_4 budget for the HOPE 2012 campaign is nearly closed, such that the moderate fluctuations on the source data (CS, [OH], etc.) lead to very large relative uncertainties of the small missing H_2SO_4 production term, and concomitantly the time series for the SCI concentration (Fig. SI-3) shows extreme variability reflecting this noise on the source data. On average, the [SCI] obtained is low, $(2 \pm 3) \times 10^4$ molecules cm^{-3}, with no values in the time series exceeding 10^5 molecule cm^{-3}.

Repeating the above analysis using the low $k_{SCI+SO2}$ value of Mauldin III et al. and Berndt et al. yields concentrations of $(1.6 \pm 2) \times 10^6$ and $(1 \pm 3) \times 10^6$ molecule cm^{-3} for the HUMPPA-COPEC and HOPE campaigns, respectively. It is interesting to notice that both values estimated with the fast and low $k_{SCI+SO2}$ rate coefficient are in agreement with the concentrations calculated from measured VOC and O_3 for polluted and pristine environments, 1.9×10^6 molecules cm^{-3} and 4.5×10^4 molecules cm^{-3} respectively, from a previous study (Welz et al., 2012).

3.2 Measured unsaturated VOC

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

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

Where $k_{VOC_i+O_3}$ is the rate coefficient between the VOC$_i$ and ozone (Table SI-2), Y_{SCI} is the yield of SCI in the ozonolysis reaction, and L_{SCIsyn} is the total loss of *syn*-SCI. We assume [SCI] ≈ [SCI$_{syn}$] following the model described by Novelli et al. (2014b), which accounts for many possible losses of SCI including the reaction with water dimers and unimolecular decomposition. The latter study suggests that *anti*-acetaldehyde oxide and formaldehyde oxide react quickly with water and water dimers and that their contributions can be neglected. A yield of SCI formation (Y_{SCI}) of 0.4 was estimated based on the data by Hasson et al. (2001). The steady state concentration of SCI for the HUMPPA-COPEC 2010 campaign was calculated using the measured data for [O$_3$] and [VOC$_i$] and an average value of 40 s^{-1} (Novelli et al., 2014b) for L_{SCIsyn} as this value was found to be rather constant and mainly dependent on the unimolecular decomposition rate of the SCI. Equation 3 allows for the calculation of a time series of SCI (Fig. SI-4) yielding an average [SCI] of ~ (5 ± 4) x 10^3 molecules cm^{-3}.

During the HOPE 2012 campaign a larger number of unsaturated organic trace gases, both anthropogenic and biogenic, were measured (Table SI-1). For Y_{SCI} the same value of 0.4 was used while for L_{SCIsyn} the value of 32 s^{-1}, obtained from the model described by Novelli et al.

(2014b) for the rural European environment, was used. Using these values in Eq. 3 results in [SCI] = (7 ± 6) x 10^{3} molecules cm^{-3}, obtained as an average of the SCI time series (Fig. SI-5). It should be noted that recent work on the unimolecular decomposition (Fang et al., 2016b;Long et al., 2016;Smith et al., 2016) yields loss rates significantly faster than used here; this implies that the [SCI] obtained here could be an overestimate.

3.3 OH reactivity

During HUMPPA-COPEC 2010, between 27th July and 12th August, an average OH reactivity, R = 9.0 ± 7.6 s^{-1}, was measured. On average, the majority of the measured OH reactivity (R_{unex} = 7.4 ± 7.4 s^{-1}), 80 %, was not accounted for by the measured organic and inorganic trace gases (Fig. SI-6). Biogenic emissions comprised up to ~ 10 % of the total measured OH reactivity and up to half of the calculated OH reactivity (Fig. SI-6). As the measurement site was located in a pristine forest environment, affected only little by anthropogenic emissions (Williams et al., 2011), it is likely that a large fraction of the unexplained OH reactivity was formed by unmeasured primary emissions by the vegetation and secondary products of oxidation. By assuming that the unmeasured VOC are unsaturated, and by using a lumped rate coefficient, k_{VOC+OH}, between OH and the fraction of unspeciated VOC of 7 x 10^{-11} cm^{3} $molecule^{-1}$ s^{-1}, typical for an OH addition to a carbon-carbon double bond (Atkinson et al., 2004;Peeters et al., 2007), it is possible to estimate the concentration [$VOC_{unknown}$] of VOC that would be necessary to close the OH reactivity budget (Eq. 4).

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

Using Eq. 4, a time series for [$VOC_{unknown}$] with an average of (1 ± 1) x 10^{11} molecules cm^{-3} is obtained. This value is substituted into Eq. 3 and a lumped rate for reaction of [$VOC_{unknown}$]

and O_3 of 7 x 10^{-17} molecules cm^{-3} is used. This value is based on the rate coefficient of the measured VOC with O_3 weighted with their abundance (Table SI-1). The same Y_{SCI} and L_{SCIsyn}, of 0.4 and 40 s^{-1}, respectively, were used as described in section 3.2. With these values, a time series of SCI (Fig. SI-7) with an average of ~ (1 ± 1) x 10^5 molecules cm^{-3} is obtained. To this SCI concentration estimate, we add the SCI formed from the measured unsaturated VOC, [SCI] = (5 ± 4) x 10^3 molecules cm^{-3}, to obtain the total SCI across all VOC. As this estimate requires assumptions for the rate coefficient between [$VOC_{unknown}$] and OH and O_3, a sensitivity study probing the upper and lower bounds of this estimate is described in the supplementary information.

During the HOPE 2012 campaign the total OH reactivity was on average 3.5 ± 3.0 s^{-1}. Using the measured trace gas concentrations it is possible to calculate the expected OH reactivity (Fig. SI-8). Table SI-2 lists all the species included in the calculation of the OH reactivity with their rate coefficient with OH. An average value of 2.7 ± 0.7 s^{-1} was calculated. Figure SI-8 shows that half of the measured OH reactivity can be explained by methane, carbonyl compounds (mainly acetaldehyde and propanal) and inorganic compounds which were present in higher concentrations compared to the HUMPPA-COPEC 2010 campaign (Table SI-2). On average, 24 % of the measured OH reactivity remains unexplained by the measured trace gases. In contrast to the HUMPPA-COPEC 2010 campaign, in HOPE 2012 a more complete speciation of VOC was measured (Table SI-1) and the site was influenced by relatively fresh anthropogenic emissions. With the extensive VOC speciation available, the reactivity budget can virtually be closed, but any remaining unexplained OH reactivity could still be due to unmeasured VOC. The time series for this unexplained OH reactivity, typically about ~ 1 s^{-1}, shows very large variability as it reflects the statistical noise of the small difference between measured and calculated OH reactivities, both of which are associated with variability. The resulting [SCI] time series (Fig. SI-9) is also highly variable, and yields a low average SCI concentration of (2.0 ± 1.5) x 10^4 molecules cm^{-3}, with no values exceeding 6 x 10^4 molecule cm^{-3}.

The total SCI is then obtained by summing the SCI predicted from the measured VOC and from the unexplained OH reactivity, leading to a total SCI concentration of (7 ± 6) x 10^3 molecules cm^{-3}.

3.4 Unexplained OH production rate

During the HUMPPA-COPEC 2010 campaign, the comprehensive measurements (Williams et al., 2011) allowed the calculation of a detailed OH budget (Hens et al., 2014). Most of the OH production during daytime is due to photolysis of O_3 and recycling of HO_2 back to OH via reactions with NO and O_3. This result holds for both high ($R > 15$ s^{-1}) and low ($R \leq 15$ s^{-1}) OH reactivity episodes during the campaign. While the OH budget can be closed during daytime ($J(O^1D) > 3 \times 10^{-6}$ s^{-1}) for low OH reactivity periods, during periods with high OH reactivity there was a large unexplained production rate of OH, $P_{OH}^{unexplained}$ = (2 ± 0.7) x 10^7 molecule cm^{-3} s^{-1}, which can thus be surmised to originate from VOC chemistry. In addition, for both periods, during night time ($J(O^1D) \leq 3 \times 10^{-6}$ s^{-1}), the IPI-LIF-FAGE and the CIMS instruments both measured non-negligible OH concentrations (Hens et al., 2014) where most of the OH production was from unknown sources ($P_{OH}^{unexplained}$ = 1 ± 0.9 x 10^6 molecule cm^{-3} s^{-1} (1σ) and $P_{OH}^{unexplained}$ = 1.7 ± 0.7 x 10^7 molecule cm^{-3} s^{-1} (1σ) for low and high reactivity, respectively). Our hypothesis is that ozonolysis of VOC could represent the missing OH source. Indeed, formation of OH from oxidation of unsaturated VOC has been shown to be an important source of OH in winter, indoors and during night time (Paulson and Orlando, 1996;Geyer et al., 2003;Ren et al., 2003;Heard et al., 2004;Harrison et al., 2006;Johnson and Marston, 2008;Shallcross et al., 2014). As OH formation from ozonolysis proceeds through Criegee intermediates (Fig. 2), we can attempt to estimate a SCI concentration from the OH budget. First, we estimate from the unexplained OH reactivity $P_{OH}^{un\exp lained}$ a so-called unexplained O_3 reactivity, $\Sigma(k_{VOC+O3}$ x [$VOC_{unidentified}$]), assuming a certain yield of OH from ozonolysis of unsaturated VOC. Next, we estimate a yield of SCI based on available literature data, and finally we combine both to estimate the SCI concentration required to close the OH budget. In contrast to the previous estimates, an average value is obtained for the SCI, and not a time series, as we start from the average $P_{OH}^{un\exp lained}$, as reported in Hens et al. (2014).

Assuming that all unexplained OH production, $P_{OH}^{un\exp lained}$, comes from VOC ozonolysis with a certain OH yield Y_{OH} we obtain:

$$P_{OH}^{un\exp lained} = k_{voc+O_3} \times [VOC_{unidentified}] \times [O_3] \times Y_{OH} \qquad (5)$$

where $VOC_{unidentified}$ includes the VOC not considered in the OH budget performed by Hens et al. (2014), i.e. the VOC causing the unknown OH reactivity discussed above. The average total OH yield from ozonolysis, Y_{OH}, is estimated at about 0.6 based on observed OH yields from the literature (Atkinson et al., 2006). OH formation from ozonolysis occurs through two channels (Fig. 2): prompt formation by the decomposition of chemically activated CI^*, and delayed OH by formation of SCI followed by their thermal decomposition; there are also product channels not yielding OH. The prompt yield of OH, $Y_{OH}^{CI^*}$ is estimated at ~ 0.4 from SCI scavenging experiments (Atkinson et al., 2004); the remaining yield Y_{OH}^{SCI} is then formed from SCI, where $Y_{OH} = Y_{OH}^{CI^*} + Y_{OH}^{SCI}$ and hence $Y_{OH}^{SCI} \approx 0.2$.

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

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

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

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

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

The measured $P_{OH}^{unexplained}$ and [O_3], and the estimates of the other parameters allow us to calculate the factor k_{voc+O_3} × [$VOC_{unidentified}$]. Substituting this factor into Eq. 6 yields an estimate of the steady state concentration of SCI_{syn}. With a value for $P_{OH}^{unexplained}$ of 1 x 10^6 molecules cm^{-3} s^{-1} as observed for low reactivity episodes and at night during HUMPPA, a steady state concentration of SCI_{syn} of (2 ± 2) x 10^4 molecules cm^{-3} is calculated. For high reactivity episodes during HUMPPA-COPEC 2010, the missing $P_{OH}^{unexplained}$ of 2 x 10^7 molecules cm^{-3} s^{-1} results in a SCI concentration of (4 ± 4) x 10^5 molecules cm^{-3}. To obtain the total SCI concentration, we then need to add the non-OH-producing SCI. Here we assume that these are mostly *anti*-SCI or H_2COO, both of which react rather quickly with H_2O or $(H_2O)_2$ (Taatjes et al., 2013;Chao et al., 2015;Lewis et al., 2015), and that their contribution can be neglected. We thus obtain that [SCI] ≈ [SCI_{syn}]. To this we add the SCI concentration calculated from the measured unsaturated VOC (section 3.2), (5 ± 4) x 10^3 molecules cm^{-3}, to obtain the SCI formed from all VOC.

For HOPE 2012 it is difficult to accurately derive an OH budget due to the lack of information on the HONO concentration, which can represent an important primary source of OH. A detailed analysis of the OH production and loss during the campaign thus requires a detailed model study to derive HONO concentrations, which is outside the scope of this paper. Hence, an estimate on the SCI from a possible missing OH production rate during the HOPE 2012 campaign is not included here.

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

3.5 Robustness of the [SCI] estimates

Figure 3 summarises the steady state concentration of SCI calculated on the basis of the H_2SO_4 budget, the measured unsaturated VOC concentration and OH reactivity (R), and the OH budget for the HUMPPA-COPEC 2010 and HOPE 2012 campaigns. By considering the lower and the highest values estimated from the measured VOC and from the missing H_2SO_4 oxidant for both campaigns, respectively, the steady state concentration of SCI is calculated to be between 5 x 10^3 and 2 x 10^6 molecules cm^{-3} for the boreal forest environment during the HUMPPA-COPEC 2010 campaign and between 7 x 10^3 and 1 x 10^6 molecules cm^{-3} for rural Germany during the HOPE 2012 campaign (Table 2). The SCI concentrations calculated using these approaches represent a best-effort estimate made for the environments studied here based on the available data; due to the many uncertainties related to the chemistry of SCI both in production and loss processes these estimates span about two orders of magnitude.

The estimate of the SCI concentration from the sulfuric acid budgets relies on the rate of oxidation of SO_2 to H_2SO_4. As indicated in section 3.1, two significantly different rate coefficients for the reaction of SCI with SO_2 are currently available. One coefficient is high, ~ 3.3 ± 2 x 10^{-11} cm^3 $molecule^{-1}$ s^{-1}, while the other is several orders of magnitude lower, 5 x

10^{-13} cm^3 $molecule^{-1}$ s^{-1}. Justifications of the differences in the values due to the diverse procedures, i.e. direct detection of SCI + SO_2 for the high rate coefficient and detection of H_2SO_4 for the lower one, are difficult, while recent measurements tend to agree with the highest value. This casts doubts on the highest obtained SCI concentrations of ~ 10^6 molecules cm^{-3}. In addition, the remaining three estimates strongly depend on the yield of SCI, k_{VOC+O_3} and L_{SCIsyn}. Among these, the parameter with the highest uncertainty is the loss rate of *syn*-SCI, L_{SCIsyn}, as it is based on relatively few studies, which report large differences between the observations. In this study, a value of 40 s^{-1} and of 32 s^{-1}, based on previous model analysis (Novelli et al., 2014b), for the HUMPPA-COPEC 2010 and HOPE 2012 campaigns respectively, were used. Recent work (Smith et al., 2016;Fang et al., 2016a;Long et al., 2016) suggests a faster unimolecular decomposition rate for the acetone oxide Criegee intermediate, exceeding 10^2 s^{-1} in ambient conditions. It is currently not clear whether this rate applies to more substituted SCI as formed from monoterpenes but the use of these higher decomposition rate in the model by (Novelli et al., 2014b) would result in a total L_{SCIsyn} of ~ 110 s^{-1}. This loss rate would decrease the estimated SCI concentration by almost a factor of 3, closer to the lower estimates not exceeding 10^5 molecule cm^{-3}; this also casts doubt on the highest estimates given in Figure 3. Therefore, an average estimated SCI concentration of about 5 x 10^4 molecules cm^{-3}, with an order of magnitude uncertainty, is considered more appropriate for both campaigns.

4 The source of the OH background signal

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

4.1 Correlation of OH_{bg} with temperature

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

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

4.2 Correlation of OH_{bg} with unexplained OH reactivity

As described in section 3.3, during the HUMPPA-COPEC 2010 campaign high average OH reactivity was observed (~ 9 s^{-1}), of which between 60 % and 90 % cannot be explained by the loss processes calculated from the measured species (Nölscher et al., 2012). A large unexplained fraction of the reactivity has often been observed, especially in forested environments (Di Carlo et al., 2004;Sinha et al., 2008;Edwards et al., 2013) indicating a large fraction of undetected BVOC and/or secondary oxidation products. The OH_{bg} shows some correlation with the measured unexplained OH reactivity at 18 m, for the period on the ground (R = 0.4), and the measured unexplained OH reactivity at 24 m, for the period on the tower (R = 0.4) (Fig. 6). If we consider only night time data, i.e. $J(O^1D) \leq 3 \times 10^{-6}$ s^{-1} (Hens et al., 2014), we obtain better agreement between the two datasets for both ground and tower periods. During the night a large fraction of observed OH production (section 3.4) could not be explained, which can tentatively be attributed to formation of OH from ozonolysis of BVOC, suggesting that the background OH could be related to such a process. Correlation between the OH_{bg} and the OH reactivity was also observed in a study by Mao et al. (2012) in a Ponderosa pine plantation (California, Sierra Nevada Mountains) dominated by isoprene where even higher OH reactivity was observed (~ 20 s^{-1}).

During the HOPE 2012 campaign such a correlation with the unexplained OH reactivity was not observed (R = 0.1). The OH reactivity was, on average, 3 times less than during the campaign in Finland and, as shown in section 3.3, of which 50 % can be explained by reaction of OH with methane, formaldehyde, acetaldehyde, inorganic compounds (NOx, SO_2, CO) and anthropogenic VOC. On average only 17 % of the OH reactivity is caused by reaction of OH with BVOC in this environment (Fig SI-8), dropping to 10 % during the night. The unexplained OH reactivity is not influenced by distinguishing between day and night time data suggesting a small contribution of non-measured BVOC. As this site is more strongly affected by anthropogenic emissions (Table SI-2) compared to the site in Finland, assuming that the OH_{bg} originates from BVOC driven chemistry, a lack of correlation between OH_{bg} and OH reactivity can be expected.

4.3 Correlation of OH_{bg} with ozonolysis chemistry

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

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

This campaign, from July 10th to August 19th 2012, encompasses a time period, from 1st to 3rd of August 2012, which was characterized by tree cutting in the vicinity of the measurement site. During this period a significantly larger fraction of unexplained OH reactivity, up to 40 % (Fig. SI-13), was observed. The relative contribution of measured BVOC and inorganic compounds did not change, while the presence of unidentified BVOC emitted from the trees as a result of the stress induced on the plants from the cutting activity, caused the larger fraction of unexplained reactivity. Figure 7 shows the correlation between OH_{bg} and the product k_{O3}[VOC][O_3] of measured unsaturated VOC concentration (Table SI-1), [O_3] and the relevant ozonolysis rate coefficients. In red are depicted the data points belonging to the tree cutting period, which naturally correspond to a larger OH_{bg} concentration for similar concentrations of measured VOC during the rest of the campaign, as the additional contribution from the non-identified BVOC is neglected. The overall correlation appears to be pretty poor in particular due to the few points scattering in the lower right corner. These points all belong to three consecutive days, from 26th to 28th of July, which were characterised by high temperature and large concentrations of BVOC (Table SI-3). As noticeable in Figure 4, during those three days the OH_{bg} strongly deviates from the temperature trends and reaches lower values. At present, the reason for such a low concentration of $OH_{bg,}$ during a period which should favour its formation if it originates from SCI, is unclear. The instrument was left unattended at the site and the drop in the quality of the signals required its shutdown on the evening of the 28th of July. However, as no evidence was found to suggest an error in the data the points have not been omitted. Excluding that period yields a correlation factor of R = 0.65. The correlation line intercept could arise for a number of reasons. Unmeasured components of the OH reactivity (i.e. unspeciated VOCs) are not accounted for in the calculation, and doing so would shift the data to higher [VOC], decreasing the positive intercept. This is also consistent with a higher intercept for the cutting tree period where a larger unexplained OH reactivity was observed. It is also conceivable that the intercept is in part due to an additional, non-ozonolysis source of background OH. One candidate for the night time periods could be NO_3 as found in the work by Fuchs et al. (2016). Unfortunately, there was no measurement of the NO_3 radical during the HOPE 2012 campaign, but based on previous studies at the site (Handisides et al., 2003), a concentration up to 14 pptv of NO_3 could be present and could have a detectable impact.

Apart from the possible partial origin of OH_{bg} from NO_3 or other interferences, there are also indications that the background OH could originate from ozonolysis of unsaturated biogenic compounds. The correlation analysis requires that all VOCs are accounted for, and omitting large contributions from unspeciated VOCs, as evidenced e.g. by OH reactivity measurements, can be expected to reduce the correlation as observed in the case of HUMPPA-COPEC 2010. The reason for the lack of correlation during the period from 26th to 28th July 2012 during HOPE-2012 characterised by large BVOC emissions remains unclear.

4.4 Correlation of OH_{bg} with $P(H_2SO_4)_{unex}$

During both campaigns, measurements of H_2SO_4, SO_2, OH and CS (condensation sink) were performed allowing the calculation of the sulfuric acid budget in the gas phase. As shown by Mauldin III et al. (2012), during the HUMPPA-COPEC 2010 campaign the well-known SO_2 oxidation process by OH (Wayne, 2000) (Eq. 1) was not sufficient to explain the measured concentration of H_2SO_4. As shown in section 3.1, half of the production rate of H_2SO_4, ~ 1 x 10^4 molecules cm^{-3} s^{-1}, cannot be explained by reaction with OH radicals (Fig. 8). The missing oxidant is assumed to be SCI, as discussed in section 3.1, because of their fast reaction rate with SO_2. As our hypothesis about the origin of the OH_{bg} supports this assumption, we compared the $[H_2SO_4]_{unex}$ observed during the HUMPPA-COPEC 2010 campaign with the OH_{bg} multiplied by SO_2 for the ground-based period when the instruments (HORUS and CIMS) measured side-by-side (Fig. 9). The two datasets indicate a correlation coefficient of R = 0.6 suggesting that whichever species is responsible for the oxidation of SO_2 is related to the formation of OH within the HORUS instrument.

Note that for the HOPE 2012 campaign the same budget calculation shows only a small fraction (10 %) of unexplained H_2SO_4 production rate (Fig. 1).

Assuming SCI to be the unknown SO_2 oxidant, the results observed in both campaigns are in agreement with the modeling study by Boy et al. (2013), who analyzed measurements at the same sites described in this study. Similar to our result, they found a larger contribution of SCI in the formation of H_2SO_4 for the boreal forest compared to rural Germany. As the OH concentration differs by, on average, less than 50 % between the two environments, a similar concentration of SCI in HOPE to that calculated for HUMPPA-COPEC 2010 would contribute up to 30 % in the formation of H_2SO_4. However, the H_2SO_4 budget during this campaign can approximately be closed by only considering the measured OH concentrations, suggesting that the concentration of SCI in this environment is smaller than that during the HUMPPA-COPEC 2010 campaign. This is consistent with the calculation in section 3 based on the smaller reactivity and hence smaller VOC concentration in this environment

4.5 Scavenging experiments

A series of scavenging tests of the OH_{bg} was performed during the HOPE 2012 campaign to help identify the interfering species. SO_2 was chosen as scavenger for the species causing the OH_{bg}, as it has been shown in several laboratory studies to react quickly with SCI ($k \sim 3.3 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}) mostly independently of their structure (Taatjes et al., 2014). The injection of SO_2 was performed through the IPI system (Novelli et al., 2014a) together with an OH scavenger. First the OH scavenger propane was injected within IPI to remove the atmospheric OH; subsequently, SO_2 was injected in addition to the OH scavenger (Fig. 10). The concentration of SO_2 is small enough not to scavenge SCI inside the low pressure section of the instrument, nor is it additionally removing atmospheric OH within the IPI system as the lifetime of OH by reaction with SO_2 is 200 times that of propane. With the addition of SO_2 (1 x 10^{13} molecules cm^{-3} in the sampled air) it is possible to suppress the OH_{bg} signal from the instrument to within the zero noise, indicating that the OH_{bg} signal originates from an SCI-like species that reacts with SO_2 and decomposes unimolecularly to OH.

4.6 SCI as a source of background OH

During the HUMPPA-COPEC 2010 campaign the background OH showed a strong exponential relationship with temperature (R = 0.8) and it correlates with unexplained OH reactivity (R = 0.5), which suggests correlation with BVOC, with ozone (R = 0.7), and also with the $P(H_2SO_4)_{unex}$ (R = 0.6). During the HOPE 2012 campaign a weak exponential correlation with temperature was recognized (R = 0.5) but no correlation was observed with OH reactivity. The OH_{bg} correlated with the product of ozone and unsaturated VOC for most of the campaign (R = 0.6) although not for a period of three days at the end of July with partly higher BVOC-O_3 turnover. In addition, during HOPE 2012 the OH_{bg} signal was scavenged by the addition of SO_2.

All evidence presented indicates that substantial parts of the OH_{bg} originate from a species formed during the ozonolysis of unsaturated VOC that decomposes into OH, is removable by SO_2 and, if present in a significant concentration, increases the H_2SO_4 production. We are currently not aware of any chemical species, other than SCI, known to oxidise SO_2 at a fast enough rate and also decompose into OH. In addition, HORUS was shown to be sensitive to the OH formed after unimolecular decomposition of SCI in the low-pressure region of the instrument (residence time 2 ms) in controlled laboratory studies (Novelli et al., 2014b).

During the HUMPPA-COPEC 2010 campaign, the correlation with OH reactivity improved when considering only data during night time, the period during which a higher fraction of the production rate of OH could not be accounted for (Hens et al., 2014). Indeed, during the night recycling via HO_2+NO is low due to the negligible NO concentration, therefore a different path of formation of OH is expected. One likely path could be the formation of OH from excited and stabilised CI formed from ozonolysis of unsaturated compounds.

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

Attempts to analyse the absolute concentration of SCI based on our OH_{bg}, however, indicates that this hypothesis is not without difficulties. A particular problem is that to date no method is available to produce and quantify a known concentration of a specific SCI conformer, which precludes the absolute calibration of SCI-generated OH. *A priori*, it seems unlikely that the IPI-LIF-FAGE instrument calibration factor for ambient OH, i.e. sampled from outside the instrument through the nozzle, is identical to the sensitivity for OH generated inside. The transmission factor through our nozzle pinhole is currently not known for OH radicals; the calibration factor used for ambient OH accounts for this transmission as well as for e.g. OH losses on the walls, alignment of the white cell, transmission optics, and response of the MCP. These last three factors should affect the OH generated from any interfering species similarly, while wall losses and transmission through the pinhole are different and possibly also differ between SCI conformers. Additionally, different SCI vary in their unimolecular decomposition rates and hence affect calibration by a different time-specific OH yield. For example, theoretical studies (Vereecken and Francisco, 2012) and laboratory experiments (Smith et al., 2016) indicate that acetone oxide will decompose faster than *syn*-acetaldehyde oxide causing the formation of a different amount of OH, which in turn will also be affected by different loss rates in the low pressure segment of the instrument. Thus, it is not possible to convert the internal OH to an absolute SCI concentration since the mixture of SCI is not known. At best one could obtain an "average" sensitivity factor, if one knew the OH_{bg} formed from a series of reference SCI conformers, and if the ambient SCI speciation is known and not too strongly dependent on reaction conditions. To further illustrate the need of a SCI-specific calibration, we try to simply calculate the external [SCI] from the internal OH_{bg} signal strength, calibrated based on the combined experimental and modelling study by Novelli et al. (2014b). For a SCI mixture that behaves identical to syn-CH_3CHOO, the OH_{bg} from the HUMPPA-COPEC 2010 campaign would then indicate an external [SCI] $\geq 2 \times 10^7$ molecules cm^{-3}, well above the estimates presented in section 3. Moreover, the observed OH_{bg} signal interpreted in this way would imply an ambient OH production exceeding 4×10^8 molecules cm^{-3} s^{-1}, clearly in disagreement with known chemistry, and also inconsistent with our estimates (Table 2). If we assume a faster decomposition rate for the SCI of 200 s^{-1}, a higher fraction of the SCI decomposes in the low-pressure region, i.e. 80 % compared to 25 % for $k_{uni} = 20\ s^{-1}$. This leads to a higher OH signal per SCI, and from this a [SCI] of 4×10^6 molecules cm^{-3}, though the implied ambient OH production would remain significantly too high. Thus, the conversion of the OH signal to an absolute concentration of ambient SCI is not unambiguous without full SCI speciation and knowledge of their chemical kinetics. Note furthermore that these [SCI] estimates would represent a lower limit as we only observe SCI that decompose to OH, whereas e.g. *anti*-SCI convert to acids/esters.

In an effort to work towards SCI-specific calibration, we probed the transmission of OH and *syn*-CH_3CHOO through the nozzles and the low-pressure region in the instrument, with explorative laboratory tests using a traditional nozzle and a molecular beam skimmer nozzle, where the latter has much thinner sidewalls and a significantly narrower gas expansion, strongly reducing wall contact. The laboratory test showed that the OH radical has a 23 % higher transmission through the molecular beam nozzle compared to the traditional nozzle. The *syn*-acetaldehyde oxide did not show any statistical difference in the transmission between the two nozzles. This indicates that (a) SCI and OH have a different transmission efficiency and most likely different wall losses, underlining that the OH calibration factor is not applicable to SCI for ambient measurements, and (b) that the calibration factor for OH obtained for ambient OH alone does not allow the quantification of the absolute OH concentration in the low-pressure section of the FAGE instrument. This is the fundamental reason why the earlier simple estimate of [SCI] and OH production leads to strong over-estimations.

In addition to the above effects, one should also consider that OH-production from SCI in the low-pressure section might be catalysed to proceed at rates beyond their ambient counterpart, biasing our interpretation of their ambient fate. The catalysis might involve wall-induced isomerisation of the higher-energy *anti*-SCI to the more stable, OH-producing *syn*-SCI, which would artificially increase the *syn*:*anti* ratio. Another possibility is the evaporation of clusters stabilizing the SCI, as it is known that SCI efficiently form complexes with many compounds, including water, acids, alcohols, hydroperoxides, HO_x radicals, etc. (Vereecken and Francisco, 2012). Redissociation of secondary ozonides (SOZ) seems less important, except perhaps the SOZ formed with CO_2 (Aplincourt and Ruiz-López, 2000), which has no alternative accessible unimolecular channels. At present, insufficient (if any) information is available to assess the impact of such catalysis.

Taking into account the factors considered above, and assuming that the estimates for the SCI concentration in both environments are correct, it appears unlikely that SCI are responsible for such a large OH_{bg} signal as observed by the HORUS instrument. If SCI were to be solely responsible for the OH_{bg} signal, the HORUS instrument would need to be far more sensitive to the detection of SCI than to the detection of OH radicals by, for example, pinhole losses that are 100 times smaller for SCI than for OH radicals. The evident discrepancy between the qualitative evidence in support of the SCI hypothesis and the current quantitative difficulty in reconciling the OH_{bg} signal with the estimated ambient concentration of SCI does not allow an unequivocal identification of the origin of the OH_{bg} within our system. It cannot be excluded that multiple species are contributing to the OH_{bg} signal. NO_3 chemistry during night time has been identified as a possible source of OH_{bg} in the LIF-FAGE instrument of the FZ-Jülich (Fuchs et al., 2016). However, in the case of the large observed night time OH_{bg} concentrations during HUMPPA-COPEC 2010, the measured night time NO_3 concentrations were below 1 ppt and therefore too small to explain the observed OH_{bg}.

5 Conclusions

We estimated a steady state concentration of SCI for the HUMPPA-COPEC 2010 and the HOPE 2012 campaigns based on a large dataset. Starting from four different approaches, i.e. based on unaccounted (i.e. non-OH) H_2SO_4 oxidant, measured VOC concentrations, unexplained OH reactivity or unexplained production rates of OH, we estimated the concentration of SCI to be between ~ 10^3 and ~ 10^6 molecules cm^{-3}. The highest values in this range are linked to an assumed low rate coefficient for SCI + SO_2 of 5 x 10^{-13} cm^3 molecule^{-1} s^{-1} (see section 3.1), which is at odds with a larger body of more direct measurements on this rate coefficient. Hence, higher SCI values appear to be relatively less likely. We thus obtain an average SCI concentration of about 5 x 10^4 molecules cm^{-3}, with an order of magnitude uncertainty, for both campaigns. At such concentrations, SCI are expected to have a significant impact on H_2SO_4 chemistry during the HUMPPA-COPEC

2010 campaign while during the HOPE 2012 campaign their impact is much smaller and possibly negligible. Additionally, it was shown that, based on the yields and unimolecular decomposition rate applied in this study, SCI do not have a large impact on the OH production compared to the direct OH generation from ozonolysis of unsaturated VOC. During both campaigns, the IPI-LIF-FAGE instrument detected an OH background signal that originates from decomposition of one or more species inside the low pressure region of the instrument. The source compound of the OH_{bg} was shown to be unreactive towards propane but to be removed by SO_2, and a relationship was found with the unaccounted H_2SO_4 production rate. It correlates with temperature in the same way as the emission of terpenes and, in most but not all measurements periods, with the product of unsaturated VOC and ozone as well as with the OH reactivity. While it is not possible at the moment to unequivocally state that OH_{bg} originates from stabilised Criegee intermediates, the observations are consistent with known SCI chemistry. The contribution of SCI to the observed OH_{bg} cannot be quantified until a calibration scheme for SCI in the IPI-FAGE system has been developed.

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

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Table 1. Average concentration (molecule cm^{-3}), with 1σ variability, of trace gases relevant for this study.

Compound	HUMPPA-COPEC 2010	HOPE 2012
SO_2[a]	$(1.4 \pm 1.7) \times 10^{10}$	$(2.2 \pm 2.3) \times 10^{9}$
H_2SO_4[a]	$(2 \pm 2) \times 10^{6}$	$(8.5 \pm 8.5) \times 10^{5}$
OH[a]	$(7 \pm 8) \times 10^{5}$	$(1.6 \pm 1.6) \times 10^{6}$
O_3[a]	$(1.1 \pm 0.2) \times 10^{12}$	$(1.1 \pm 0.3) \times 10^{12}$
Σ[VOC][a,b]	$(7.3 \pm 7.1) \times 10^{9}$	$(9.8 \pm 9.0) \times 10^{9}$
OH Reactivity[c]	9.0 ± 7.6	3.5 ± 3.0
Condensation sink (CS)[c]	$(10 \pm 4.0) \times 10^{-3}$	$(7 \pm 3) \times 10^{-3}$

a, Units: molecules cm^{-3}.

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

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

c, Units: s^{-1}.

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

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

Approach	**HUMPPA-COPEC 2010**	**HOPE 2012**
Missing H_2SO_4	$(2.3 \pm 2) \times 10^4$ [a]	$(2.0 \pm 3) \times 10^4$ [a]
	$(1.6 \pm 2) \times 10^6$ [b]	$(1 \pm 3) \times 10^6$ [b]
Measured unsaturated VOC	$(5 \pm 4) \times 10^3$	$(7 \pm 6) \times 10^3$
Unexplained OH reactivity	$(1 \pm 1) \times 10^5$	$(2 \pm 1.5) \times 10^4$
Unexplained OH production	$(2 \pm 2) \times 10^4$ [c]	n. a.
	$(4 \pm 4) \times 10^5$ [d]	n. a.

a, $k_{SCI+SO2} = 3.3 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}

b, $k_{SCI+SO2} = 5 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}

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

d, $P_{OH}^{unexplained} = 2 \times 10^7$ molecule cm^{-3} s^1

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

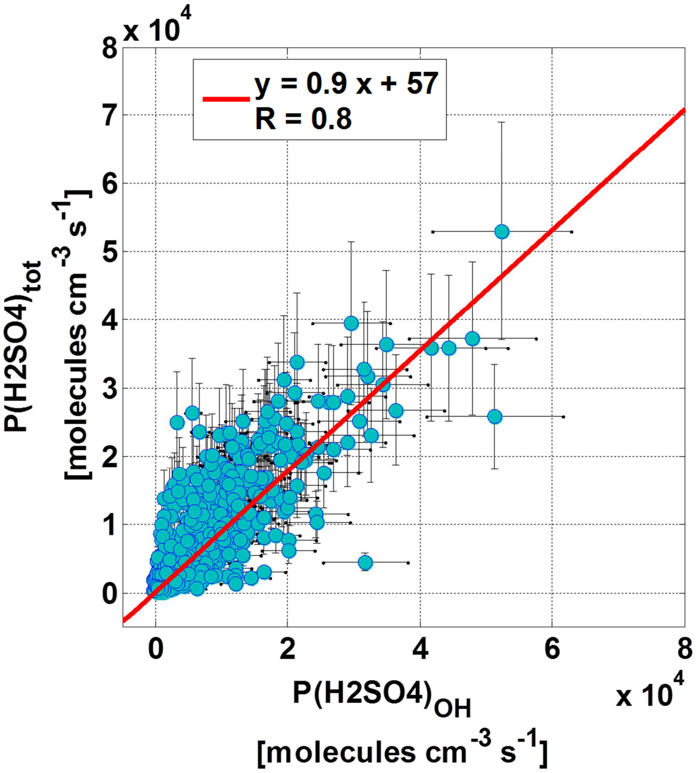

Figure 1. Total production rate of H_2SO_4 ($P(H_2SO_4)_{tot}$) as a function of the production rate of H_2SO_4 from the reaction between OH and SO_2 during the HOPE 2012 campaign. The linear regression, following the method of York et al. (2004), yields a slope of 0.9 ± 0.02 and a intercept of 57 ±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

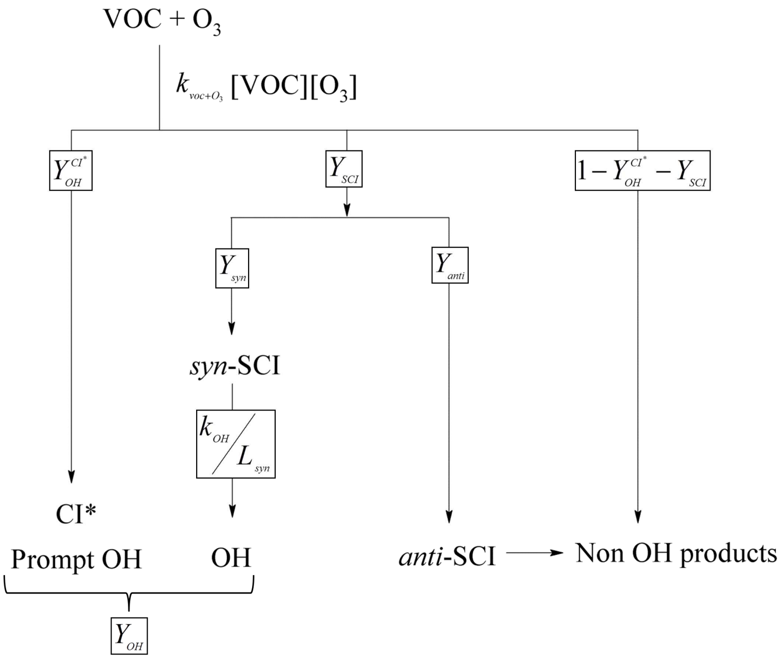

Figure 2. Schematic representation of the formation of OH from the ozonolysis of unsaturated VOC.

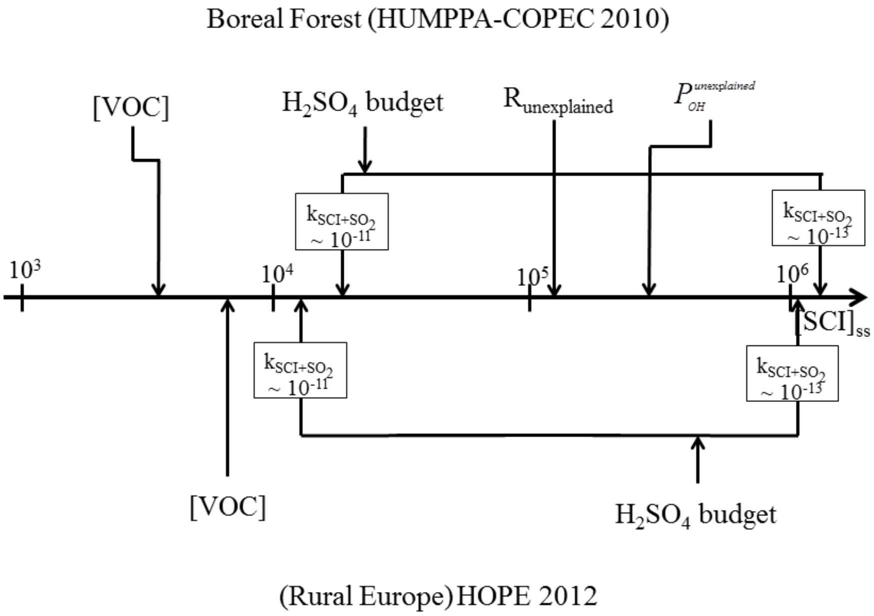

Figure 3. Schematic overview of the estimated steady state concentration of SCI ($[SCI]_{ss}$, molecules cm^{-3}) observed during the HUMPPA-COPEC 2010 and HOPE 2012 campaigns. For both campaigns the SCI estimate is based on the unsaturated VOC concentration measured, [VOC], and the H_2SO_4 budget using different SCI+SO_2 rate coefficients ($k_{SCI+SO2}$ in cm^3 $molecule^{-1}$ s^{-1}). In addition, during the HUMPPA-COPEC campaign SCI can be calculated from the unexplained OH reactivity, $R_{unexplained}$, and unexplained OH production, $P^{OH}_{unexplained}$. See main text for more details (Section 3).

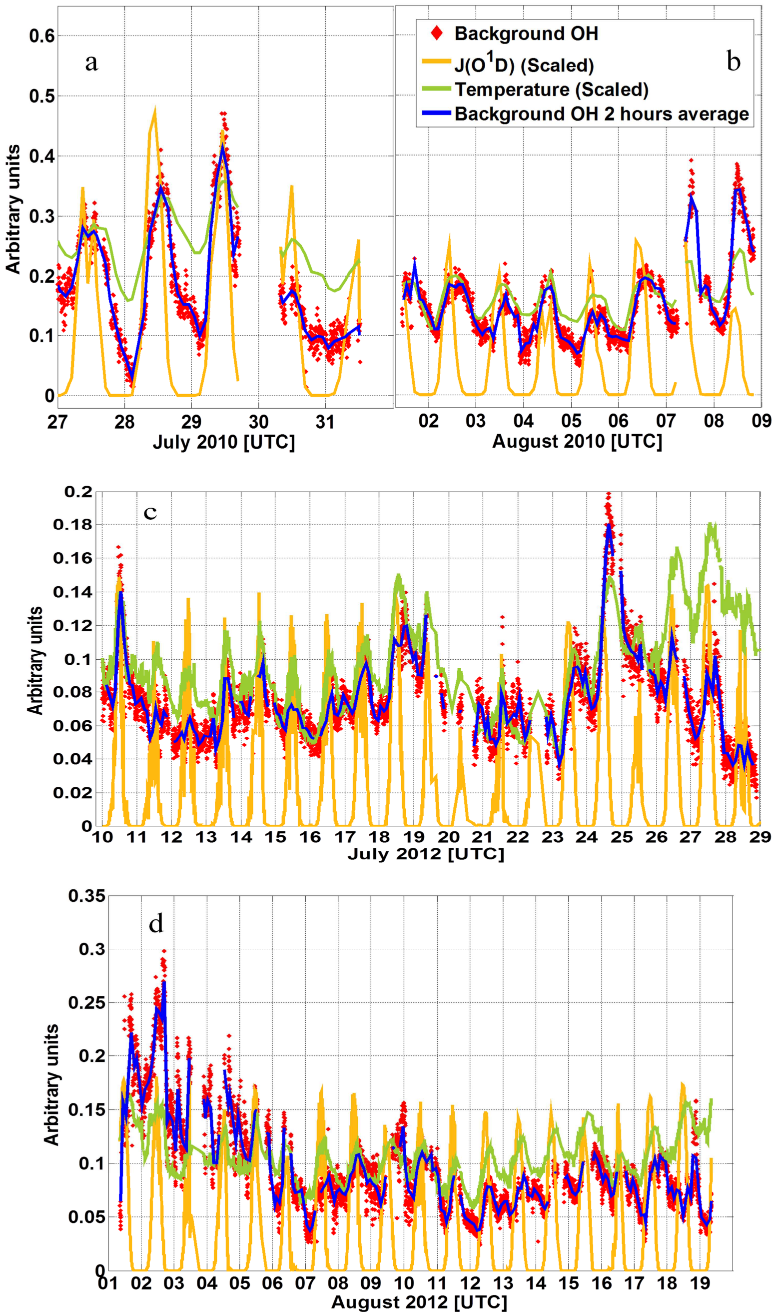

Figure 4. Background OH (red diamonds) measured during the HUMPPA-COPEC 2010 (a, ground and b, tower) and the HOPE 2012 (c, July and d, August) campaigns together with scaled J(O^{1}D), multiplied by 4 x 10^4 and 4 x 10^3 for HUMPPA-COPEC 2010 and HOPE 2012, respectively (orange), and scaled temperature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

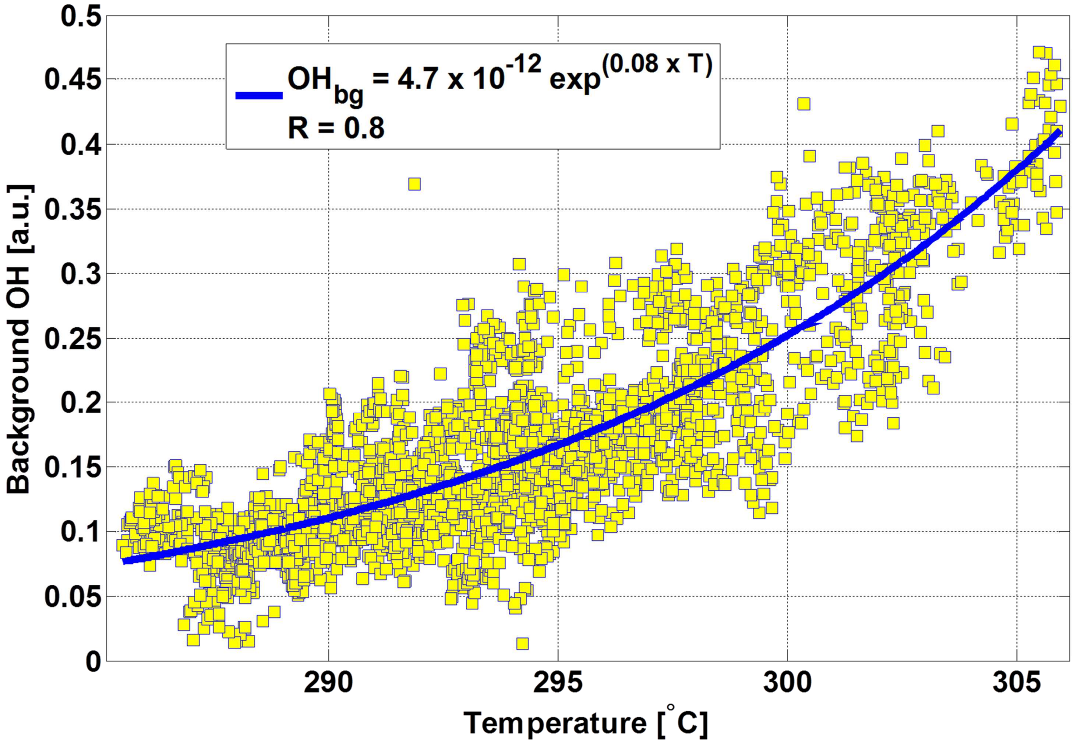

Figure 5. Background OH as a function of the temperature during the HUMPPA-COPEC 2010 campaign.

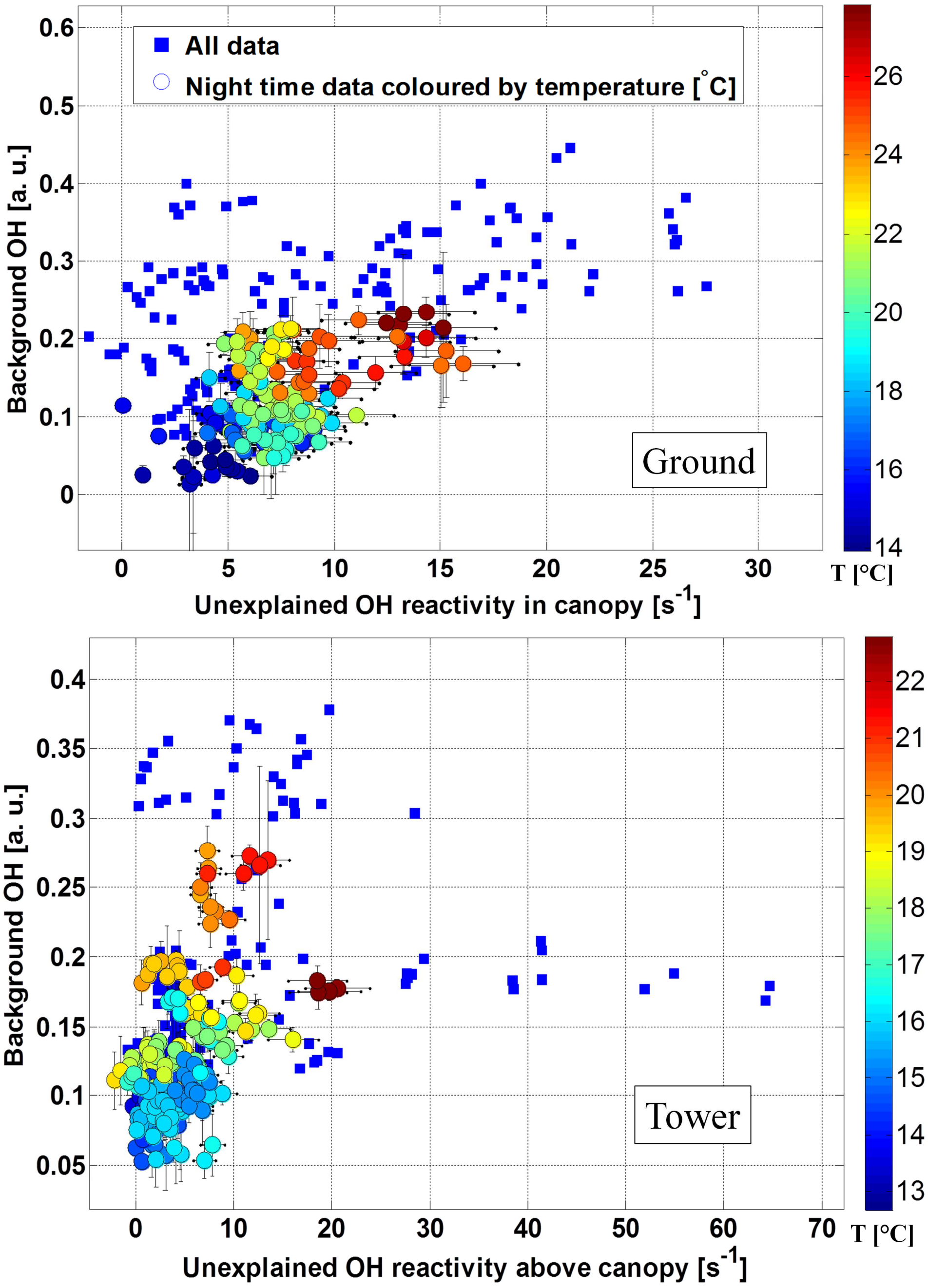

Figure 6. Background OH as a function of unexplained OH reactivity for ground and tower period measurements during the HUMPPA-COPEC 2010 campaign. Squares represent the daytime data, bullets represent night time data and are coloured accordingly to temperature (right legend).

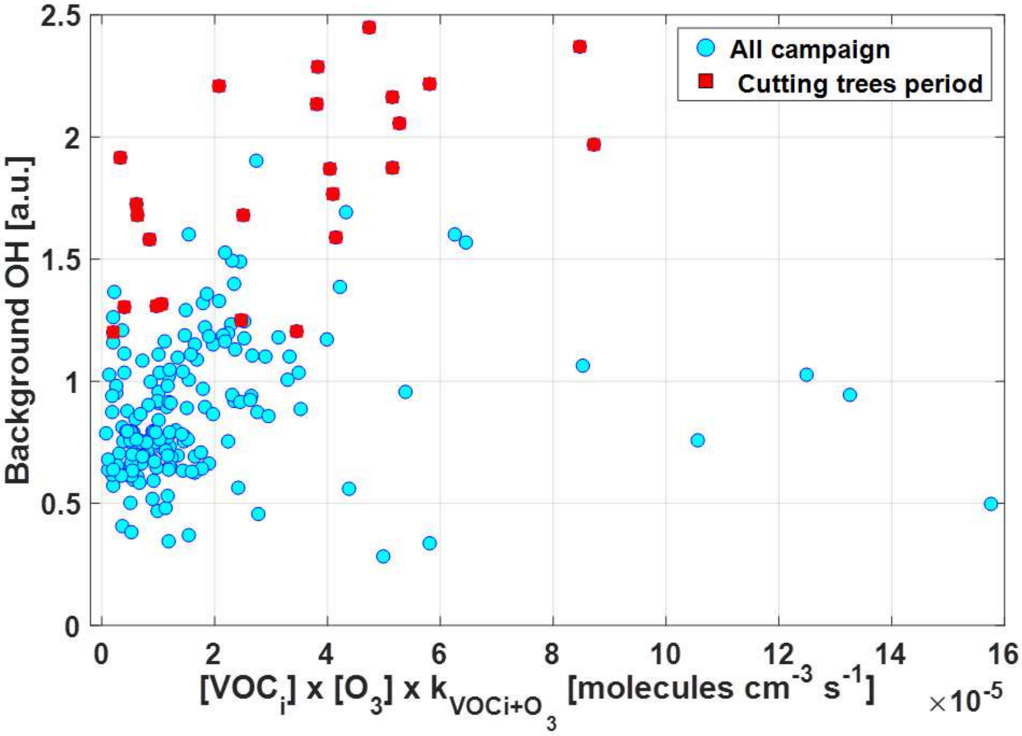

Figure 7. Background OH as a function of the sum of the product of the measured unsaturated VOC-ozone turn-over (Table SI-1), during the HOPE 2012 campaign. The blue points refer to the entire field campaign excluding tree cutting, which occurred between 1st and 3rd of August 2012, described by the red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

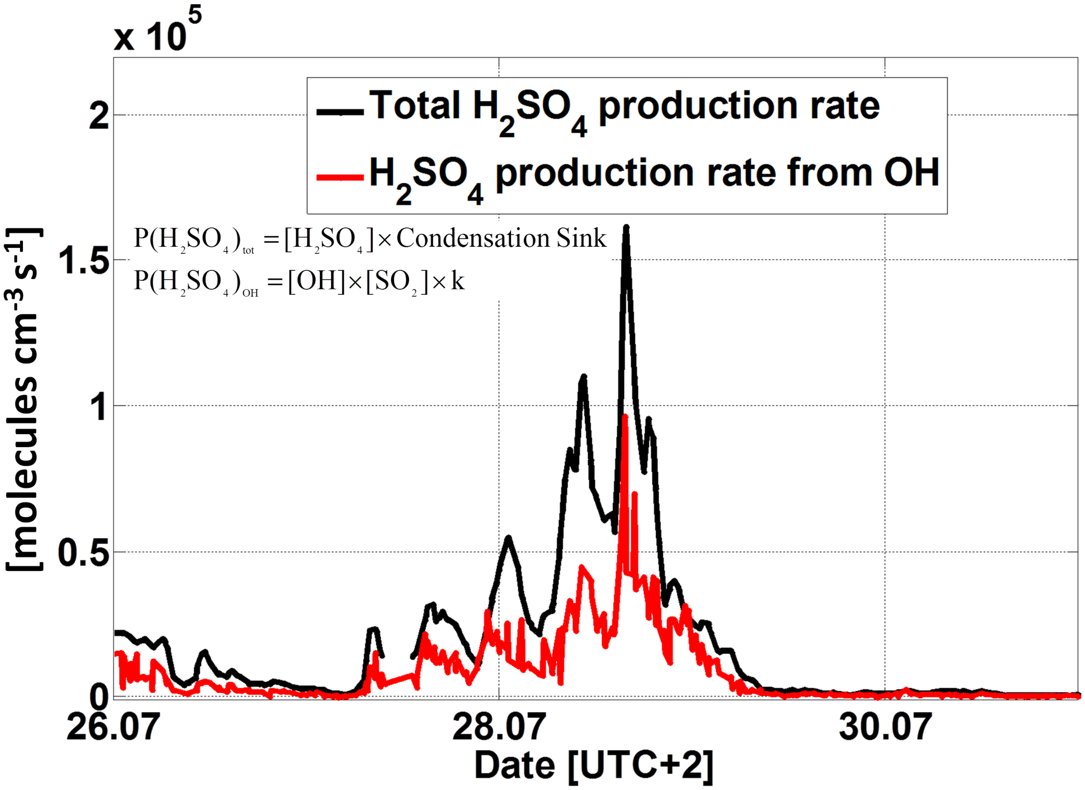

Figure 8. Comparison of the total H_2SO_4 production rate (black line), calculated from the measured H_2SO_4, and the production rate of H_2SO_4 (red line) involving only the oxidation process of SO_2 by OH for the ground measurements during the HUMPPA-COPEC 2010 campaign.

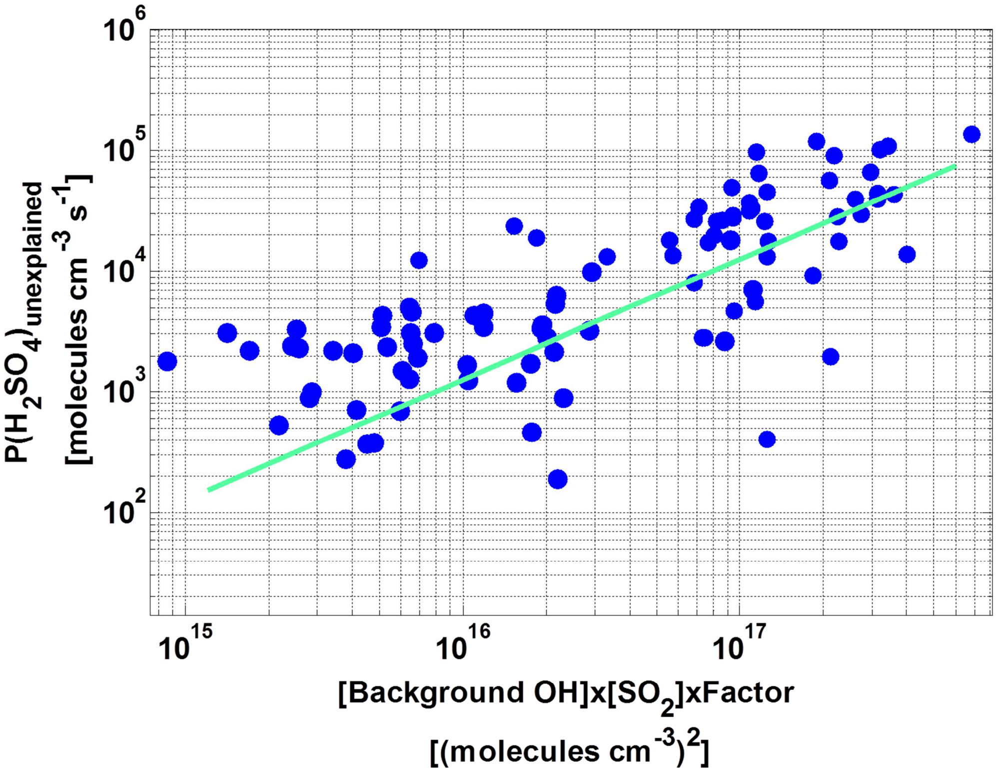

Figure 9. The production rate of H_2SO_4 unaccounted for by the oxidation of SO_2 by OH as a function of the OH_{bg} multiplied by SO_2 concentration during the ground measurements of the HUMPPA-COPEC 2010 campaign. OH_{bg} is expressed in molecules cm^{-3} equivalents of OH.

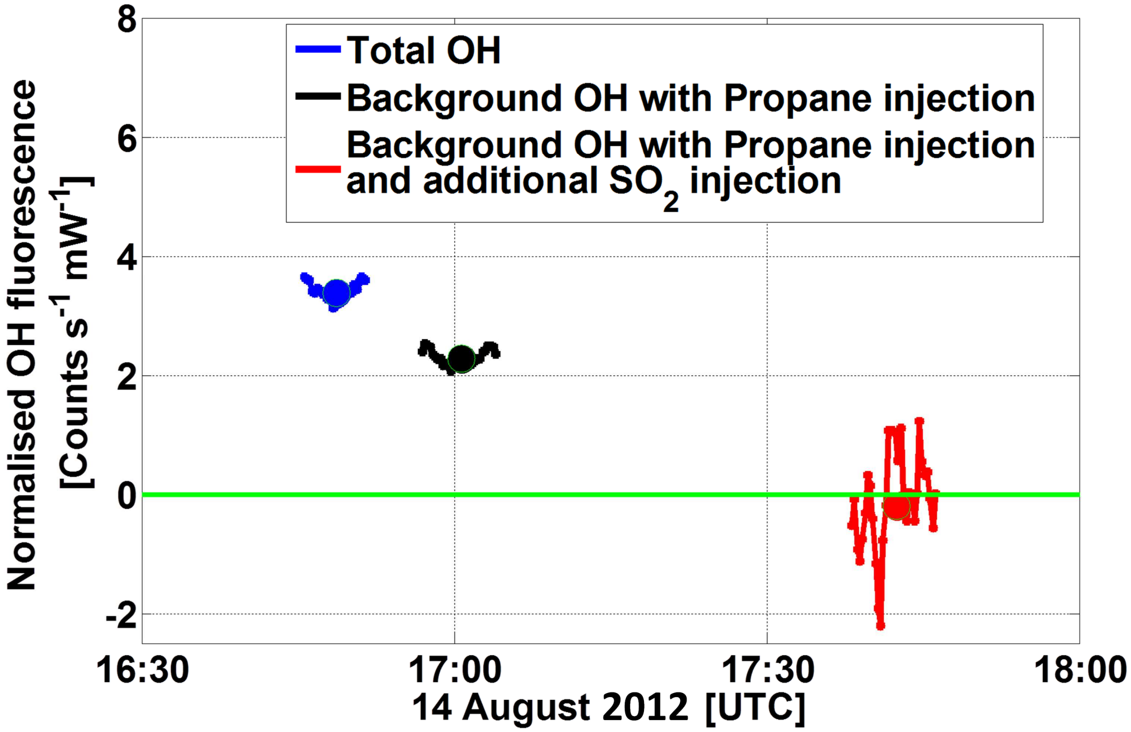

Figure 10. SO_2 injection test within IPI during the HOPE 2012 campaign. The blue data points represent the total OH measured when no injection is performed. The black data points represent the background OH measured while injecting propane (2.5 x 10^{15} molecules cm^{-3}) scavenging > 90 % of ambient OH. The red signal is the background OH observed when SO_2 (1 x 10^{13} molecules cm^{-3}) is injected in addition to propane.

Supplementary information

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

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Assessment of the available rate coefficients for the SCI + SO_2 reaction

The disagreement between the rate coefficient for the SCI + SO_2 reaction obtained by Mauldin III et al. (2012) and Berndt et al. (2012), 5×10^{-13} cm^3 $molecule^{-1}$ s^{-1}, and the one obtained by a number of other groups (Welz et al., 2012;Taatjes et al., 2013;Liu et al., 2014b;Sheps et al., 2014;Stone et al., 2014;Chhantyal-Pun et al., 2015;Newland et al., 2015a;Newland et al., 2015b;Foreman et al., 2016;Zhu et al., 2016), 3.3×10^{-11} cm^3 $molecule^{-1}$ s^{-1}, is not straightforward to explain.

A first factor is that Mauldin III et al. (2012) and Berndt et al. (2012) measure the rate of formation of H_2SO_4 rather than the loss of SCI by SO_2. Theoretical and experimental results (Carlsson et al., 2012;Ahrens et al., 2014) indicate that SO_3 is the main product of the SCI + SO_2 reaction, with a yield near 100% at all reaction conditions considered. Barring secondary chemistry removing SO_3 prior to its reaction with H_2O to form H_2SO_4, which seems unlikely under their reaction conditions, the H_2O_4 yield should match the SCI loss. Earlier theoretical work by Vereecken et al. (2012) suggested that the secondary ozonide (SOZ) formed as an intermediate from the reaction between larger SCI and SO_2 could stabilize and undergo bimolecular reaction without formation of SO_3; the loss of SOZ would then reduce SO_3 formation, explaining the difference in the rate coefficients for the different experiments. However, more recent theoretical work (Kuwata et al., 2015) found additional low-lying pathways that make collisional stabilization of the SOZ unlikely. Experiments by Carlsson et al. (2012) and Ahrens et al. (2014) observed high yields of SO_3 close to unity suggesting that the SOZ is not lost under the conditions used, i.e. in chambers with high concentrations of reactants and in the absence of water.

A second factor is that the reaction conditions used by Mauldin III et al. (2012) and Berndt et al. (2014) differ from the other studies, i.e. they were performed either at ambient air conditions or with lower concentrations of reagents and in the presence of water, while the remaining experiments were typically performed under lower pressures, without efficient colliders present. The mechanism of the SCI+SO_2 reaction as obtained by several authors (Vereecken et al., 2012;Kuwata et al., 2015;Jiang et al., 2010;Kurtén et al., 2011) all indicate a barrierless formation of a pre-reactive complex or cycloadduct. This type of reactions typically show faster rate coefficients at higher pressures due to lower redissociation of the adduct; this is corroborated by the theoretical study on the pressure dependence by Kuwata et al. (2015) who finds no pressure dependence up to 10132.5 hPa and an increase in the effective rate coefficient for higher pressures. Experimental studies of the pressure dependence (Liu et al., 2014b;Huang et al., 2015;Chhantyal-Pun et al., 2016) do not show extensive pressure dependence up to 300 Torr, and all show a positive pressure dependence, in line with the currently accepted reaction mechanism. The Carlsson et al. (2012) experiments at 1013.51 hPa likewise can be fitted using a faster CI + SO_2 rate coefficient of 1 x 10^{-11} cm^3 $molecule^{-1}$ s^{-1}. This suggests that the reaction conditions used by Mauldin III et al. and Berndt et al. would likely lead to faster rate coefficients, especially for larger SCI as used in Mauldin III et al. due to the lower redissociation rate and hence higher thermalization yield of the intermediates.

A third factor is that the Mauldin III et al. examine SCI formed from larger terpenoids, rather than the smaller SCI examined in the remaining studies. A larger SCI should mean a longer lifetime for the SOZ intermediate, especially as this longer lifetime makes collisional thermalization more efficient. Hence the large SOZ might indeed live long enough to react in bimolecular reactions prior to dissociation to SO_3, contrary to smaller SOZ. Unfortunately, SOZ chemistry has not been studied in detail; for the current case the reaction with e.g. H_2O

could be a potential loss process. A prerequisite for this scavenging to be effective is that no H_2SO_4 precursor should be formed. This scavenging of the SOZ intermediate would however not apply to the experiments of Berndt et al., which examined CH_3CHOO and $(CH_3)_2COO$ Criegee intermediates, similar in size to those used in the studies yielding higher rate coefficients. For SCI of this size, the RRKM master equation analysis of (Kuwata et al., 2015) predicts very fast SOZ decomposition.

Finally, an alternative explanation could be based on analysis of the studies by Mauldin III et al. (2012) and Berndt et al. (2012). In their experiments, the rate of the SCI+SO_2 reaction is derived relative to the total loss rate of SCI, L_{SCI}, as it governs the steady-state concentration of SCI with negligible SO_2 present. This L_{SCI} has a value on the order of ~ 3 to 5 s^{-1} in both experiments. Since these studies, a large body of experimental and theoretical data has become available, regarding the reactivity of SCI towards many coreactants present in the reaction mixture (Taatjes et al., 2013;Ouyang et al., 2013;Ahrens et al., 2014;Buras et al., 2014;Liu et al., 2014a;Stone et al., 2014;Sheps et al., 2014;Welz et al., 2014;Lewis et al., 2015). From this new data, we should consider that a total loss rate of about 4 s^{-1} is an underestimate. In a previous study by Novelli et al. (2014) a value of L_{SCI} = 40 s^{-1} under atmospheric conditions was proposed. A re-analysis of the study by Mauldin III et al. (2012) using L_{SCI} = 40 s^{-1} and the measured yield of SCI for α-pinene of 0.1 (Donahue et al., 2011), results in a rate coefficient for the α-pinene-derived SCI + SO_2 reaction of 2.6×10^{-11} cm^3 $molecule^{-1}$ s^{-1}. Likewise, for the other compounds examined in the two studies (Berndt et al., 2012;Mauldin III et al., 2012), the derived rate of SCI+SO_2 would shift significantly towards the higher values obtained in the other studies (Welz et al., 2012;Taatjes et al., 2013;Liu et al., 2014b;Sheps et al., 2014;Stone et al., 2014). One must consider, though, that the study by Berndt et al. (2012) included a measurement of k_{loss}, based on the observed H_2SO_4 formation from the steady state SCI in the absence of SO_2. Hence, this second explanation is only viable if another source of H_2SO_4 exists in the system; this has already been suggested by Newland et al. (2015a) based on their SO_2 oxidation experiments.

Still, as these considerations for the lower values by Mauldin III et al. (2012) and Berndt et al. (2012) are merely speculative, we will consider both 3.3×10^{-11} cm^3 $molecule^{-1}$ s^{-1} and 5×10^{-13} cm^3 $molecule^{-1}$ s^{-1} as possible rate coefficients for the SCI + SO_2 reaction in the current budget analysis.

Sensitivity study on the unexplained OH reactivity SCI estimate

The estimate of SCI from the unexplained OH reactivity data contains larger uncertainties compared to the previous estimates as the rate coefficient for ozonolysis of unsaturated compounds varies by up to three orders of magnitude. In addition, the rate coefficient between OH and unsaturated compounds, depending on whether these are unsaturated NMHC or OVOC, primary emissions, or secondary oxidation products, varies by an order of magnitude. A sensitivity study was done on the SCI estimates from the unexplained OH reactivity to attempt to account for this uncertainty in rate coefficients. It is possible to calculate a lower limit for the SCI concentration by using the highest rate coefficient between OH and unsaturated compounds, 1×10^{-10} cm^3 $molecule^{-1}$ s^{-1} (Atkinson et al., 2006) combined with a slow rate coefficient for the unsaturated compounds and ozone, 1×10^{-17} cm^3 $molecule^{-1}$ s^{-1} (Atkinson et al., 2006), leading to a [SCI] = $(8.7 \pm 8.0) \times 10^3$ molecules cm^{-3}. For the upper limit, a slower rate coefficient for OH and unsaturated OVOC, ~ 3×10^{-11} cm^3 $molecule^{-1}$ s^{-1} (Atkinson et al., 2006;Teruel et al., 2006) together with a higher rate coefficient with O_3, 1×10^{-16} cm^3 $molecule^{-1}$ s^{-1} (Atkinson et al., 2006) results in a concentration of [SCI] = $(3 \pm 3) \times$

10^5 molecules cm^{-3}. These are the values obtained for the HUMPPA-COPEC 2010 campaign. For the HOPE 2012 campaign, the same assumptions would yield a lower and an upper limit of (1 ± 0.2) x 10^3 molecules cm^{-3} and (2.9 ± 0.7) x 10^4 molecules cm^{-3}, respectively.

Table SI-1. Average concentrations with 1σ standard deviation of measured unsaturated VOC during the HUMPPA-COPEC 2010 and HOPE 2012 campaigns, together with the rate 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	$(1.8 \pm 1.8) \times 10^{9}$	$(2.2 \pm 2.2) \times 10^{9}$	1×10^{-14} exp(-1995/T)
α-pinene	$(2.7 \pm 3) \times 10^{9}$	$(1.5 \pm 1.5) \times 10^{9}$	8.1×10^{-16} exp(-640/T)
β-pinene	$(1.9 \pm 6.6) \times 10^{8}$	$(9 \pm 9) \times 10^{8}$	1.4×10^{-15} exp(-1270/T)
3-carene	$(1.7 \pm 2) \times 10^{9}$	$(5.6 \pm 4.7) \times 10^{8}$	$4.8 \times 10^{-17,\ b}$
myrcene	$(2.6 \pm 2.7) \times 10^{8}$	$(2.2 \pm 1.6) \times 10^{8}$	2.7×10^{-15} exp(-520/T)
limonene	n.a.	$(2.9 \pm 2.1) \times 10^{8}$	2.8×10^{-15} exp(-770/T)
sabinene	n.a.	$(9.2 \pm 9.6) \times 10^{8}$	$8.2 \times 10^{-17,\ b}$
γ-terpinene	n.a.	$(1 \pm 1) \times 10^{8}$	$1.5 \times 10^{-16,\ b}$
2-methylpropene	n.a.	$(4.2 \pm 2.5) \times 10^{8}$	2.7×10^{-15} exp(-1630/T)
but-1-ene	n.a.	$(1.4 \pm 4.2) \times 10^{8}$	$1.2 \times 10^{-17,\ a,b}$
propene	n.a.	$(4.7 \pm 3.7) \times 10^{8}$	5.5×10^{-15} exp(-1880/T)
cis-2-butene	n.a.	$(6.1 \pm 3.0) \times 10^{7}$	3.2×10^{-15} exp(-965/T)
ethene	n.a.	$(7.3 \pm 9.0) \times 10^{9}$	9.1×10^{-15} exp(-2580/T)

a, rate coefficient from Adeniji et al. (1981).
b, at 298 K
1 ppbv = 2.46×10^{10} molecules cm^{-3} at 295K and 1013 hPa.

Table SI-2. Average concentrations with 1σ standard deviation of measured trace gas during the HUMPPA-COPEC 2010 and HOPE 2012 campaigns, with the rate coefficients of the 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 ± 1.8) x 10^{9}	(2.2 ± 2.0) x 10^{9}	2.7 x 10^{-11} exp(390/T)
α-pinene	(2.7 ± 3) x 10^{9}	(1.5 ± 1.5) x 10^{9}	1.2 x 10^{-11} exp(440/T)
β-pinene	(1.9 ± 6.6) x 10^{8}	(9 ± 9) x 10^{8}	7.4 x 10^{-11},[a,b]
3-carene	(1.7 ± 2) x 10^{9}	(5.6 ± 4.7) x 10^{8}	8.8 x 10^{-11},[a,b]
myrcene	(2.6 ± 2.7) x 10^{8}	(2.2 ± 1.6) x 10^{8}	3.3 x 10^{-10},[b,c]
limonene	n.a.	(2.9 ± 2.1) x 10^{8}	3 x 10^{-11} exp(515/T),[d]
sabinene	n.a.	(9.2 ± 9.6) x 10^{8}	1.2 x 10^{-10},[a,b]
γ-terpinene	n.a.	(1 ± 1) x 10^{8}	1.7 x 10^{-10},[b]
MACR	(1.0± 0.9) x 10^{10}	(1.4 ± 0.9) x 10^{9}	8 x 10^{-12} exp(380/T)
ethanol	(3.6 ± 2.2) x 10^{10}	(1.8 ± 1.1) x 10^{10}	3.2 x 10^{-12} exp(20/T)
methanol	(1.0 ± 1.4) x 10^{11}	(9.0 ± 3.4) x 10^{10}	9 x 10^{-13},[b]
ozone	(1.1 ± 0.2) x 10^{12}	(1.1 ± 0.3) x 10^{12}	1.7 x 10^{-12} exp(-940/T)
SO_2	(1.4 ± 1.7) x 10^{10}	(2.3 ± 2.2) x 10^{9}	2 x 10^{-12},[b]
H_2O_2	(1.1 ± 1.0) x 10^{10}	n.a.	1.7 x 10^{-12},[b]
HO_2	(9.0 ± 9.5) x 10^{8}	(1.4 ± 8.6) x 10^{8}	4.8 x 10^{-11} exp(250/T)
NO	(6.5 ± 7.0) x 10^{8}	(3.8 ± 5.0) x 10^{9}	1.3 x 10^{-11},[b]
NO_2	(9.5 ± 5.0) x 10^{9}	(3.8 ± 2.4) x 10^{10}	1.1 x 10^{-11},[b]
CO	(3.0 ± 1.2) x 10^{12}	(2.8 ± 0.4) x 10^{12}	2.1 x 10^{-13},[b]
HONO	(3.4 ± 3.1) x 10^{9}	n.a.	6.0 x 10^{-12},[b]
propanal	n.a.	(5.8 ± 3.0) x 10^{9}	4.9 x 10^{-12} exp(405/T)

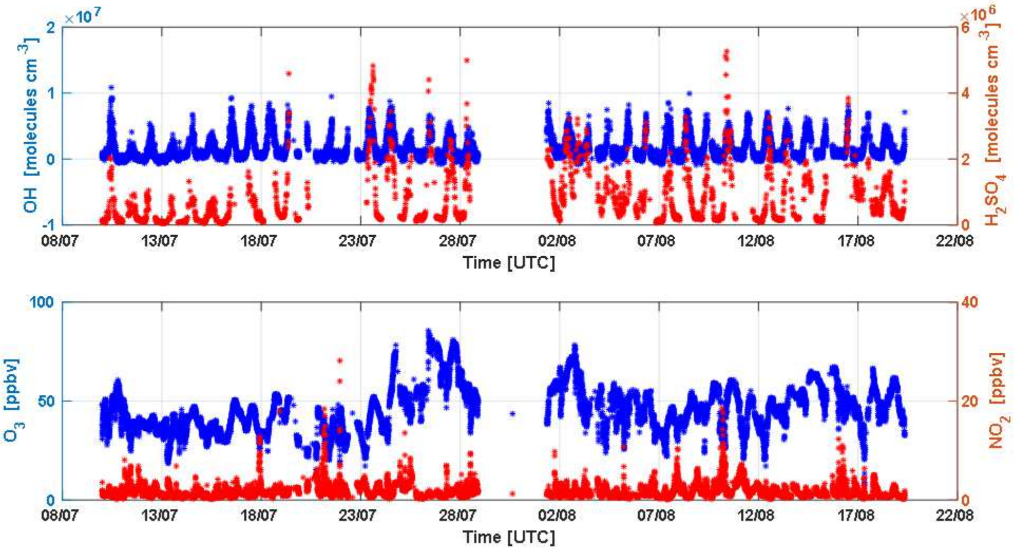
acetaldehyde	(1.8 ± 1.0) x 10^{10}	(2.9 ± 1.4) x 10^{10}	1.5 x $10^{-11,\ b}$
formaldehyde	(1.4 ± 1.6) x 10^{10}	(2.1 ± 0.4) x 10^{10}	8.5 x $10^{-12,\ b}$
acetone	(8.2 ± 3.8) x 10^{10}	(6.0 ± 2.2) x 10^{10}	1.8 x $10^{-13,\ b}$
CH_4	(4.4 ± 0.07) x 10^{13}	(4.3 ± 0.1) x 10^{13}	6.4 x $10^{-15,\ b}$
2-methylpropene	n.a.	(4.2 ± 2.5) x 10^{8}	6.1 x $10^{-11,\ a,b}$
but-1-ene	n.a.	(1.4 ± 4.2) x 10^{8}	3.1 x $10^{-11,\ a,b}$
propene	n.a.	(4.7 ± 3.7) x 10^{8}	2.9 x $10^{-11,\ b}$
cis-2-butene	n.a.	(6.1 ± 3.0) x 10^{7}	6.4 x $10^{-11,\ b}$
ethene	n.a.	(7.3 ± 9.0) x 10^{9}	7.8 x $10^{-12,\ b}$
p-xylene	n.a.	(7.2 ± 5.2) x 10^{8}	2.0 x $10^{-11,\ a,b}$
benzene	(2.1 ± 1.9) x 10^{9}	(8.0 ± 4.0) x 10^{8}	1.2 x $10^{-12,\ a,b}$
ethylbenzene	n.a.	(2.3 ± 2.1) x 10^{8}	7.0 x $10^{-12,\ a,b}$
Toluene	(6.1 ± 3.0) x 10^{9}	(1.2 ± 0.7) x 10^{9}	5.6 x $10^{-12,\ a,b}$
ethane	n.a.	(1.8 ± 0.3) x 10^{10}	4.8 x 10^{-11} exp(250/T), ^{a}
propane	n.a.	(5.6 ± 3.6) x 10^{9}	1.1 x $10^{-12,\ a,b}$
methylpropane	(1.8 ± 2.3) x 10^{9}	(1.4 ± 0.9) x 10^{9}	2.1 x $10^{-12,\ a,b}$
butane	(1.8 ± 1.6) x 10^{9}	(2.0 ± 1.2) x 10^{9}	2.3 x $10^{-12,\ a,b}$
2-methylbutane	(1.6 ± 1.2) x 10^{9}	n.a.	3.6 x $10^{-12,\ a,b}$
n-pentane	(1.0 ± 0.9) x 10^{9}	(5.6 ± 5.0) x 10^{9}	3.8 x $10^{-12,\ a,b}$

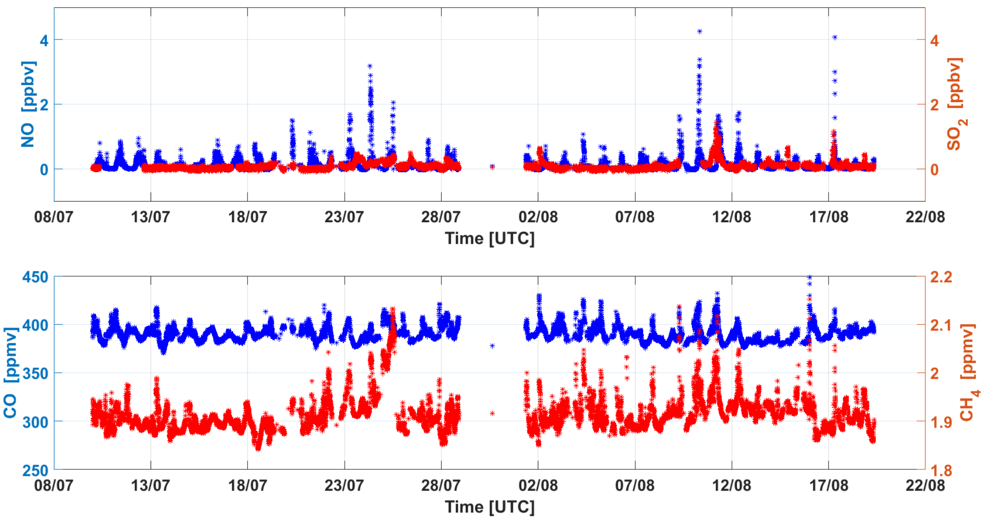
a, rate coefficient from (Atkinson and Arey, 2003).
b, at 298 K.
c, rate coefficient from (Hites and Turner, 2009)
d, rate coefficient from (Braure et al., 2014)
1 ppbv = 2.46 x 10^{10} molecules cm^{-3} at 295K and 1013 hPa.

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

	Σ[VOC] [molecules cm^{-3}]	Temperature [ºC]
HOPE 2012 campaign	$(5 \pm 4) \times 10^{9}$	16 ± 3
26th to 28th of July 2012	$(1.3 \pm 0.9) \times 10^{10}$	22 ± 3

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


×10^7
2
1
0
-1
OH [molecules cm^-3]
×10^6
6
4
2
0
H2SO4 [molecules cm^-3]
08/07
13/07
18/07
23/07
28/07
02/08
07/08
12/08
17/08
22/08
Time [UTC]
100
50
0
O3 [ppbv]
40
20
0
NO2 [ppbv]
08/07
13/07
18/07
23/07
28/07
02/08
07/08
12/08
17/08
22/08
Time [UTC]


4
2
0
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4
2
0
SO2 [ppbv]
08/07
13/07
18/07
23/07
28/07
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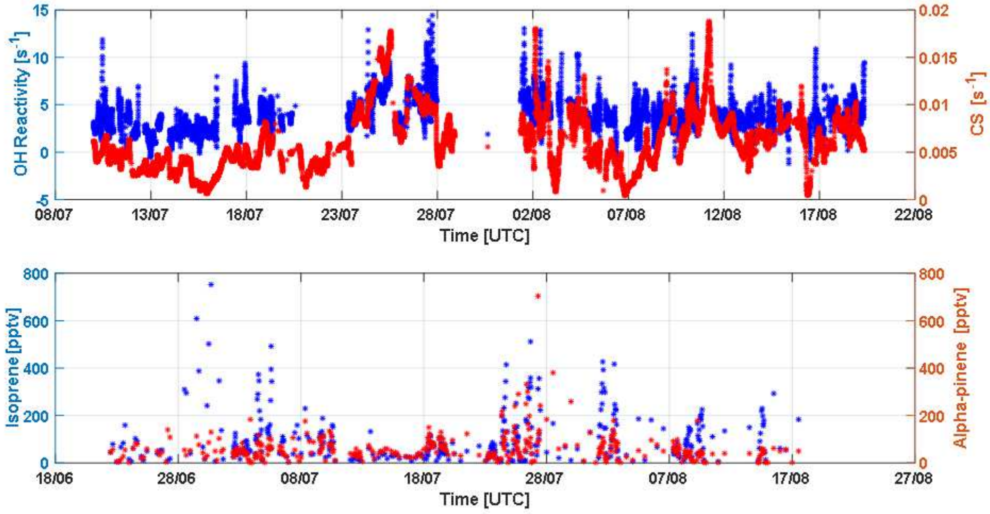
07/08
12/08
17/08
22/08
Time [UTC]
450
400
350
300
250
CO [ppmv]
2.2
2.1
2
1.9
1.8
CH4 [ppmv]
08/07
13/07
18/07
23/07
28/07
02/08
07/08
12/08
17/08
22/08
Time [UTC]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10
5
0
-5
OH Reactivity [s^-1]
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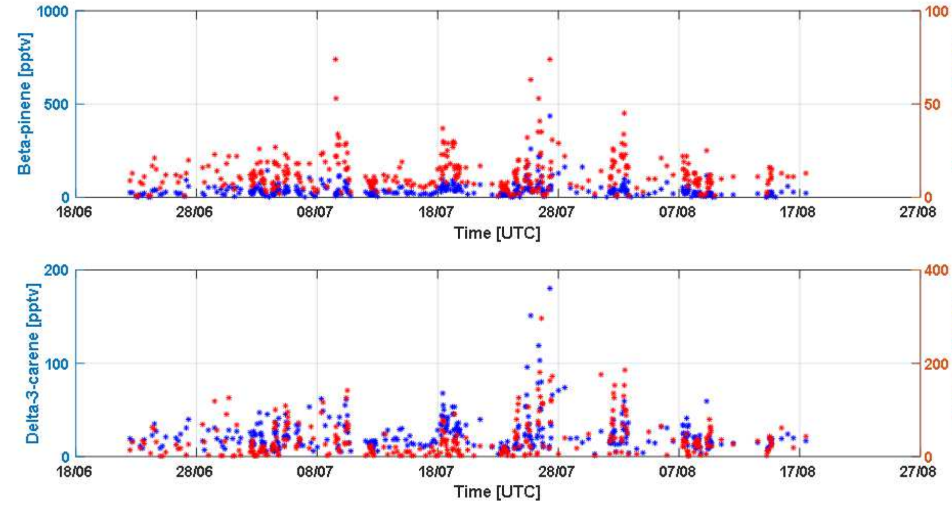
0.015
0.01
0.005
0
CS [s^-1]
08/07
13/07
18/07
23/07
28/07
02/08
07/08
12/08
17/08
22/08
Time [UTC]
800
600
400
200
0
Isoprene [pptv]
800
600
400
200
0
Alpha-pinene [pptv]
18/06
28/06
08/07
18/07
28/07
07/08
17/08
27/08
Time [UTC]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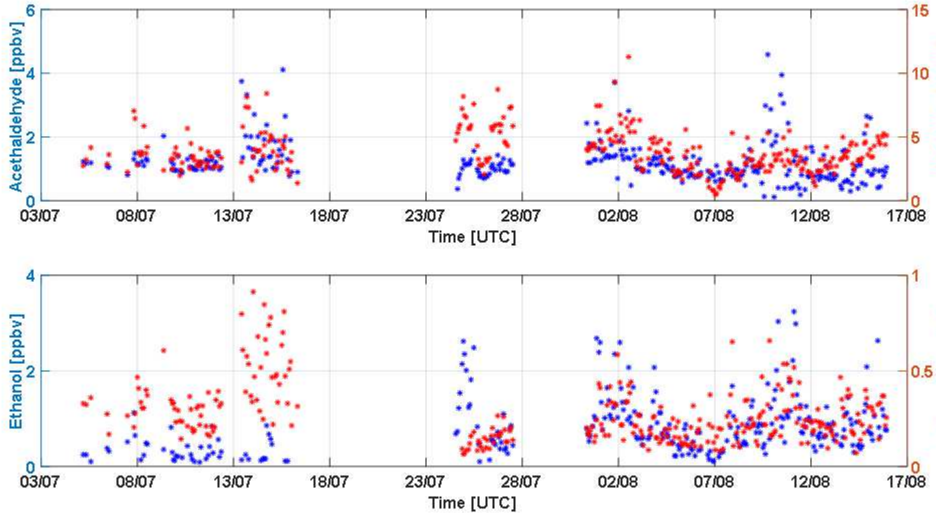
Limonene [pptv]
100
50
0
18/06
28/06
08/07
18/07
28/07
07/08
17/08
27/08
Time [UTC]
Delta-3-carene [pptv]
200
100
0
Sabinene [pptv]
400
200
0
18/06
28/06
08/07
18/07
28/07
07/08
17/08
27/08
Time [UTC]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2
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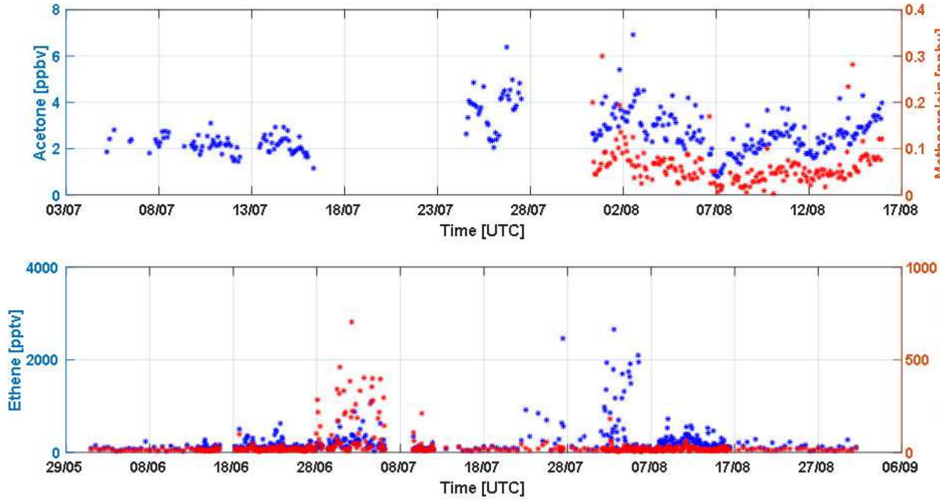
10
5
0
03/07
08/07
13/07
18/07
23/07
28/07
02/08
07/08
12/08
17/08
Time [UTC]
Ethanol [ppbv]
4
2
0
Propanal [ppbv]
1
0.5
0
03/07
08/07
13/07
18/07
23/07
28/07
02/08
07/08
12/08
17/08
Time [UTC]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6
4
2
0
Methacrolein [ppbv]
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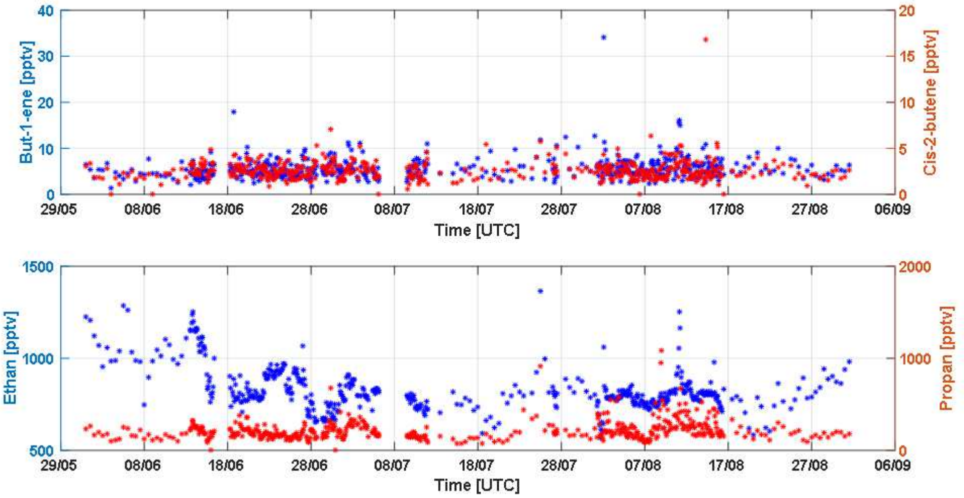
0.3
0.2
0.1
0
03/07
08/07
13/07
18/07
23/07
28/07
02/08
07/08
12/08
17/08
Time [UTC]
Ethene [pptv]
4000
2000
0
Propene [pptv]
1000
500
0
29/05
08/06
18/06
28/06
08/07
18/07
28/07
07/08
17/08
27/08
06/09
Time [UTC]


But-1-ene [pptv]
Cis-2-butene [pptv]
Ethan [pptv]
Propan [pptv]
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29/05
08/06
18/06
28/06
08/07
18/07
28/07
07/08
17/08
27/08
06/09
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30
20
10
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15
10
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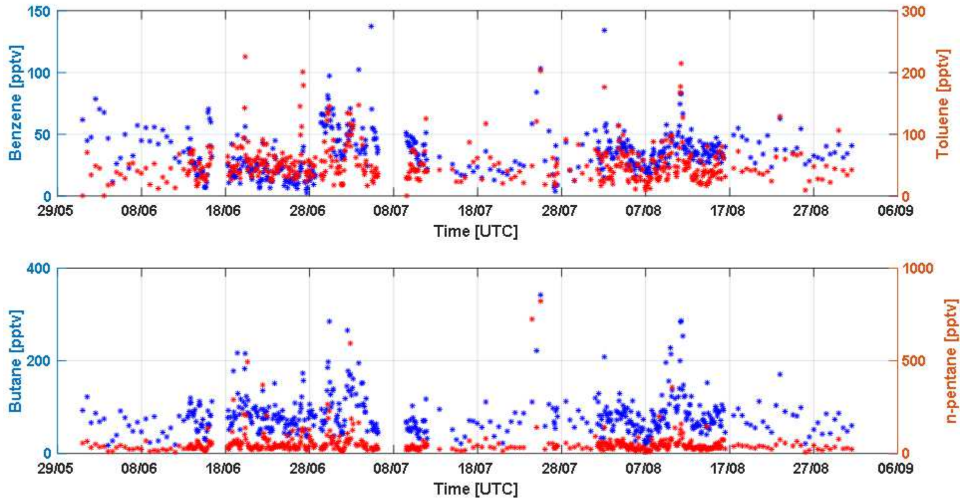
1000
500
2000

1


Benzene [pptv]
Toluene [pptv]
Butane [pptv]
n-pentane [pptv]
Time [UTC]
29/05
08/06
18/06
28/06
08/07
18/07
28/07
07/08
17/08
27/08
06/09
150
100
50
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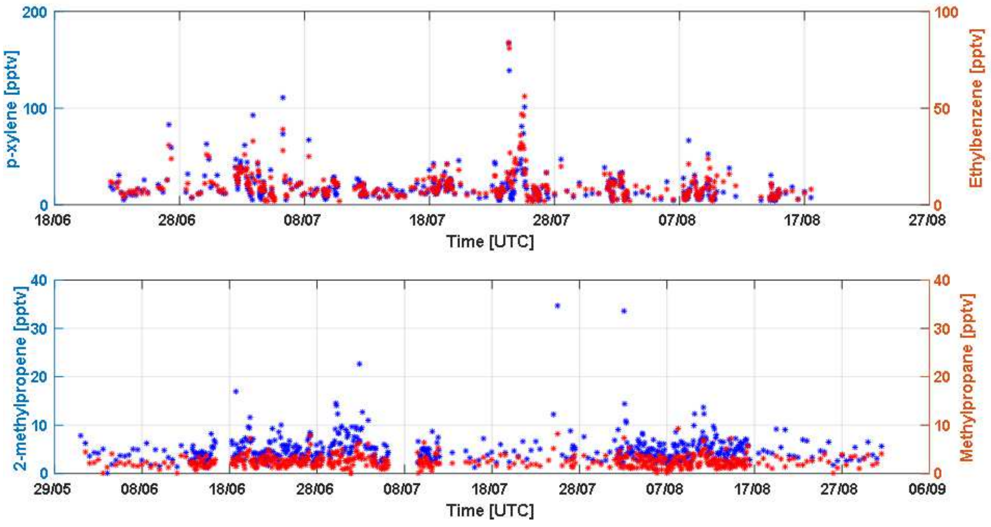
300
200
400
1000
500

2


p-xylene [pptv]
Ethylbenzene [pptv]
2-methylpropene [pptv]
Methylpropane [pptv]
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18/06
28/06
08/07
18/07
28/07
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27/08
29/05
08/06
06/09
200
100
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30
20
10

3

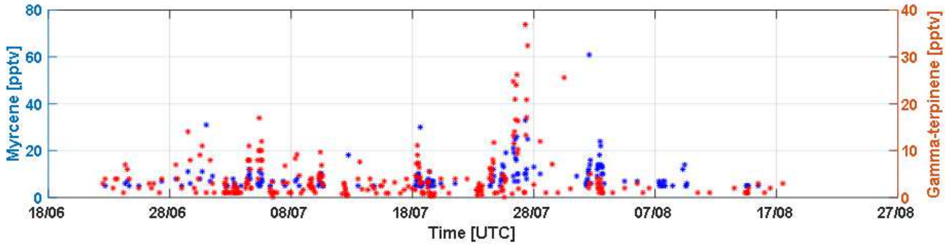

Figure SI-1. Time series of trace gases measured during the HOPE 2012 campaign.

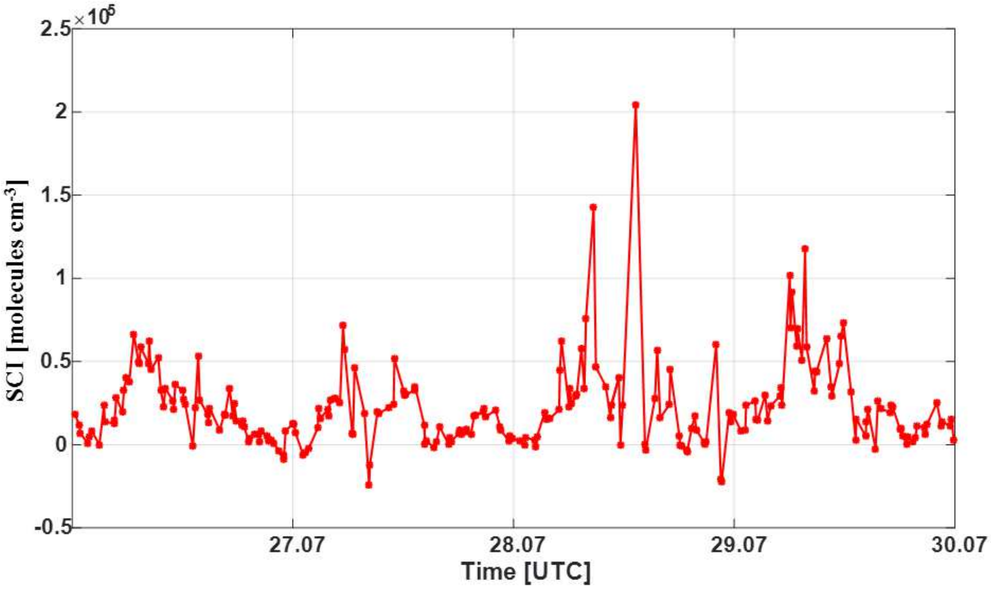

Figure SI-2. SCI time series as calculated from the sulfuric acid budget during the HUMPPA-COPEC 2010 campaign.

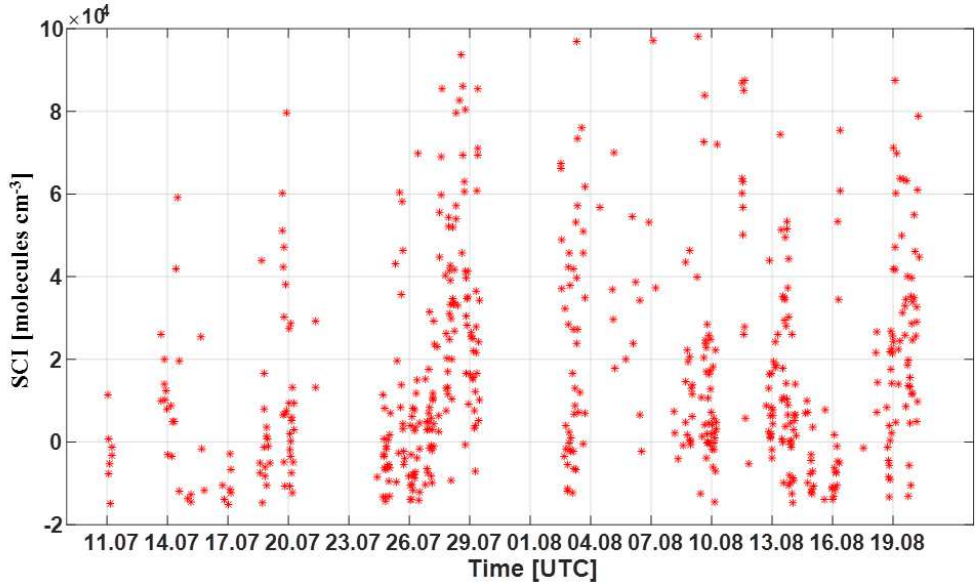

Figure SI-3. SCI time series as calculated from the sulfuric acid budget during the HOPE 2012 campaign.

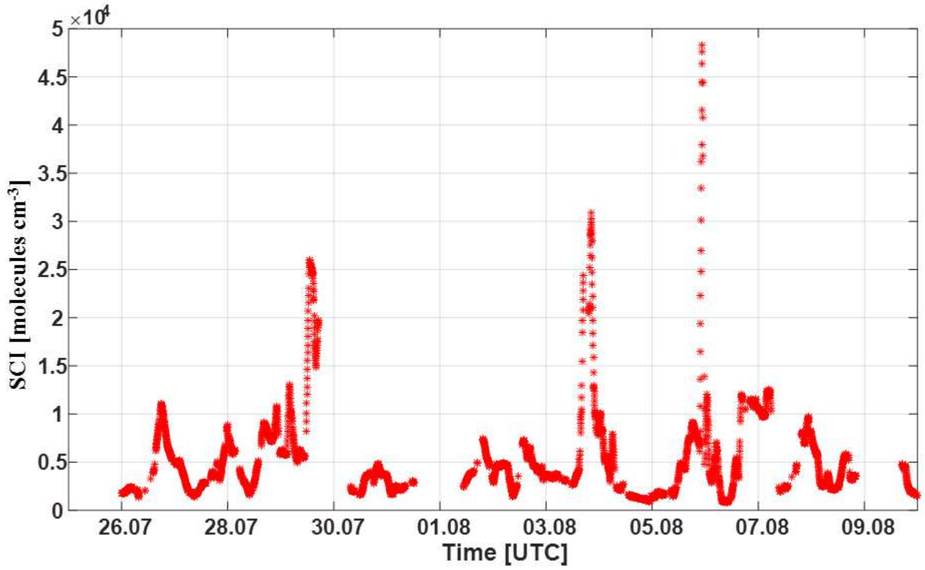

Figure SI-4. SCI time series as calculated from the measured unsaturated VOC during the HUMPPA-COPEC 2010 campaign.

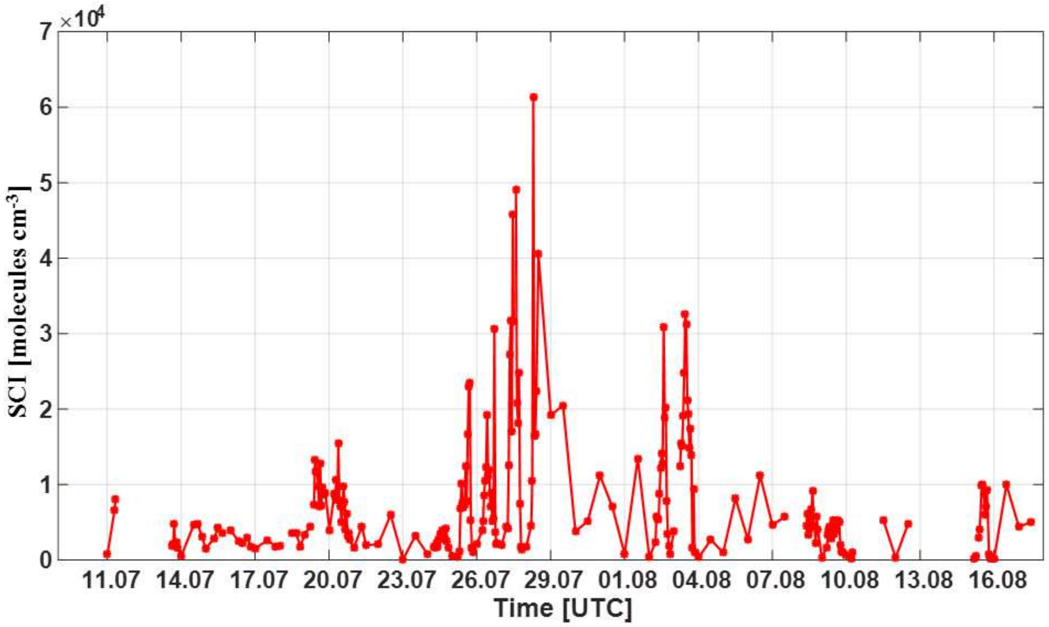

Figure SI-5. SCI time series as calculated from the measured unsaturated VOC during the HOPE 2012 campaign.

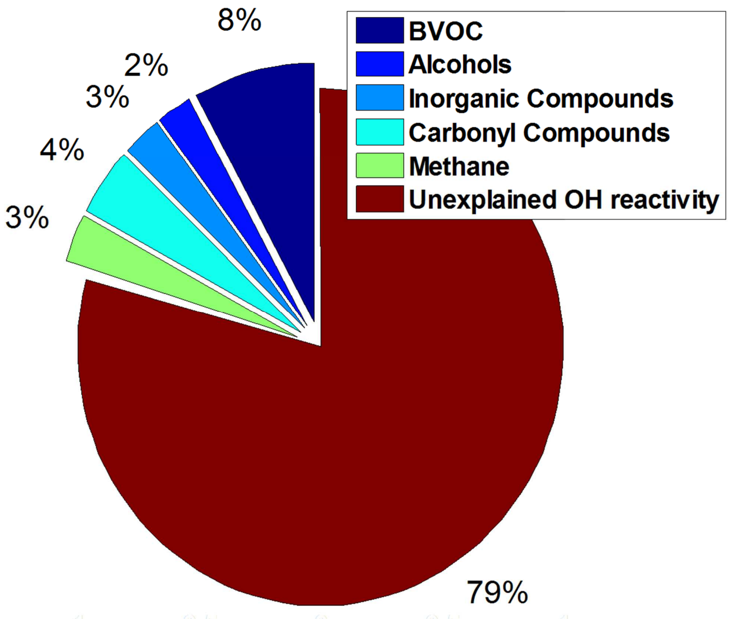

Figure SI-6. Contributions of measured trace gases to the measured OH reactivity during the HUMPPA-COPEC 2010.

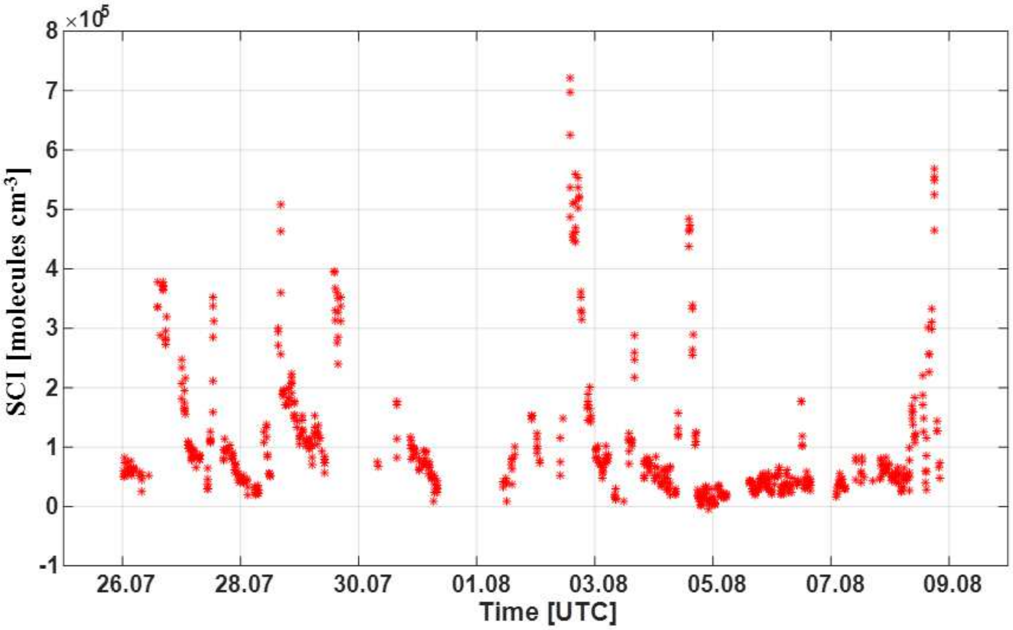

Figure SI-7. SCI time series as calculated from the unexplained OH reactivity during the HUMPPA-COPEC 2010 campaign.

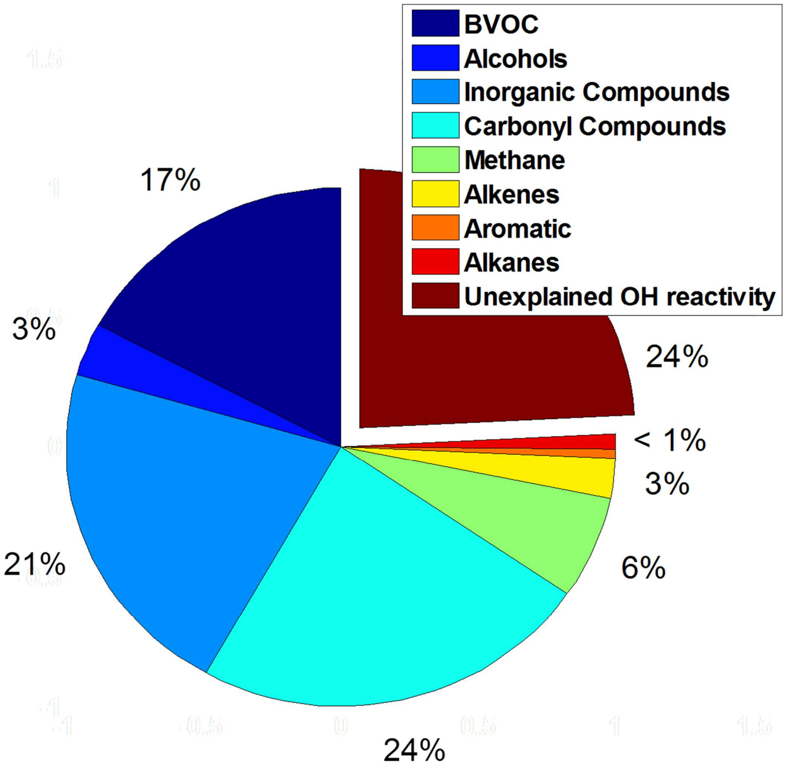

Figure SI-8. Contributions of measured trace gases to the measured OH reactivity during the HOPE 2012.

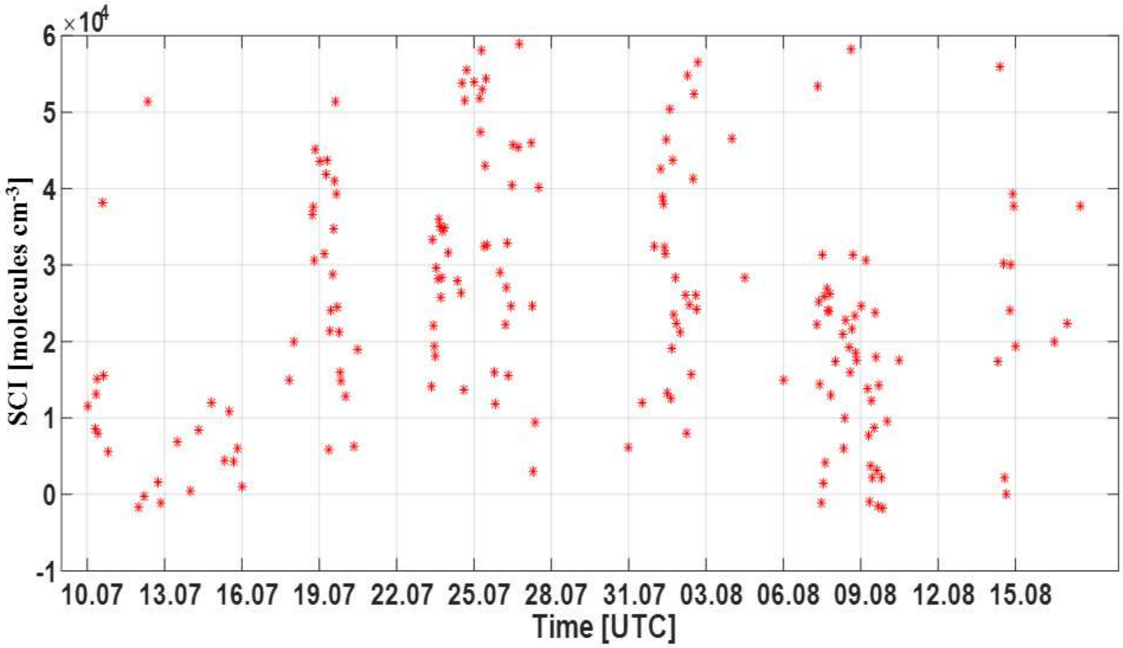

Figure SI-9. SCI time series as calculated from the unexplained OH reactivity during the HOPE 2012 campaign.

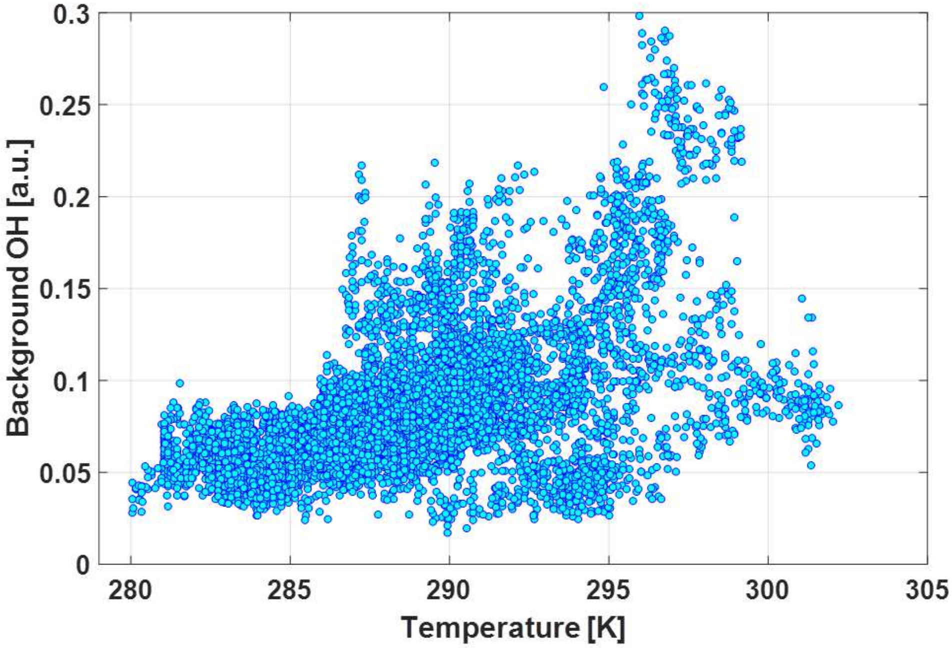

Figure SI-10. Background OH as a function of temperature during the HOPE 2012 campaign.

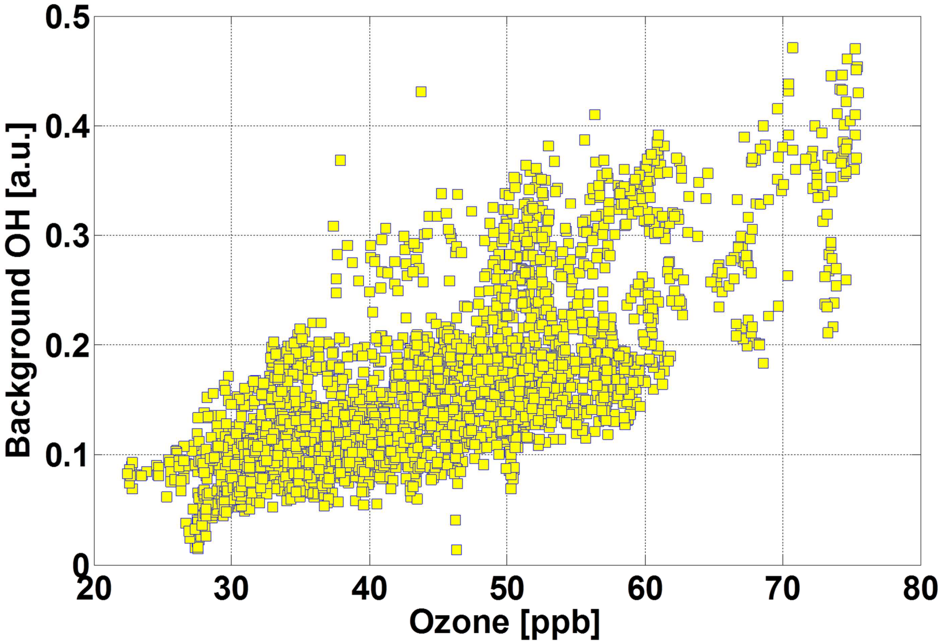

Figure SI-11. Background OH as a function of the ozone concentration during the HUMPPA-COPEC 2010 campaign.

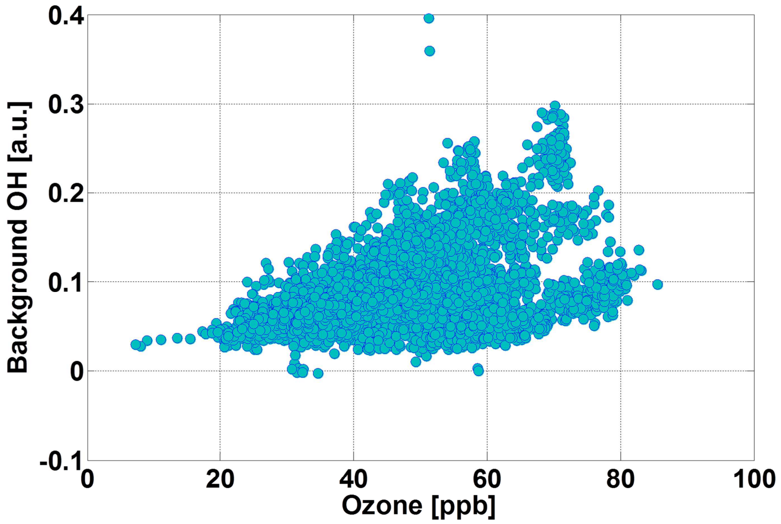

Figure SI-12. Background OH signal as a function of ozone concentration during the HOPE 2012 campaign.

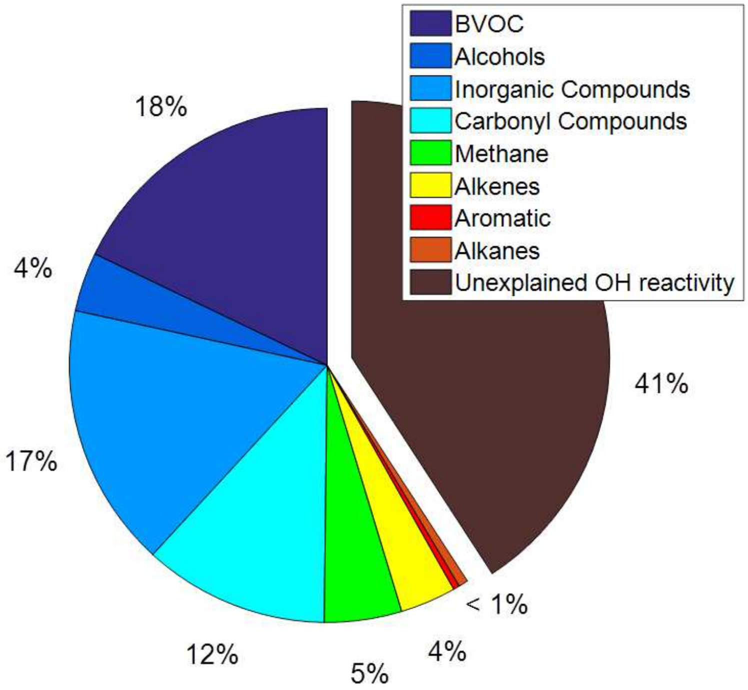

Figure SI-13. Contribution of measured trace gases to the measured OH reactivity during HOPE 2012 between the 1st and 3rd of August 2012.

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