Response to Reviewers

Anonymous Referee #1

Thank you for the helpful comments. Our responses can be found below.

1) Sections of the instrument description are not clear. For example, from the diagram in Figure 1 it is not clear to me what the sample flow path is or where the sample is actually collected. Is it pulled straight through the entire column, or is it trapped on the 4-port valve? What is the purpose of pump M? What is the purpose of flow tube F? A few more of these sorts of questions come up throughout the comments below"

We have made the following changes in order to improve the instrument description section:

- Fig. 1 has been updated so that the different instrument flow paths are differentiated from each other. We now highlight the flow paths of direct CIMS sampling, GC trapping, and GC elution. We believe this makes it clear that diluted air is pulled through the column during trapping. This update also makes it clear that the GC pumps either pull air from the instrument inlet or pull air through the column for sample collection.

- We have included an improved description on how air is subsampled into the column while referencing specific components labeled in Fig. 1 in order to better describe their purpose. An example of such changes to the manuscript can be seen on page 5 lines 17-20.

- The purpose of the flow tube is to ensure the analyte stream is well mixed prior to chemical ionization by CF_3O^-. This has been clarified on page 4 lines 1-3.

2) Sections of the instrument calibration are not clear. For example, it is mentioned that some compounds have sampling losses, but then there is no further mention or discussion of this. Calibration appears to rely in some way on a different c-ToF, but exactly how that is being used is not clear. It sounds like not all compounds have authentic/synthesized standards, and if not, how are retention times determined? Estimating collection and transfer efficiency by comparing GC-CIMS signal to CIMS signal likely suffers from an assumption of equal transmission of all isomers, but it is not clear if that is being accounted for because there is little discussion of how it is being applied.

Although details of instrument calibration were presented in the supplement, but we agree that the main text lacked necessary detail. We have rewritten the calibration section, pulling information from the supplement to discuss instrument sensitivity and better clarify how peak assignment and retention times were determined. Issues

regarding the transmission of individual isomers is now discussed in more detail in the discussion section. Additional information of how this was addressed is provided below.

3) Demonstrating the capabilities by field deployment is a valuable addition, but the authors seem to be focusing more on the actual isoprene oxidation chemistry and science than in thinking about this as a proof-of-concept. Several detailed chemical questions regarding unimolecular reactions, etc., are addressed and discussed all within a few short paragraphs, which does relatively little to advance the instrumentation aspect of the paper, but is also too detailed and dense to give a good discussion of the scientific advances. My strong recommendation is focus on this section only as a proof-of-concept. For instance, a major advantage of this technique is the time-resolved dataset the authors show no timeseries of concentrations or isomer ratios, or demonstrations of the continuous operation other than inferring it from the diurnal patterns.

We have rewritten this section to focus more on the instrument data as a proof-of-concept. Although we still use isoprene oxidation products to demonstrate the capabilities of this instrument, we only briefly touch on the chemistry to describe the relevance of these compounds in the atmosphere and highlight conclusions we can draw with this isomer-specific data set. We have also updated Fig. 9 to includes a time series of the four ISOPOOH/IEPOX isomers, rather than just the diurnal averages. This demonstrates the impact of continuous operation during a portion of the PROPHET campaign.

<u>Technical Comments</u>

Page 2 line 3: "can also lead to a scenario" sounds a bit odd to me, maybe just "Chemical oxidation can cause OVOCs to increase....".

The wording has been changed to "*Chemical oxidation can also cause OVOCs to increase…*"

Page 2 line 5: Use "In addition" or "also", but probably not both

We have removed "also" from the sentence.

Page 2 line 27: The GC paragraph sounds like it is about GC in general, in which case it would be a much larger discussion. I think the authors are mostly discussing field-deployabe/in-situ GCs here, which should be made clear.

This paragraph has been reworded to ensure that the reader knows we are discussing field-deployable GCs and not GCs in general.

Page 2 line 30-31: Though I realize it is not possible to make this list of GC-based OVOC measurements comprehensive, there are a few absences that stand out. I

would include some of Allen Goldstein's measurements in this list, perhaps Millet et al., JGR 2005 which saw MVK and methacrolein as well as other OVOCs, and arguably SVTAG as I believe it can see many oxygenated gases (Zhao et al., AS&T 2013). I would also include the NOAA GC, such as Goldan et al., JGR 2004, and/or some of Jessica Gilman's work.

We have added the following citations: Millet et al., JGR 2005, Zhao et al. AS&T 2013, Goldan et al. JGR 2004 and Lerner et al. AMT 2017

Page 3 line 22: I don't understand how the air is subsampled. Is there a sample loop or something? Oh, on the head of the column - so is there a valve in the CIMS interface? There needs to be some more clarity on how sampling happens

As mentioned in the response to the first comment, we have updated Fig.1 to reflect the different instrument flow paths and have reworded this section to add more clarity to how GC sampling occurs. The air is pulled through a column (which is pre-cooled to -20 C) and analytes are trapped at the column head. Valves downstream of the column determines whether the sample gas is pulled to a scroll pump or into the CIMS (flow tube or ion source).

Page 3 line 17: What is "Low pressure" about it? It seems like a regular GC approach to me: trapping cold, then heating and pushing through N2 to a vacuum detector. I gather the "LP" aspect is the large bore column, which reduces carrier gas pressures? A short mention or discussion of this would be helpful.

Thank you for this comment. We know highlight the pressure at which the GC operates (noting the location of this pressure measurement in Fig. 1) which is less than 260 mbar during compound separation. We have also provided an additional paragraph (page 5, lines 26) in order to provide more details about the benefits of this technique. It reads: *"…low pressures support the use of short, large bore columns without significant loss in peak separation. This becomes especially advantageous during cryotrapping as this large I.D. column allows for a greater volume of analytes to be pulled through and trapped, beneficially impacting the instrument signal to noise. In addition, low pressure conditions also allow for faster analysis times and lower elution temperatures (Table 2). The decrease in analysis time provides this instrument with sufficient time resolution to capture diurnal variations in measured species (one GC cycle per hour), while lower elution temperatures allow this method to be used on thermally-labile species, extending the range of compounds that can be analyzed."*

Page 3 line 28: The compounds aren't separated by the temperature controller, they are separated by the GC, using a ramp controlled by the controller.

We have changed the wording of this sentence.

Page 3 line 29: "each plate" is not that clear. Do the author's mean "on either side of the GC manifold/housing"?

We have rewritten this section such that this wording is no longer used. We have also updated Fig. 2 to show the approximate locations of the heaters on the GC assembly making it clear that the heaters are located on the outside surfaces of the GC manifold.

Page 3 line 30: What is the purpose of the flow tube? It makes a big difference later, but it's not clear what the function is. I would think interaction with ions, but seems to happen latter.

As mentioned above, we have added additional details on page 4 lines 1-3. The purpose of the flow tube is to ensure the analyte stream is well mixed prior to chemical ionization by CF_3O^-.

Page 6 line 16-21: FT and HS is asymmetric naming, with one after the approach and the other after the result. FT and IS (ion source) would be preferred,

We now use this recommended naming scheme.

Page 6 line 23: It's not clear why introduction at the source causes longer interaction times. Does fragmentation affect/complicate calibration?

Introduction at the source allows analytes to interact as soon as CF_3O^- forms, rather than later downstream (as in the case of FT introduction). The interaction time between the analytes and the ions increases by approximately 10 fold. This information has been added to this section.

Fragmentation does occur and can cause some discrepancies between the GC signal and the direct CIMS sampling, as discussed in the main text. However, by comparing chromatograms obtained by sending the flow to the IS vs FT, we can see that the concentrations determined by these two methods are comparable once the enhancement factor is accounted for. We do note that we see more fragmentation ions when operating in IS mode, but this is likely due to the higher signal to noise, which would allow us to observe them unlike when performing GCs through the FT. The section now includes this information.

Page 7 line 14: When the authors say "directed" do they mean direct sampling, or analysis by GC? Given the fragmentation in the HS method, it seems to me that the latter is necessary.

The compounds are sampled into the flow tube directly (without passing through the GC). The passage has been reworded to make this clear.

Page 7 line 15: Which standards are available/synthesized and which are not? Later, for instance in Figures 7, 10, and 11, the author's seem to know the elution orders of many specific isomers - are these all from authentic or synthesized standards?

Authentic standards were used to determine instrument sensitivity, while a combination of synthesized standards (which varied in purity) and chamber experiments were used to determine GC elution order. The section has been rewritten to provide a better understanding of how elution order was determined. Assignment of many of the isoprene products is described in Teng et al., 2017.

Page 7 line 16-20: It is not clear what the purpose of the c-ToF-CIMS is, or where it is discussed or first mentioned. Is it that there are known sensitivities with that instrument, so that is the purpose of the average sensitivity difference? How does it help to compare to the c-ToF? This paragraph needs generally more explanation to be made clearer.

We have extensive calibration of the HRToF-CIMS using four gas standards (HCN, SO2, hydroxyacetone and glycoaldehyde). These calibration gases are simultaneously sampled on the cToF which uses the same ion chemistry as the HRToF-CIMS and for which we know the sensitivities of many other compounds. Because we observed that the cToF-CIMS was 1.4x more sensitive than the HRToF-CIMS for the standard gases used, we applied this factor across all analytes to estimate the HRToF sensitivities to the compounds discussed in this study. As mentioned above, this information was originally available in the Supplement but has been moved to the main manuscript to reduce confusion.

Page 8 line 27: for which species are losses observed?

We have observed poor transmission of IEPOX. We make mention of this and clarify how we can determine its transmission when ISOPOOH (which has higher transmission) is present.

Page 9 line 2-3: This is an interesting approach that potentially provides very nice confirmation of compounds for which standards aren't available. However, do the authors know that all isomers are transferred equivalently, and that all isomers can be seen? If total isomer-resolved signal is less than direct CIMS signal, that could be due to incomplete transmission of all isomers as seems to be implied by the author's, but it could also be due to complete transmission of one isomer but not the others, or complete transmission of all observed isomers but the presence of non- or poorly-observed other isomers. It is not clear to me that this approach fully works, and no effort is made to validate it here.

We have provided proof-of-concept of using this approach in the field using IHN which has high transmission through the GC. We also agree that poor transmission can be due to a single isomer rather than a sum of all isomers. This has been observed to be the case of the two isomers of IEPOX (GC transmission = 67%) compared to ISOPOOH (GC transmission ~ 100%). We now clarify how we can use this method in laboratory experiments to distinguish between which isomer(s) are responsible for compound with poor transmission, without the use of synthesized standards.

Page 9 Section 3.2: Dilution will solve the humidity problem, but only reduces and does not solve the problem of reactions on the adsorbent from ozone or other oxidants. To collect these compounds, an ozone scrubber is probably out of the question, but have the author's done any tests to evaluate the impact of ozone on these compounds under typical sampling conditions?

In response to this comment, we have performed additional experiments in which we trapped ozone from an air sample containing 200 ppb ozone on the column. In this experiment, we oxidize isoprene under high NOx conditions to produce IHN. We use IHN because its reaction rates with ozone are isomer-specific. In addition, during this oxidation approximately 100 ppb of NO_2 was produced, providing another oxidant to test. There was no evidence that either oxidant affected the IHN, even at higher dilutions (15x) and colder trapping temperatures (-50C). This information has been added in the discussion section.

Page 10, Section 4: How long were these campaigns and/or measurement periods?

We have now included dates to specify when and for how long for each campaign took place.

Page 10, line 18: "Isomers" is a more common term than "mass analogous", or the authors could use "isobaric", the mass spectrometric term for having the same mass

We have changed "mass analogues" to "isobaric,"

Figure 3d-f: Both axes are CIMS signals, but one is labeled normalized IHN signal, and the other as CIMS signal. Why not label the right as m/z 104 signal, or water signal or something comparable?

We have changed the axes labels of Fig 3 to reflect these changes.

Figure 8: The period of GC elution (black line) seems to have significantly lower scatter, even during background periods - is that real, and if so why is that?

Signal scatter is lower during the GC elution. We proposed an explanation for that in the caption stating: "*Changes in the amount of flow entering the ion source during direct CIMS and GC-CIMS sampling directly correlate with the signal to noise seen during each operating mode. The increased flow rate through the ion source during the GC sampling mode results in higher ion counts and increased signal to noise*."

Anonymous Referee #2:

Thank you for the carful read of our manuscript. We have addressed the comments and modified our manuscript accordingly.

Instrument description section:

Suggest devoting significantly more time on the first paragraph describing the instrument and Figure 1. Even if the details of this are in previous papers. The title speaks of low pressure chromatography but the words "low pressure" are mentioned only two times and with very little description of it, how it works, what pressures the GC operates under etc.

We agree and the following changes have been made in response to this comment:

- Fig. 1 has been updated and now differentiates different instrument flow paths including direct CIMS sampling, GC trapping and GC elution.

- The first paragraph of this section has been expanded and now briefly contrasts laboratory studies described in previous papers with this automated GC-CIMS design.

- We have included an additional paragraph under the GC subsection to further discuss the low pressure chromatography. This includes listing the pressure that the GC operates (< 260 mbar depending on if passing the GC output through the ion source or flow tube) at as well as the benefits that result from operating under these conditions. This passage reads: *"As mentioned above, connecting the GC outlet directly to the mass spectrometer allows the entire column to remain at sub-ambient pressures during elution… low pressures support the use of short, large bore columns without significant loss in peak separation. This becomes especially advantageous during cryotrapping as this large I.D. column allows for a greater volume of analytes to be pulled through and trapped, beneficially impacting the instrument signal to noise. In addition, low pressure conditions also allow for faster analysis times and lower elution temperatures (Table 2). The decrease in analysis time provides this instrument with sufficient time resolution to capture diurnal variations in measured species (one GC cycle per hour), while lower elution temperatures allow this method to be used on thermally-labile species, extending the range of compounds that can be analyzed."*

It is not clear at all how the cryofocusing is accomplished. Please clarify this section and take the time and space to describe the different parts of Figure 1 –

particularly the cryofocus and low pressure aspects of the GC. The very high flow rates are an interesting aspect of the design and this should be highlighted and explained.

We have taken better care to better describe how cryofocusing is accomplished while referencing several components labeled in Fig. 1. Also, as mentioned above, further discussing the low pressure aspect of this GC also highlights the high flow rates of this instrument.

Since this paper is about the description of an automated field-hardened instrument, provide more details on how the various components of the instrument are fitted together and how the automation was accomplished. The description of the instrument is not concise and does not have a good flow.

More detail has been provided, particularly in the GC section. This section has also been rearranged to highlight key design components followed by a concise description of sample collection and elution operating parameters.

Often very indirect language is used which results in the manuscript being too wordy perhaps at the expense of not providing concise details.

An example: 5/11: "During the collection of analytes on the head of the column, it is important that the temperature remains stable, as sizable fluctuations in temperature adversely affects the chromatography. To control the trapping set point…"

Could be replaced by something like: A PID control loop using heaters and the resistance temperature detector (RTD, F3102, Omega) located on the GC column ring (Fig. 2, #2 on diagram) were used to maintain fine control over the temperature set points during cryofocusing. This is needed to obtain reproducible chromatography.

Suggest going through the Instrument description sections and make clear declarative statements where possible and appropriate of the instrument design. Provide details needed for the reader to grasp the primary design features and justification for them without having to refer to previous papers.

The specific example and other instances in the instrument description now use more direct language. Primary design features and justification for their use are now described in more detail in both the instrument description and discussion sections

5/12: To control the trapping set point, we utilize the heaters and the resistance temperature detector (RTD, F3102, Omega) located on the GC column ring (Fig. 2, #2 on diagram)

Perhaps show the heaters on the diagram

We have updated Figure 2 and heater locations were added to the diagram.

5/14: In addition, during trapping we only use the solenoid valve connected to the 0.15 mm I.D. restrictor as this valve provides a CO2 flow that is adequate to maintain the GC temperature (~10 slm)

?????

We apologize for the confusion. We have reworded the passage to clarify the purpose of the different CO_2 valves.

Calibrations and backgrounds:

7/15: However, as standards are not available for many species mentioned in this work, these calibration experiments were simultaneously performed on the c-ToF-CIMS to directly compare the compound sensitivities between these two instruments. On average, the c-ToF-CIMS was 1.4 times more sensitive…

I know what you mean here and it is explained further in the supplement but please rewrite more clearly in the main section as other readers will not get this on a quick read through.

We have rewritten this passage and incorporated some information that was provided in the supplement to make the calibration procedure clearer to the reader.

7/21: We use two methods to quantify the instrumental background signals caused by interfering ions present at targeted analyte masses. In the first method, the instrument undergoes a "dry zero" where the CIMS flow tube is overfilled with dry nitrogen so that no ambient air is sampled during this time. In this method, the humidity within the instrument changes substantially compared with ambient measurements. The second method passes….

How do the two methods compare?

The following text has been added to the section as a response to this comment: "*The dry zero is most similar to the GC measurements and can assess the health of the instrument over the course of a campaign (i.e. these backgrounds should not change over time), while the ambient zero captures background signals that are adjusted for the water dependent sensitivity of the compounds measured during direct CIMS sampling.*"

Discussion

8/16: The largest technical challenge in developing a field-deployable GC was the design of a sampling system capable of collecting and separating compounds with minimal analyte degradation.

Why is this true for a field-deployable system? Seems that you need those same characteristics for a laboratory based system. The difference in a field – deployable system one would think is in getting the sample undisturbed to the instrument which is not addressed – and possibly trivial if the right sampling manifold is used (also not discussed). Referring to my opening comments, the question here is whether more of the details of the system – or a similar prototype system are discussed in previous papers. I suggest that these details be repeated here for the reader. Address what was specifically done in the field-deployable GC versus the prototype laboratory system.

We agree. The goal of this section was to discuss the difficulty of minimizing losses while transmitting reactive compounds through this GC system, rather than the difficulty of constructing a field-deployable GC as a whole. As such we've rearranged this section to better reflect this. In addition, parallels between this GC system and the laboratory prototype have been added to the Instrument Description section. This is necessary to highlight the automated nature of this instrument.

Field Performance:

10/9: "However, instrument upgrades performed prior to the Caltech study were able to greatly reduce GC downtime and significantly improved the chromatography, despite other operating conditions remaining mostly unchanged."

This in a nutshell exemplifies the main problem with the paper. What were the instrument upgrades? Isn't this what the paper is supposed to be about?

We have removed this passage from this section and it is now incorporated in Section 2 when we discuss features of the GC design. Additional information about these upgrades are also provided in the Supplement.

Figures:

Fig 1. Enlarge the LP-GC portion of the drawing with better detail on the valving and cryofocusing aspects

The authors have updated Fig. 1 as described in a previous comment. We have also included better detail on some of the valves (e.g. the 4-port valve at the head of the column)

Fig 2. Enlarge drawing and add heaters on solenoid positions

Fig 2. has been updated to include more information, including heater position on the assembly.

Small thing…

4/22: For the studies detailed in this paper…unnecessary to start the sentence with this. Check paper for other such incidences

This text was removed and other instances in this paper were corrected as well.

Low-pressure gas chromatography with chemical ionization mass spectrometry for quantification of multifunctional organic compounds in the atmosphere

Krystal T. Vasquez[1], Hannah M. Allen[1], John D. Crounse[2], Eric Praske[1], Lu Xu[2], Anke C. Noelscher[2*], and Paul O. Wennberg[2,3]

[1]Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA 91125, USA
[2]Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA 91125, USA
[3]Division of Engineering and Applied Science, California Institute of Technology, Pasadena, CA 91125, USA
[*]now at: Deutscher Wetterdienst, Technische Infrastruktur, Frankfurter Straße 135, Offenbach am Main, Germany

Correspondence to: Krystal T. Vasquez (kvasquez@caltech.edu) and Paul. O. Wennberg (wennberg@caltech.edu)

Abstract. Oxygenated volatile organic compounds (OVOCs) are formed during the oxidation of gas phase hydrocarbons in the atmosphere. However, analytical challenges have hampered ambient measurements for many of these species, leaving unanswered questions regarding their atmospheric fate. We present the development of an *in situ* gas chromatography (GC) technique that, when combined with the sensitive and specific detection of chemical ionization mass spectrometry (CIMS), is capable of the isomer-resolved detection of a wide range of OVOCs~~by addressing several~~. The instrument addresses many of the issues typically associated with chromatographic separation of such compounds (e.g., analyte degradation). The performance of ~~this~~ the instrumentation is assessed through data obtained in the laboratory and during two field studies. We show that this instrument is able to successfully measure otherwise difficult-to-quantify compounds (e.g., organic hydroperoxides and organic nitrates) and observe the diurnal variations of a number of their isomers.

1 Introduction

The composition of the atmosphere is determined through a dynamic array of chemical emission, transport, deposition and photochemical processing. Our ability to accurately predict future trends of both air quality and climate change depends on understanding these processes. Of particular interest is the photooxidation of non-methane hydrocarbons (NMHCs) ~~that, due to their high abundance,~~ which influence the distributions of key atmospheric constituents such as ozone (O_3) and secondary organic aerosol (SOA). While decades of research have provided much insight into the link between atmospheric composition and chemistry, significant knowledge gaps still persist and the atmospheric degradation pathways of many NMHCs remain poorly understood.

The gas phase oxidation of NMHCs is typically initiated by one of several atmospheric oxidants (~~e.g.~~i.e., OH, NO_3, or O_3) converting these hydrocarbons into oxygen-containing, often multifunctional, intermediates. These first-generation oxygenated volatile organic compounds, or OVOCs, can undergo further transformations through a number of competing physical and photochemical sinks (Atkinson and Arey, 2003; Mellouki et al., 2015), each of which can have a unique effect on the atmosphere.

Some OVOCs can undergo photochemical fragmentation to smaller species, often through conversion of NO to NO_2 leading to local ozone formation, while others (such as those with longer atmospheric lifetimes) can be transported downwind prior to oxidation, extending their effects to regional and global scales. Chemical oxidation can also ~~lead to a scenario in which the OVOCs~~ cause OVOCs to increase their functionality, creating large, low-volatility, multifunctional products that partition into the particle phase and contribute to the formation and growth of aerosol. In addition, it has ~~also~~ been shown that significant portions of OVOCs can be removed from the atmosphere through fast deposition processes (Nguyen et al., 2015) which can greatly affect the chemical cycling of many important compounds.

It is the relative importance of each possible sink that establishes the dominant tropospheric fate of these compounds and thereby the impact of their hydrocarbon precursors (Koppmann and Wildt, 2008). This seemingly straightforward relationship can quickly become complicated however, especially for larger compounds ($>C_3$). A prime example of this can be seen during the OH oxidation of isoprene, a highly abundant and reactive biogenic VOC, which produces six isomeric peroxy radicals (RO_2). Changes in the relative abundance of these radicals can result in vastly different ratios of its OVOC products (Orlando and Tyndall, 2012; Teng et al., 2017; Wennberg et al., 2018), allowing isoprene to either have a profound effect on ozone and SOA through its bimolecular reaction products—isoprene hydroxy nitrates (IHN) and isoprene hydroxy hydroperoxides (ISOPOOH), respectively—or on the OH radical which ~~can be~~ is recycled during the subsequent chemistry of products ~~that arise~~ formed from the unimolecular RO_2 reaction channel (e.g. hydroperoxy aldehydes or HPALDs; Peeters et al., 2014). These structural effects are also apparent throughout the later generation chemistry of isoprene and other NMHCs ~~,~~ and the outputs of global chemistry transport models can be quite sensitive to this isomer-specific chemistry. For example, ozone production, in particular, has been shown to be highly dependent on the assumed yields and reaction rates of specific organic nitrate isomers (Squire et al., 2015), which together determine the net NO_x recycling capabilities of each compound.

Despite its importance, our understanding of this intricate chemistry has been hindered by the lack of instrumentation capable of providing isomer-resolved measurements of important OVOCs. Recent progress has been made in this respect for laboratory studies (e.g., Bates et al., 2014, 2016; Lee et al., 2014; Teng et al., 2015, 2017; Schwantes et al., 2015; Praske et al., 2015, 2018). Analytical techniques for ambient measurements, however, either suffer from high detection limits and/or large instrumental losses of these reactive analytes (Vairavamurthy et al., 1992; Apel et al., 2003, 2008; Clemitshaw, 2004), and so the focus has been typically on smaller, more abundant compounds ~~(Mellouki et al., 2003; Koppmann and Wildt, 2008; Hellén et al., 2017)~~ (Mellouki et al., 2003; Goldan et al., 2004; Koppmann and Wildt, 2008; Hellén et al., 2017).

Gas chromatography (GC) can reach the detection limits needed to measure a variety of larger OVOCs by preconcentrating analytes prior to separation and utilizing detection methods such as flame ionization detection (FID) or electron impact mass spectrometry (EI-MS) (Ras et al., 2009). As a result, this technique is ~~becoming~~ increasingly popular and has ~~recently been used~~ been or is currently being developed for the *in situ* detection of carbonyls ~~(Apel et al., 2003)~~(Apel et al., 2003; Zhao et al., 2013), organic acids (Hellén et al., 2017), organic nitrates (Mills et al., 2016) and other oxygenated organic compounds ~~(e.g., Clemitshaw, 2004; K~~ (e.g., Clemitshaw, 2004; Millet et al., 2005; Goldan et al., 2004; Koppmann and Wildt, 2008; Roukos et al., 2009; Lerner et al., 2017). Nevertheless, these field-deployable GC techniques come with their own analytical challenges as the non-specificity of common detectors such as GC-FID and overall difficulty in differentiating fragmentation patterns of isobaric and isomeric

species with GC-MS can create data sets that hide the intricacies of crucial structure-activity relationships of individual compounds. In addition, the multifunctional nature of these compounds makes them highly reactive, increasing the likelihood that they will be lost or converted into different species through surface-enhanced reactions that can occur at various stages of GC analysis. Converted species can be subsequently detected (e.g., Rivera-Rios et al., 2014), thus identifying such artifacts necessitates authentic calibrations even for species not being targeted. Due to the lack of commercially available standards for many species of interest, this can quickly become labor intensive or simply not feasible, leading to large uncertainties in these types of measurements and much confusion regarding chemical mechanism elucidation.

Here, we present the development and deployment of a new gas chromatography method that uses the highly sensitive detection of chemical ionization mass spectrometry (CIMS) for the near real-time detection of a number of OVOCs. With this instrumentation, we address many of the historical issues associated with the use of gas chromatography for atmospheric field sampling, allowing for the preservation of difficult-to-measure compounds and enabling isomer-resolved measurements of a wide array of compounds. Compounds discussed in this study are shown in Table ~~1.~~ 1. To distinguish between ~~different~~ isomers of the hydroxynitrates, ISOPOOH, HPALD and ~~ICN~~isoprene carbonyl nitrates (ICN), we employ an abbreviated naming scheme in which the first number denotes the carbon position where the oxidant originally adds to the parent alkene and the second denotes the position of the additional functional group (e.g. for 1,2-IHN the hydroxy group added to the C1 carbon of isoprene, followed by a ~~nitroxy~~ nitrooxy group at C2).

2 Instrument Description

~~A simplified schematic of the GC-HR-ToF-CIMS is shown in Fig. 1. It~~ The GC-HRToF-CIMS integrates the use of a metal-free, low-pressure gas chromatograph (LP-GC) positioned upstream of a high-resolution time-of-flight chemical ionization mass spectrometer (~~HR-ToF-CIMS~~HRToF-CIMS, TofWerk/Caltech)~~, allowing for two~~ . This combination allows for two main sampling modes: (1) direct atmospheric sampling for the real-time quantification of gas-phase species (hereafter, direct CIMS sampling), and (2) GC-CIMS analysis for the collection, separation and quantification of ambient isomer distributions of select OVOCs. The overall design of this instrumentation is based upon an existing testbed that has been used in previous laboratory studies ~~(e.g., Bates et al., 2014; Lee et al., 2014; Teng et al., 2015, 2017; Schwantes et al., 2015).~~ (e.g., Bates et al., 2014; Lee et al., 2014; . However, in those studies, the GC prototype required a short length of the column to be manually submerged into a chilled isopropanol bath; a set up that is cumbersome, if not impossible, to use outside of a laboratory setting. These studies were also performed under very low humidities. Here, we have ~~automated and~~ field-hardened this design such that ~~its novelty comes from the capability to operate~~ GC operation is automated and chromatography is reproducible under a variety of field conditions~~with minimal maintenance as it captures real-time data through a programmed sampling routine.~~ . A simplified schematic of the GC-HRToF-CIMS is shown in Fig. 1, highlighting the main flow paths of direct CIMS sampling (orange) as well as GC trapping (blue/purple) and eluting (red/purple). Details of the GC automation are discussed in Sect. 2.2.

2.1 ~~HR-ToF-CIMSThe HR-ToF-CIMS~~ HRToF-CIMS

The HRToF-CIMS builds upon methods developed with a previous custom-built quadropole CIMS ~~(Crounse et al., 2006, later upgraded to a~~ (Crounse et al., 2006, later upgraded to a cToF-CIMS). Ambient air is drawn at high flow rate (~2000 slm, P ~1 atm) through a custom Teflon-coated glass inlet (3.81 cm I.D x 76.2 cm long~~) after which a~~ ; Fig. 1B). A small fraction of ~~the~~ this flow is sub-sampled perpendicular to the main flow in order to discriminate against large particles ~~that may be present. This sub-sampled gas stream can be~~ and debris, and directed to the CIMS, the GC, or a zeroing system through short lengths of 6.35 mm O.D. PFA tubing. When measured directly by the CIMS, ~~the sample first~~ ambient air, diluted with dry N_2, flows through a fluoropolymer-coated (Cytonix PFC801A) glass flow tube (Fig. 1F) ~~maintained at 35 before undergoing~~ to ensure a well-mixed gas stream prior to chemical ionization by ~~a~~ CF_3O^- reagent ~~ion~~ ions (*m/z* 85)~~whose~~ . The flow tube pressure is held at 35 mbar and samples ambient air at a constant flow rate of 180 sccm as regulated by a critical orifice (Fig. 1G). This ambient air is then diluted by a factor of 10 with dry N_2 (Fig. 1I). Two valves located upstream of this orifice ensure a constant mass flow through the flow tube by pumping on the inlet (~0.5 slm). When the instrument switches to a different analysis mode (e.g. performs a GC or zeroes), these valves are toggled to overfill the flow tube with dry nitrogen and prevent ambient air from being sampled through this flow path.

The CF_3O^- ion chemistry has been described in ~~more~~ detail elsewhere (Huey et al., 1996; Amelynck et al., 2000a, b; Crounse et al., 2006; Paulot et al., 2009a, b; St. Clair et al., 2010; Hyttinen et al., 2018). Briefly, CF_3O^- is formed by passing 380 sccm of 1 ppmv CF_3OOCF_3 in N_2 through a cylindrical tube (Fig. 1~~G~~H) containing a layer of polonium-210 (NRD LLC ~~Po-2021~~P-2021, initial activity: 10 mCi). Alpha-particles produced from the radioactive decay of the polonium react with the N_2 gas to produce electrons which react rapidly with CF_3OOCF_3 to produce ~~the~~ CF_3O^- ~~ion. The reagent ion interacts with the~~ ions which, in turn, react with analytes by forming cluster (*m/z* = analyte mass + 85) or fluoride transfer (*m/z* = analyte mass + 19) product ions~~allowing~~ . This method allows for the detection of small organic acids and other oxygenated multifunctional compounds with high sensitivity (LOD $\approx$ 10 pptv during direct sampling for 1 s integration period) and minimal fragmentation.

Following ionization, the ions are directed via a conical hexapole ion guide into the high resolution mass spectrometer (Tofwerk) which collects data for masses between *m/z* 19 and *m/z* 396 at 10 Hz time resolution. The ~~HR-ToF-CIMS~~ HRToF-CIMS has a mass resolving power of ~3000 ~~m/dm~~m/Δm, allowing for the separation of some ions with different elemental composition but the same nominal mass.

2.2 GC

2.2.1 Design and Automation

Chromatographic separation of analytes is achieved on a short ~~,~~ (1-m), megabore column encased between two aluminum plates~~, each measuring~~ . These plates measure 130 mm x 130 mm x 5 mm (total mass = 466 g~~,~~), creating the compact design shown in Fig. 2~~)~~. The column ~~sits~~ is housed within a rectangular groove (0.8 mm wide x 2.4 mm deep) machined into ~~one~~ the bottom plate, which serves to ~~both~~ hold the column in place~~and allow for it to make~~ , and provides for good thermal contact with the metal as it ~~makes 2.5 loops~~ loops 2.5 times around the plate. The temperature of the ~~GC~~ metal assembly can

be controlled over a large range ~~, cooling to -60~~(−60°C ~~using liquid and warming to ~200~~to 200°C~~, reaching a~~ ; maximum heating rate of 42°C min^{-1} ~~with its electrical heating system (described in Section 2.2.1) . In addition, the entire GC system is completely automated and the majority of its processes operate in parallel with direct CIMS sampling to allow for minimal interruptions in instrument sampling. The GC system is modularized, containing its own separate control system, enabling its use with other detectors.~~

2.2.2 ~~Operating Parameters~~

~~For the studies detailed in this paper, air is subsampled from the main instrument inlet and directed into the cryocooled 0.53 I.D. RTX-1701 megabore column (Restek) at a flow rate of 220 . Ambient air is diluted by a factor of 15 to 30, depending on the relative humidity of the sample, and the targeted compounds are collected over a 10-minute period on the column head at -20. As discussed in later sections, the choice of the dilution and trapping temperature is a compromise between adequately cryofocusing the maximum amount of analytes while avoiding the collection of water. After collection, a Teflon solenoid valve (SH360T042, NResearch) is switched allowing carrier gas to enter the column at a constant flow rate of 5 (Horiba ZS12, Fig. 1N). The compounds are separated using a programmable temperature~~) using a combination of CO_2 coolant and an electrical heating system that consists of a temperature ramping controller (Watlow F4 series)~~and several resistance~~ , heaters (~400 total watts~~,~~ ; KH series, Omega~~) adhered to the outside of each plate. The automated temperature program proceeded as follows: a 3 minute temperature ramp to 20(~13) , followed by a 3ramp to 50, followed by a 10increase to 120for a total temperature ramping time of 20 minutes. Following completion of the temperature program, the column is held at 120for an additional two minutes to remove remaining analytes~~; Fig. 2A) and three resistance temperature detectors (RTDs, F3102, Omega; Fig. 2B, numbered). Sample collection and elution are controlled using automated solenoid valves (NResearch) to direct gas to one of a number of vacuum outlets (Fig. 1F, H and Q). These processes occur in parallel with direct CIMS sampling to minimize interruptions in data collection.

2.2.2 ~~GC Cooling System~~

~~The GC assembly~~ The GC is cooled through the evaporation and expansion of liquid CO_2 ~~entering~~ which enters from the center of each plate ~~. The~~ and flows along eight radial grooves. An o-ring seal ~~contains~~ forces the CO_2 ~~and causes it to exit via ports machined into the plate~~ to exit through ports located near the radius of the column. ~~To achieve sufficient time resolution for the GC measurements (1 cycle per hour), the column must cool to the cryotrapping set point within a short time period regardless of ambient temperatures. However, we also wish to minimize the~~ The movement of the CO_2 ~~usage, reducing the maintenance required in the field.Thus~~ from the center to the outside of the plate establishes a temperature gradient in the same direction. Symmetry enables the entire column to remain at a similar temperature, in spite of this gradient. In contrast, a previous version of this GC assembly used during this instrument's first deployment allowed CO_2 to enter from a single point along the column diameter (See Supplement Fig. S1), resulting in large temperature gradients across the column and degradation of the chromatography (e.g. irregular peak shapes).

The CO_2 flow is controlled ~~into the GC plates using~~ by two solenoid valves (Series 9, Parker; Fig. 1S) connected to ~29 cm x 0.25 mm ID and ~35 cm x 0.15 mm I.D. PEEK restrictors. With both valves open, a total CO_2 flow rate of 25 slm (as gas) is admitted to cool the GC assembly ~~from 67~~to -20°C within the allotted 10 minute period. ~~To conserve~~ During trapping, only the solenoid valve connected to the 0.15 mm I.D. restrictor remains open to minimize CO_2 ~~while maintianing the trappingtemperature, only a single valve is opened (see below).~~

2.2.2 ~~Cyrotrap Temperature Control~~

~~During the collection of analytes on the head of the column, it is important that the temperature remains stable, as sizable fluctuations in temperature adversely affects the chromatography. To control~~ usage. Fine control over the GC temperature was accomplished by utilizing a PID control loop with the ~~trapping set point, we utilize the~~ heaters and the ~~resistance temperature detector (RTD , F3102, Omega)~~ RTD located on the ~~GC~~ column ring (Fig. 2, #2~~on diagram)in a PID control loop. In addition, during trapping we only use the solenoid valve connected to the 0.15 I.D. restrictor as this valve provides a flow that is adequate to maintain the GC temperature (~10).~~

). Additional efficiency was gained by insulating the GC assembly with Nomex™ felt and wrapping the felt with Kapton tape to prevent water vapor from diffusing to and condensing on the cold plates~~. The entire instrument was placed~~ , as well as placing the entire instrument in a temperature-controlled, weatherproofed enclosure ~~. This~~ (See Sect. 2.4). Altogether, this resulted in reproducible temperature profiles with minimal temperature gradients across the column (less than 2°C) during field operation (See Supplement Fig. ~~S1~~S2).

2.2.2 ~~Column Humidity Management~~Operating Parameters

~~Because compounds are trapped at sub-ambient temperatures, relative humidity inside the column can easily reach 100% during ambient sampling. This is problematic not only because co-trapped water and ice clog the column, but also because many species of interest are highly reactive and can readily hydrolyze (Koppmann and Wildt, 2008; Roukos et al., 2009; Lee et al., 2014; Teng et . We address this issue by diluting the ambient air with dry prior to cryotrapping to reduce the RH below the ice point at -20(1.3water vapor). This is illustrated in Fig. 7 during GC analysis of isoprene hydroxy nitrate (IHN)at high RH (~50%) with three different sampledilutions. When water is trapped during the lowest dilution (5x) , the column flow is observed to decrease over time (~~ To initiate sample collection, ambient air is subsampled from the main instrument inlet (1 slm; Fig. 1N) and diluted by a factor of 15 to 30 (Fig. ~~7A) , indicating the formation of an ice blockage. In addition, the isomer distribution of IHN is dramatically altered, as seen by the loss of 1, 2-IHN (first peak, Fig. 7D) and the corresponding formation of an isoprene diol, its hydrolysis product (Fig~~1M), depending on the relative humidity (RH) of the sample. ~~7G) . However, at the two higher dilutions (15x and 20x), the column flow remains relatively stable throughout the trapping period~~ The diluted air is pulled through the pre-cooled 0.53 mm I.D. RTX-1701 megabore column (Restek) by a flow-controlled pump (220 sccm; Fig. 1Q) and targeted compounds are cryofocused on the head of the column over a 10-minute period at −20°C (As discussed in later sections, the choice of the dilution and trapping temperature is a compromise between adequately cryofocusing the maximum amount of analytes while avoiding the collection of water). Following collection, a four-port Teflon solenoid valve (SH360T042,

NResearch) is switched, allowing N_2 carrier gas to enter the column at a constant flow rate of 5 sccm (Horiba Z512, Fig. 1P) and two 3-way valves (225T032, NResearch) are toggled to direct the column effluent either to the flow tube (Fig. 1F) or the ion source (Fig. ~~7B-C) —consistent with minimal ice formation—and the isomer distribution of IHN is preserved between the two runs (Fig. 7E-F). Some water is retained~~ 1H) of the mass spectrometer—in both configurations, the entire length of column is held under low pressure conditions (< 260 mbar at P_1 [Fig. 1]). Compounds are then separated on the column ~~even at these higher dilutions, but it was likely trapped downstream of the analytes, limiting its interactions with IHN~~using the following automated temperature program: a 3 minute temperature ramp to 20°C (~13°C min^{-1}), followed by a 3°C min^{-1} ramp to 50°C, followed by a 10°C min^{-1} increase to 120°C for a total temperature ramping time of 20 minutes. Following completion of the temperature program, the column is baked at 120°C for an additional two minutes to remove remaining analytes.

~~During sampling, the operating dilution is chosen based on ambient relative humidity measurements. The effectiveness of the dilution is verified by monitoring the water signal (*m/z* 104) which should quickly fall to background levels during elution when minimal water is retained (as seen in Fig. 7E-F). For the data shown here, we diluted the samples by a factor of 15 during laboratory studies and by a factor of 20 to 30 in the field studies. The high sample dilution demands a very high sensitivity to be able to adequately quantify many of the compounds of interest, which is achievable on this instrument due to the chemical ionization technique used (discussed below). Even so, ambient mixing ratios of several of the targeted analytes described here pushed the detection limits of the instrumentation, leading to increased uncertainty, especially when deconvolution is required prior to integration of chromatographic peaks~~As mentioned above, connecting the GC outlet directly to the mass spectrometer allows the entire column to remain at sub-ambient pressures during elution (180 mbar [into ion source] or 260 mbar [into flow tube] at P_1). This allows for low pressure chromatography which provides several advantages over conventional GC methods (Sapozhnikova and Lehotay, 2015). For instance, low pressures support the use of short, large bore columns without significant loss in peak separation. This becomes especially advantageous during cryotrapping as this larger I.D. column allows for a greater volume of analytes to be sampled, beneficially impacting the instrument signal to noise. In addition, low pressure conditions also allow for faster analysis times at lower elution temperatures (Table 2). The decrease in analysis time provides this instrument with sufficient time resolution to capture diurnal variations in measured species (one GC cycle per hour), while lower elution temperatures allow this method to be applied for analysis of thermally-labile species, as discussed in later sections.

2.3 GC/CIMS Interface

Following the column, a 100 - 200 sccm N_2 pickup flow (Fig. 1P~~R~~) is added to the 5 sccm column flow to decrease the residence time in the PFA tubing connecting the GC to the mass spectrometer. ~~A Teflon solenoid valve (225-T032, NResearch) then directs~~ As mentioned above, solenoid valves direct the analytes into the CIMS instrument, either through the flow tube (similar to direct CIMS sampling) or directly into the ion source. Unlike direct ambient sampling, it is possible to pass the GC flow through the ion source as oxygen is not retained on the column during trapping. ~~Oxygen~~ In other cases, oxygen that enters the ion source is ionized (O_2^-) and causes interferences at many *m/z*.

Figure 3 shows a comparison of two chromatograms obtained by these different analysis modes. Introduction via the flow tube (hereafter "FT" mode; Fig. 3, blue) allows for interaction of analytes with only CF_3O^- (and CF_3O^- derived) reagent ions, providing a straightforward comparison to the direct CIMS samples as well as quantification of the GC transmission of analytes. However, ~~as~~ due to tubing and gas flow configurations, the pressure within the column is greater under FT mode ~~, due to tubing and gas flow configurations,~~ than when directed to the ion source region~~(ΔP =~30)~~. Therefore, compounds tend to elute later and at higher temperatures, making introduction into the ion source (hereafter "~~high sensitivity~~IS" ~~or "HS"~~ mode; Fig. 3, black) the preferred analysis mode when separating more thermally-labile compounds in the current instrument configuration.

~~HS~~ IS mode also creates an enhancement in instrument sensitivity due to the increase in analyte-reagent ion ~~interactions time~~ interaction time (as the analytes can interact with CF_3O^- as soon as it forms, rather than mixing with the ions downstream) and overall drier conditions. The enhancement in sensitivity is quantified through comparison to the direct CIMS measurements, which show a multiplicative enhancement factor that is non-linearly dependent on the gas flow entering the ion source. For the instrument flows used in this work, the ion source enhancement was determined to be 9.8 ± 0.8~~as calculated by methods described in the Supplement~~, which was determined by comparing peak areas produced when operating in FT vs. IS mode (see Supplement). Additional discrepancies between ~~HS~~ IS mode and direct CIMS measurements may result from analyte interactions with the metal walls of the ionizer. In addition, ~~drect~~ direct electron attachment to analytes (often followed by fragmentation) can ~~also~~ occur in the ion source, though differences between the two GC modes are typically explained within error by the enhancement factor. These fragment ions, however, provide additional structural information. For example, different fragment ions may arise from the fragmentation of a primary nitrate versus a tertiary nitrate (see Supplement Fig. ~~S5~~S6).

2.4 Instrument Housing and Supporting Equipment

The ~~GC-HR-ToF-CIMS~~ GC-HRToF-CIMS was placed in a weatherproofed, temperature-controlled enclosure during field sampling to protect the instrument electronics and allow for efficient GC cooling. In total, the instrument enclosure measured 1.1 m x 1.7 m x 0.9 m (W x H x D), taking up a footprint of approximately 1 m^2 (Fig. 4). Weatherproofing was created by using Thermolite™ insulated paneling (Laminators, Inc.) that covered the aluminum instrument rack (80/20, Inc.) and was aided by weather stripping placed between the panels and the rack. For temperature control, two Ice Qube HVAC units (IQ1700B and IQ2700B, Blade series, cooling power = 498 and 791 W, respectively) were attached to one side of the enclosure to remove the heat produced by the ~~electronics~~instrument. During the range of ambient temperatures experienced during these studies (8.7°C - 37.8°C), the internal temperature of the enclosure remained at or below 30°C under normal operating conditions.

Along with the instrument enclosure, two scroll pumps (nXDS 20i, Edwards) were located separately from the instrument in their own weather-resistant container and were used to back the three turbomolecular pumps (Twistorr 304 FS, Agilent) and the flow tube attached to the mass spectrometer. A weather station was also co-located with the instrument during the two field studies. It included sensors for air temperature, RH, solar irradiance, wind direction, wind speed and atmospheric pressure.

2.5 Instrument Calibration~~and Instrumental Backgrounds~~

~~Calibrations were performed~~ Instrument sensitivity was assessed in the laboratory ~~to measure the sensitivity of the instrument to a number of commercially available or synthesized standards~~ using a select number of commercially-available compounds. These experiments were performed using authentic standards for hydrogen cyanide (HCN), sulfur dioxide (SO_2), hydroxyacetone (HAc) and glycolaldehyde (GLYC). The absolute concentrations of these compounds were quantitatively determined by Fourier Transform Infrared Spectroscopy (FTIR) before ~~being directed to the HR-ToF-CIMS~~ undergoing dilution and CIMS sampling (see Supplement for additional details regarding calibration procedures). However, ~~as standards are not available for many species mentioned in this work, these calibration experiments were simultaneously performed on the c-ToF-CIMS~~ because many compounds of interest are not commercially available and difficult to synthesize and purify, these four standard gases were simultaneously sampled on the cToF-CIMS (which uses the same chemical ionization technique) to directly compare the compound sensitivities between these two instruments. On average, the ~~c-ToF-CIMS was~~ cToF-CIMS was observed to be 1.4 times more sensitive than the ~~HR-ToF-CIMS for the species~~ HRToF-CIMS for the four gases tested. We used this factor to proxy sensitivities for other compounds that ~~were~~ had been previously determined for the ~~c-ToF-CIMS~~ cToF-CIMS through calibrations or estimated using ion-molecule collision rates as described in Paulot et al. (2009a), Garden et al. (2009),~~and Crounse et al. (2011)~~Crounse et al. (2011), Schwantes et al. (2015) and Teng et al. (2017).

~~We~~ For the chromatography, preliminary peak assignment was based on previous laboratory studies that were performed on the test bed this field deployable system was based upon (Bates et al., 2014; Nguyen et al., 2014; Lee et al., 2014; Praske et al., 2015; Teng , as detailed in the supplementary material of Teng et al. (2017). Many of these studies used synthesized standards which had been developed for compounds such as ISOPOOH (Rivera-Rios et al., 2014; St Clair et al., 2016), IEPOX (Bates et al., 2014), and IHN (Teng et al., 2017), while others oxidized parent hydrocarbons in a chamber and determined elution orders based on assumptions regarding physical chemistry of reaction intermediates, as in Teng et al. (2015). However, due to differences in the analytical set ups, verification of these assignments and their retention times have also been made for a number of targeted compounds through laboratory experiments described in more detail in the Supplement. The results from one of these studies is shown in Fig. 5 which compares the retention times for alkyl hydroxy nitrates derived from propene (propene HN) and three structural isomers of butene (butene HN) created in the chamber bag with chromatograms gathered in the field.

2.6 Instrumental Backgrounds

In the field, we use two methods to quantify the instrumental background signals caused by interfering ions present at targeted analyte masses. In the first method, the instrument undergoes a "dry zero" where the CIMS flow tube is overfilled with dry nitrogen so that no ambient air is sampled during this time. In this method, the humidity within the instrument changes substantially compared with ambient measurements. The second method, an "ambient zero," passes air from the main inlet through a zeroing assembly, which includes a sodium bicarbonate denuder and a scrubber filled with Pd-coated alumina pellets. The scrubbed air then enters the flow tube after instrument flows are adjusted to mimic near-ambient humidity levels~~capturing an "ambient zero" which obtains background signals that are adjusted for the water dependent sensitivity of the compounds~~.

During field sampling, both zeroing methods occur twice each hour during a six minute period that separates the CIMS and GC-CIMS measurements. The dry zero is most similar to the GC measurements and can assess the health of the instrument over the course of a campaign as these backgrounds should not change over time, while the ambient zero captures background signals that are adjusted for the water dependent sensitivity of the compounds measured during direct CIMS sampling.

2.7 Data Processing

Data from the mass spectrometer is collected using data acquisition software provided by Tofwerk (TofDaq). This data is later combined with the instrument component read-backs collected using single board computers (Diamond Systems) and converted into a MATLAB file using in-house developed scripts. To account for fluctuations in the reagent ion, observed mass signals are normalized to the signal associated with the isotope of the reagent ion ($^{13}CF_3O^-$, *m/z* 86) and its cluster with water ($[H_2O \cdot ^{13}CF_3O]^-$, *m/z* 104). The analyte signal is defined as this normalized absolute number of counts (nmcts) recorded at *m/z*.

2.7.1 ~~GC Peak Integration & Identification~~

~~To integrate the chromatographypeaks~~For the chromatography, we modified an open-source MATLAB peakfit function (O'Haver, 2017). Peak areas are determined for desired masses by subtracting a baseline and fitting the chromatograms with the appropriate peak shapes as shown in Fig. 6 for ISOPOOH and its isobaric oxidation product, isoprene epoxydiol (IEPOX, *m/z* 203; St Clair et al., 2016). ~~For many compounds, preliminary peak assignment is based on previous laboratory studies that used a combination of chamber experiments and synthesized standards in order to determine elution order (Bates et al., 2014; Nguyen et al., 2014; . However, due to differences in the analytical set ups, verification of these assignments and their retention times have also been made for a number of targeted compounds through laboratory experiments described in more detail in the Supplement. The results from one of these studies is shown in Fig. 5 which compares the retention times for alkyl hydroxy nitrates derived from propene (propene HN) and three structural isomers of butene (butene HN) created in the chamber bag with chromatograms gathered in the field.~~ These areas are then scaled by the relative CIMS sensitives of each isomer (see Supplement), ion source enhancement (if applicable) and a transmission factor. The resulting values are then normalized by volume of air collected on the column in order to obtain the corresponding ambient mixing ratios.

3 Discussion

3.1 ~~Analyte Transmission~~

~~The largest technical challenge in developing a field-deployable GC was the design of a sampling system capable of collecting and separating compounds with minimal analyte degradation. This is critical when considering that many targeted compounds are highly susceptible to irreversible losses or chemical conversion upon contact with instrument surfaces (Grossenbacher et al., 2001, 2004 . We addressed this issue through the utilization of low pressure gas chromatography which holds several known advantages~~

~~over traditional GC techniques (Sapozhnikova and Lehotay, 2015), such as creating conditions which allows compounds to elute both at lower temperatures and shorter retention times (Table 2). Lower elution temperatures better preserves thermally labile species and allows for the elution of lower volatility compounds within reasonable time scales. In addition, all wetted instrument surfaces (with the exception of the ion source) are composed of metal-free, inert materials such as PFA/PTFE Teflon, PEEK and column-phase materials. This reduces unwanted side reactions on surfaces, most notably the metal-catalyzed decomposition of compounds such as hydroxyperoxides and organic nitrates (Rivera-Rios et al., 2014; Mills et al., 2016).~~

~~Despite measures taken to improve analyte transmission , losses are still observed for some species, highlighting the importance of accurately quantifying analyte transmission through the GC column. Yet, for traditional GC-based measurements, transmission typically remains unknown which can be detrimental when there is a lack of available standards and GC response factors must be based on another compound that has a similar chemical make-up but might interact differently with the column phase. However, as previously stated, the combination of our LP-GC system with the high sensitivity of the CIMS provides two sampling modes (direct CIMS and GC-CIMS) that automatically alternate between each other in half hour increments. This allows us to compare individual chromatograms to CIMS measurements taken immediately before or during cyrotrapping in order to assess GC transmission efficiency under field conditions, without the need for external standards.~~

3.1 Sample Collection

Due to their lower volatility and highly reactive nature, the accuracy and precision of ambient OVOC measurements can be greatly limited by the sample collection method. GC sampling techniques ~~typically~~ often used in atmospheric chemistry collect gas-phase compounds on solid adsorbents (e.g., TENAX®) that have been developed to combat some of the aforementioned issues ~~(such as preventing the co-collection of water by allowing for higher trapping temperatures; Demeestere et al., 2007; Ras et al., 2009~~ (such as preventing the co-collection of water by trapping analytes at higher temperatures; Demeestere et al., 2007; Ras et al., 2009) . However, the use of OVOC-specific adsorbents have shown problems with the formation of artifacts caused by the reaction of ozone, NO_2, and other compounds trapped on the sorbent surfaces ~~(Klenø et al., 2002; Noziére et al., 2015)~~ (Klenø et al., 2002; Noziére et and can lead to significant analyte loss, especially for polar and/or labile compounds such as tertiary organic nitrates (as suggested in Mills et al. (2016)), organic hydroperoxides and other highly-functionalized compounds. In addition, high ~~humidities~~ humidity can result in increased water uptake into the sorbent materials during ambient sampling (Ras et al., 2009) requiring additional water removal steps ~~prior to collection such as~~ such as the utilization of chemical scrubbers which can react with compounds of interest (Koppmann and Wildt, 2008; Roukos et al., 2009), or trapping at above optimal temperatures which may result in the loss of more volatile compounds (Vairavamurthy et al., 1992; Roukos et al., 2009)~~or through the utilization of chemical scrubbers which can react with intended compounds (Koppmann and Wildt, 2008; Roukos et al., 2009)~~. These issues motivate our use of dilution and cryotrapping on the column to transmit a wider range of analytes through our system.

Trapping efficiency was assessed by cryofocusing a mixture of propene HN and IHN for varying amounts of time (and thus, sample volumes) in order to test for linearity of the cryotrap. Results provided in the Supplement show that the GC peak area was linearly proportional to the volumes sampled, suggesting that compounds are preserved on the column during trapping (Fig. S2). Analyte breakthrough has been monitored in the laboratory by directing the GC flow into the CIMS during trapping

to monitor analyte signals. For most compounds of interest (>C_3), there has been no evidence of breakthrough under typical trapping conditions (-20°C) when this procedure has been performed for a trapping period up to 12 minutes, though we note chromatography can be significantly degraded prior to breakthrough, as the analytes spread to larger bands on the column.

Experiments were performed to determine if oxidants such as ozone and NO_2 can interfere with targeted compounds trapped on the column. We oxidized isoprene under high NO_x conditions to produce IHN, as its isomer-specific reaction rate with ozone would make it apparent whether certain isomers were affected more than others. When we attempted to co-trap 100 ppb of NO_2 and 200 ppb of ozone, our results show no evidence that either oxidant affects the IHN trapped on the column, even at lower dilutions (15x) and lower trapping temperatures (-50°C).

3.1.1 Trapping Temperature and Column Humidity

Our trapping temperature (-20°C) was optimized on the original ~~test bed~~ laboratory prototype and was chosen as ~~the best compromise for its ability to capture compounds with a range of volatilities at the highest possible temperature and , thereby, the lowest dilution required to avoid trapping water~~ a compromise between analyte retention and avoidance of water retention. We find that trapping above -20°C results in degradation of the chromatography for several species, examples of which can be seen in the Supplement (Fig. ~~S3~~S4). However, ~~even~~ at -20°C some higher volatility compounds are ~~still~~ not trapped efficiently, resulting in irregular peak shapes (Fig. ~~S4~~S5). Further optimization of trapping conditions is needed in order to improve the chromatography for these species and further reduce the likelihood of water ~~co-trapping~~retention.

Because compounds are trapped at sub-ambient temperatures, unless special care it taken, relative humidity inside the column can easily reach 100% during ambient sampling. This is problematic because co-trapped water and ice clog the column, and many species of interest are highly soluble and reactive and readily hydrolyze (Koppmann and Wildt, 2008; Roukos et al., 2009; Lee et . We address this issue by diluting the ambient air with dry N_2 prior to cryotrapping to reduce the RH below the ice point at -20°C (1.3 hPa water vapor). This is illustrated in Fig. 7 during GC analysis of isoprene hydroxy nitrate (IHN) at high RH (~50%) with three different sample dilutions. When water is trapped during the lowest dilution (5x), the column flow is observed to decrease over time (Fig. 7A), indicating the formation of an ice blockage. In addition, the isomer distribution of IHN is dramatically altered, as seen by the loss of 1,2-IHN (first peak, Fig. 7D) and the corresponding formation of an isoprene diol, its hydrolysis product (Fig. 7G). However, at the two higher dilutions (15x and 20x), the column flow remains stable throughout the trapping period (Fig. 7B-C)—consistent with minimal ice formation—and the isomer distribution of IHN is preserved between the two runs (Fig. 7E-F). Though some water is retained on the column even at these higher dilutions, it was likely trapped downstream of the analytes, limiting its interactions with IHN.

During sampling, the operating dilution is chosen based on ambient RH measurements. The effectiveness of the dilution is verified by monitoring the water signal ($[H_2O \cdot {}^{13}CF_3O]^-$, *m/z* 104) which should quickly fall to background levels during elution when minimal water is retained (as seen in Fig. 7E-F). For the data shown here, we diluted the samples by a factor of 15 during laboratory studies and by a factor of 20 to 30 in the field studies. The high sample dilution demands a very high sensitivity to be able to adequately quantify many of the compounds of interest, which is achievable on this instrument when operating in IS mode (discussed in Sect. 2.3). Even so, ambient mixing ratios of several of the targeted analytes described here

pushed the detection limits of the instrumentation, leading to increased uncertainty, especially when deconvolution is required prior to integration of chromatographic peaks.

3.2 Analyte Transmission

In addition to rapid hydrolysis, many targeted OVOCs are highly susceptible to irreversible losses or chemical conversion upon contact with surfaces (Grossenbacher et al., 2001, 2004; Giacopelli et al., 2005; Rivera-Rios et al., 2014; Xiong et al., 2015; Mills et al., 20 . We addressed this issue through the utilization of metal-free low pressure gas chromatography. As mentioned above, this technique holds several known advantages over traditional GC methods, including elution at lower temperatures (Table 2), that make it possible to better preserve thermally labile species. In addition, all wetted instrument surfaces (with the exception of the ion source) are composed of inert materials such as PFA/PTFE Teflon, PEEK and column-phase materials. This reduces unwanted reactions on surfaces, most notably the metal-catalyzed decomposition of compounds such as hydroxyperoxides and organic nitrates (Rivera-Rios et al., 2014; Mills et al., 2016).

Despite measures taken to improve analyte transmission, losses are still observed for some species such as hydroperoxides and epoxides. This highlights the importance of accurately quantifying analyte transmission through the GC column. Yet, for traditional GC-based measurements, transmission typically remains unknown which can be detrimental when there is a lack of available standards and GC response factors must be based on another compound that has a similar chemical make-up but may interact differently with the column phase. However, the combination of our LP-GC system with the high sensitivity of the CIMS provides two sampling modes (direct CIMS and GC-CIMS) that automatically alternate between each other in half hour increments. This allows us to compare individual chromatograms to CIMS measurements taken simultaneously with cryotrapping in order to assess GC transmission efficiency under field conditions, without the need for external standards. This is done by comparing mixing ratios calculated from direct CIMS sampling measurements and the sum of the entire chromatogram signal (normalized by the amount of air trapped), which is best done when concentrations are high, and thus, measurement error is minimized. Using this method, we assess the transmission efficiency of IHN, which has been shown to have 100% transmission through a similar system (Lee et al., 2014). In the field, the percent difference of IHN mixing ratios calculated from these two measurement modes was typically less than 5%. We note that transmission less than unity can be the result of incomplete transmission of a single isomer (rather than the sum of all isomers). An example of this is in the case of ISOPOOH and IEPOX—IEPOX is transmitted more poorly through this column than ISOPOOH (Bates et al., 2014). In these cases, we use laboratory experiments to monitor discrepancies between mixing ratios obtained from direct CIMS sampling and GC-CIMS analysis and observe how these discrepancies change as we alter the isomer distribution (such as through additional oxidation of ISOPOOH). Using this method, we determine that ISOPOOH transmission is nearly 100%, while IEPOX has a transmission of about 67%.

4 Field Performance and Ambient Air Measurements

The ~~GC-HR-ToF-CIMS~~ GC-HRToF-CIMS has participated in two field studies that served as a test for this analytical method. Its first deployment occurred as part of the Program for Research on Oxidants, Photochemistry, Emissions and Transport (PROPHET) campaign ~~in summer~~ that occurred between 1 - 31 July, 2016, where it was placed on the top of a 30 m research tower surrounded by the dense forests of rural, northern Michigan. The following summer, the instrument underwent a second deployment at the California Institute of Technology (Caltech) campus in Pasadena, CA~~and sampled~~ , where measurements were taken from the roof of the 44 m tall Millikan Library ~~.~~ between 15 July and 17 August, 2017. In contrast to PROPHET, Pasadena is typically characterized as a high-NO_x, urban environment due to its proximity to Los Angeles~~. However,~~ , though biogenic emissions have also been known to influence the area (Arey et al., 1995; Pollack et al., 2013)~~, due to local urban flora and the presence of the San Gabriel Mountains to the north.~~

. During both deployments, the instrument provided a near continuous measure of OVOC concentrations, ~~though we experienced occasional interruptions~~ either through direct sampling or GC analysis. Interruptions in the GC measurements ~~at both locations~~ were primarily due to required maintenance of the cooling system ~~. However, instrument upgrades performed prior to the Caltech study were able to greatly reduce GC downtime and significantly improved the chromatography, despite other operating conditions remaining mostly unchanged.~~ (e.g. changing CO_2 tanks). When the GC was operational, data was captured during 1 h cycles in which the first half was dedicated to direct CIMS measurements and the latter half measured analytes after chromatographic separation, with the collection of ambient and dry zeros interlaced between operational modes. This sampling routine is shown in Fig. 8 for a single mass (*m/z* 232) collected during the 2017 Caltech field study.

~~The data sets described here focus on the daytime isoprene degradation products such as IHN, ISOPOOH, IEPOX and HPALD. These species are chosen because they are unique to the isoprene oxidation pathways, allowing for a more complete analysis for the atmospheric production and fate of each isomer. At PROPHET, products from the reaction pathway (ISOPOOH and IEPOX) were the most abundant among the discussed species, reaching an average maximum of ~200 pptv during a three day period (Fig. 9A). Because ISOPOOH and IEPOXare mass analogues, most~~ At PROPHET, the low NO_x environment (Millet et al., 2018) provided ideal conditions for measuring several organic peroxides, such as ISOPOOH. However, because ISOPOOH and its oxidation product, IEPOX, are isobaric, other analytical techniques are either unable to separate these two species or rely on the relative abundances of fragment ions to determine the relative contribution of each to the observed signal (Paulot et al., 2009b). With the GC-CIMS, ~~however, we are~~ we were able to physically separate the ~~isomer~~ isomers prior to quantification (Fig. 6)~~. As seen in~~ , allowing real-time information regarding the distribution of these two species (Fig. 9~~,~~). As such, we observed that IEPOX comprised about half of the total daytime signal (07:00 - 22:00 local time~~) with an average *trans:cis*~~ ; Fig. 9E), a fraction that is typically estimated through models when assessing IEPOX aerosol uptake (as in Budisulistiorini et al. (2017)). In addition, we are also able to differentiate the isomers that make up ISOPOOH and IEPOX, which can serve to highlight the isomer-specific chemistry of these compounds. A prime example is the observed daytime ratio of ~~1.2. For the ISOPOOH isomers , an average daytime~~ 1,2-ISOPOOH to 4,3-ISOPOOH~~ratio of~~ . This ratio (~7.6~~was observed. This ISOPOOH isomer ratio is much~~) is higher than expected when accounting only for

the isomer-specific bimolecular reaction rates of the isoprene peroxy radicals (Wennberg et al., 2018). ~~The higher ratio is consistent with a large sink~~ Thus, these measurements allow us to conclude that there was competitive RO_2 isomerization of the 4-OH ~~isomer via isomerization (Peeters et al., 2009; Crounse et al., 2011; Teng et al., 2017). The importance of such unimolecular chemistry is further supported by observations of known isomerization products (e.g. HPALDs;~~ isoprene peroxy radicals (Peeters et al., 2009; Crounse et al., 2011; Teng et al., 2017) during the course of this campaign.

Other multifunctional organic peroxides were also observed during this campaign, such as those seen at *m/z* 201 (Fig. 10)~~found throughout the course of the campaign.~~

~~IHN was also observed~~ . Though the CIMS signal at *m/z* 201 has previously been assigned to the HPALDs (Crounse et al., 2011) , a product of isoprene RO_2 isomerization, laboratory GC studies have determined that this signal is actually composed of several compounds (Teng et al., 2017). This is consistent with field chromatograms obtained at PROPHET, ~~though in much lesser amounts than ISOPOOH or IEPOX. Only two isomers could be identified in~~ which show up to five individual peaks at this mass-to-charge ratio. Using the peak assignment discussed in Teng et al. (2017), we assign latter two peaks in Fig. 10 as the 1-HPALD (purple) and 4-HPALD (grey), which together compose ~38% of the total GC peak area. The second peak (green) is likely the same unidentified early eluting peak seen in the ~~GC data collected during this experiment: 1,2-IHN and 4, 3-IHN with an average daytime ratio of ~2.6. We compare these IHN observations from PROPHET to measurements from the Caltech site to assess differences in~~ Teng et al. (2017) study (which also results from isoprene RO_2 ~~chemistry between the two sites. Similar to PROPHET,~~ isomerization). The two other peaks (red and orange) are unidentified and may result from different chemistry.

The GC-HRToF-CIMS has also demonstrated its ability to measure individual isomers of organic nitrates during its two deployments, as showcased by our IHN measurements. The two dominant isomers of IHN (1,2-IHN and 4,3-IHN~~were the first and second most abundant isomers of this compound observed at the Caltech site, respectively, though in this study~~) were observed at both PROPHET (with an average daytime ratio of ~2.6) and at Caltech (with an average daytime ratio of ~1.4). At Caltech, other IHN isomers were also ~~observed~~ quantified (Fig. 11), as well as an unidentified component that has been previously observed during laboratory studies (Teng et al., 2017). ~~During the Caltech study, the average daytime 1,2-IHN to 4,3-IHN ratio was ~1.4, roughly half that observed in Michigan; we suspect this difference reflects the shorter bimolecular lifetime of the ISOPOO in Pasadena (<10 s) which would limit the impact of the~~ Comparison of isomer ratios obtained from each site were used to assess the isoprene RO_2 chemistry and are consistent with competitive unimolecular reaction pathways ~~in this environment~~at PROPHET. Interestingly, the IHN ratio at PROPHET differed significantly from the corresponding ISOPOOH ratio despite the similar formation pathways of each pair of oxidation products. We suspect this reflects differences in their loss pathways ~~and hypothesize that this lower isomer ratio for the pair of nitrates may result from hydrolysis of the 1,2-IHN isomer (see also Wolfe et al., 2015; Fisher et al., 2016)~~which will be discussed further in an upcoming manuscript.

In addition to ~~daytime isoprene oxidation products~~IHN, the GC-CIMS ~~captured a wide variety of additional compounds, some of which can be identified based on previous laboratory studies~~also observed other large ($>C_3$) organic nitrates. For example, evidence of isoprene + NO_3 chemistry ~~at Caltech~~ during the Caltech experiment is indicated by the nighttime ~~abundance of~~ increase in the signal at *m/z* 230, which is assigned to the isoprene carbonyl nitrates ~~(ICN)~~(ICN; Schwantes et al., 2015).

Though only two isomers were observed during this study (Fig. 12), the distribution of these species (assigned as 4,1-ICN and 1,4-ICN) matches results from Schwantes et al. (2015) and ~~is consistent with their finding~~ may confirm the hypothesis that C1 addition of the NO_3 moiety is favored (Suh et al., 2001). As the distribution of the isoprene nitroxy peroxy radical (INO_2) is less constrained than the OH derived RO_2 counterpart, further observations of ambient ICN isomers with the GC-CIMS may lead to improved understanding of the impact of nighttime NO_3 chemistry ~~and provide additional information on the relative importance of ICN degradation pathways (e. g. photooxidation) and thus its effect on concentrations at sunrise (Müller et al., 2014; Schwantes et al., 2015).~~

~~Through the combination of chromatographic separation, high mass resolution and low-fragmentation mass spectrometry the GC-HR-ToF-CIMS will serve as a powerful tool, helping to untangle the atmospheric chemistry of many OVOCs. This is illustrated in observations of several presently unidentified compounds measured during the field studies, such as *m/z* 236 (MW 151), a~~ (Schwantes et al., 2015). In addition, a suspected nitrogen-containing compound was observed at Caltech ~~(~~at *m/z* 236 (MW 151; Fig. 13). Data obtained from direct CIMS sampling showed at least two local maxima, one occurring before sunrise and the other shortly after noon. With the addition of the GC, we find that two distinct species contribute to this instrument signal with varying contributions over the course of a day. That is, the first compound (eluting at 9.8 minutes) is responsible for the majority of the signal in the early afternoon, possibly indicative of production via photooxidation, whereas the second compound (eluting at 13.8 minutes) is most abundant between sunset and sunrise, possibly due to production from nighttime NO_3 chemistry, high photolability, a short lifetime against the OH radical, or some combination thereof.

5 Summary

We have developed an automated GC-CIMS system that ~~can capture~~ captures diurnal changes in the isomer distributions of a wide range of important OVOCs. This novel method addresses common issues typically associated with ambient GC measurements, allowing observations of compounds that have previously proven difficult to measure. We use a combination of sample dilution and temperature control to avoid the adverse effects caused by high column humidity (e.g. hydrolysis of reactive compounds). This, along with the use of LP-GC methodology, cryotrapping directly on the column and the creation of a ~~mostly~~ near metal-free GC design, reduces analyte degradation upon contact with the instrument surfaces.

Analytical performance was assessed through a combination of laboratory studies and field campaigns. ~~GC-HR-ToF-CIMS~~ GC-HRToF-CIMS has demonstrated its ability to provide continuous, reproducible measurements, effectively trapping tested species with no observable breakthrough and providing a quantitative measurement of GC transmission by utilizing its two sampling modes (direct CIMS and GC-CIMS sampling). Though additional optimization is needed to expand the number of species that can be measured using this technique, its participation in future field studies will help enable the elucidation of the chemical mechanisms of a number of species, such as the isoprene oxidation products, by providing information that will help assess how compound structure impacts its formation or atmospheric fate and thereby its effect on the global atmosphere.

Data availability. Data from the 2017 Caltech study is available at http://dx.doi.org/10.22002/D1.971. Additional data is available upon request to the corresponding authors.

Competing interests. The authors declare they have no conflict of interest

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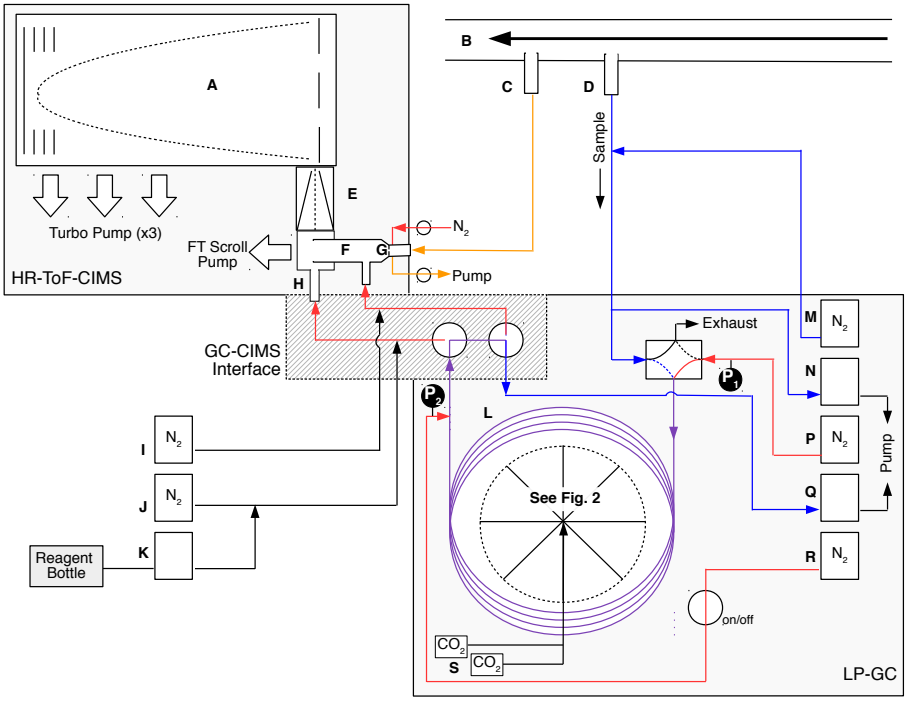


Figure 1. A simplified instrument schematic of ~~GC-HR-ToF-CIMS~~ GC-HRToF-CIMS showing the ~~HR-ToF-CIMS~~HRToF-CIMS, the LP-GC and the interface between the two systems. ~~Main~~ The main components are: (A) time-of-flight mass spectrometer; (B) teflon coated glass inlet; (C) CIMS sampling port; (D) GC-CIMS sampling port; (E) hexapole ion guide; (F) teflon coated glass flow tube; (G) critical orifice; (H) 210-Po ionization source; (~~H~~I) CIMS dilution flow; (~~I~~J) CIMS ion source dilution flow; (~~J~~K) ~~CF3OOCF3~~ CF_3OOCF_3 reagent flow; (~~K~~L) GC column and cryotrap; (~~L~~M) GC dilution flow; (~~M~~N) GC sample intake pump; (~~N~~P) GC column flow; (~~O~~Q) GC bypass pump; (~~P~~R) GC ~~N2~~ N_2 pickup flow; (S) CO_2 solenoid valves. Pressure gauges at the head and tail of the column are denoted by P_1 and P_2, respectively. Select instrument flow states are differentiated by the various line colors, where orange represents the flow path during direct CIMS sampling, blue represents the path GC trapping and red represents the path during GC elution. Analytical lines that are used during both GC trapping and eluting are purple. Diagram is not to scale.

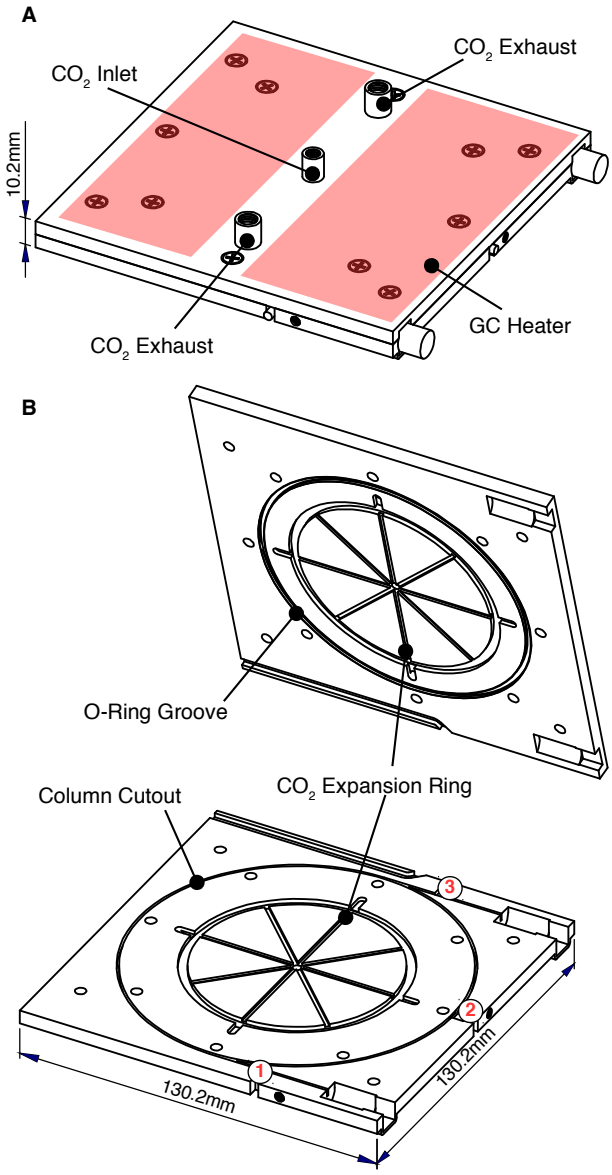


Figure 2. Schematic of the GC cyrotrap and heating unit. Column sits in a groove machined into one plate, providing good thermal contact. CO_2 enters from the center of both plates ~~(on the opposite side)~~ and expands in the eight radial spokes before exiting through four exhaust ports~~(opposite side)~~. Heaters are adhered to the outside of the GC assembly; two of these heaters are shown above in red. The temperature is measured at three locations near the column: (1) near the inlet of the column, (2) on the column ring, and (3) near the outlet of the column.

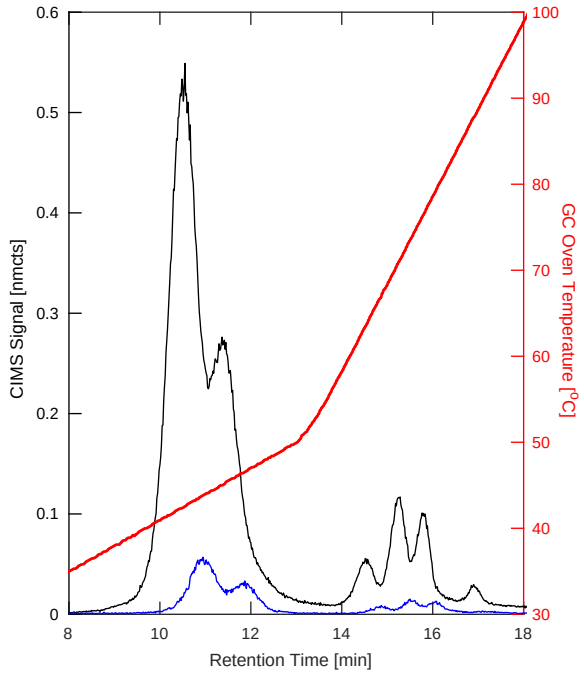


Figure 3. Comparison of chromatograms of the IHN isomers obtained from the two different GC analysis modes in which the same amount of analyte is collected on the column, but is directed into either the ion source (black) or flow tube (blue). GCs that are directed into the ion source result in approximately a 10-fold signal increase compared to flow tube GC analysis. In addition, compounds analyzed ~~by~~ via the ion source typically elute at lower temperatures compared to flow tube analysis, an advantage for sampling fragile, multifunctional compounds.

~~Comparison of GC column flow (A-C) and three chromatograms (D-F) of IHN (*m/z* 232, black) and water (*m/z* 104, blue) at three different dilutions from a high RH chamber experiment. The beginning of a chromatogram is marked when the temperature program initiates. When water is trapped during the lowest dilution (5x), column flow decreases (indicating an ice blockage) and the isomer distribution of IHN is dramatically altered as noted by a loss in the first peak (1,2-IHN) and increase in the last peak (*E* 1,4-IHN). These peak changes are marked by arrows and described relative to 4,3-IHN (*). The 1,2-isoprene diol (*m/z* 187, G), an expected product of 1,2-IHN hydrolysis, is also observed in this scenario. However, when the sample is sufficiently diluted prior to trapping, the water signal quickly falls to background levels and isomer distribution is preserved with minimal diol formation. Column flow also remains relatively stable throughout the trapping period when minimal water is maintained.~~

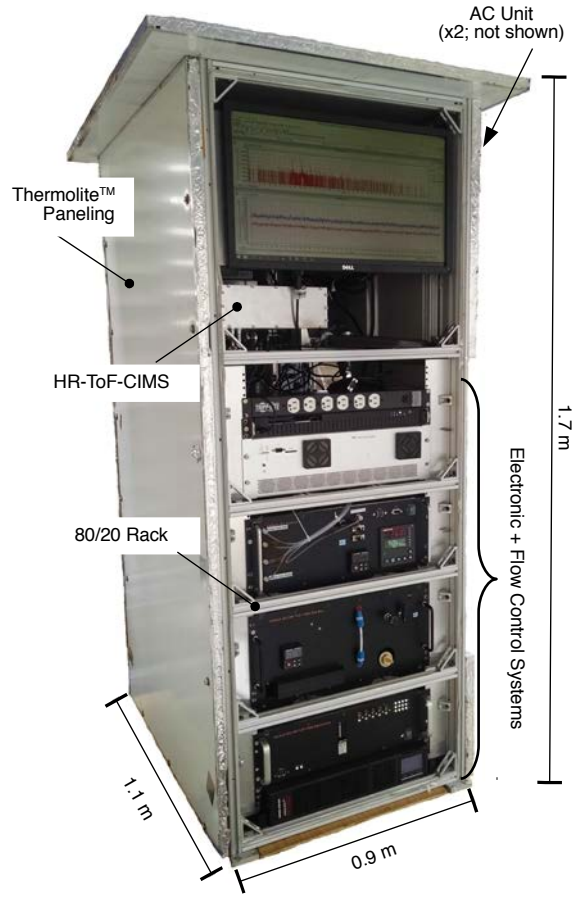


Figure 4. The weatherproofed and temperature-controlled enclosure in which the instrument resides during field sampling. The front panel of the enclosure is removed in this photo.

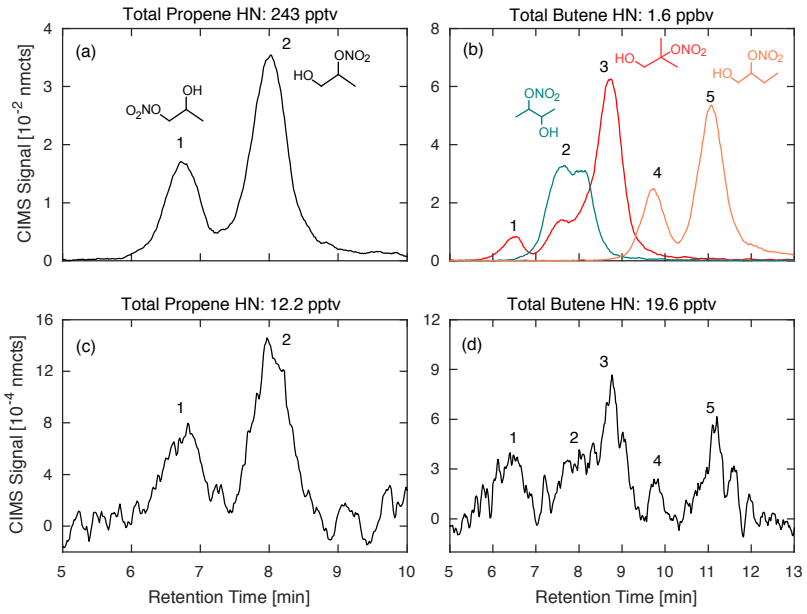


Figure 5. Comparison of hydroxy nitrates formed during chamber experiments (A-B) from propene (left) and three structural isomers of butene (right; 1-butene (orange), 2-butene (teal), and 2-methyl-propene (red); dominant hydroxynitrate structures shown) with the corresponding *m/z* signal observed during a 2017 field study in Pasadena, CA (C-D). Data shown is a 10 second average.

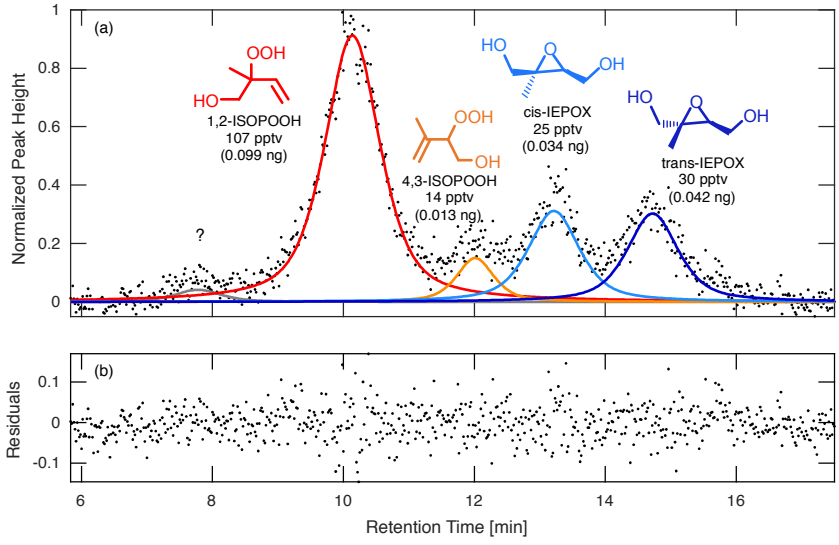


Figure 6. (A) Chromatogram, peak fits and (B) fit residuals resulting obtained from the peakfit MATLAB function for the deconvolution and integration of ambient ISOPOOH and IEPOX isomers observed during the PROPHET 2016 field study. The isomers observed during this study were 1,2-ISOPOOH (red), 4,3-ISOPOOH (orange), cis-IEPOX (light blue) and trans-IEPOX (dark blue). In addition, an unknown peak (gray) can be seen eluting at 7.8 minutes prior to the ISOPOOH and IEPOX isomer species. To obtain the ambient mixing ratios, peaks are deconvoluted and integrated using an appropriate peak shape (in this case, a Gaussian-Lorentzian blend), scaled by the relative CIMS sensitives of each isomer (see Supplement), ion source enhancement (if applicable) and estimated transmission factor, and then normalized by volume of air collected on the column. The GC signal shown here has been normalized to the largest peak height. Amounts shown in parenthesis corresponds to the amount of analyte trapped in the column.

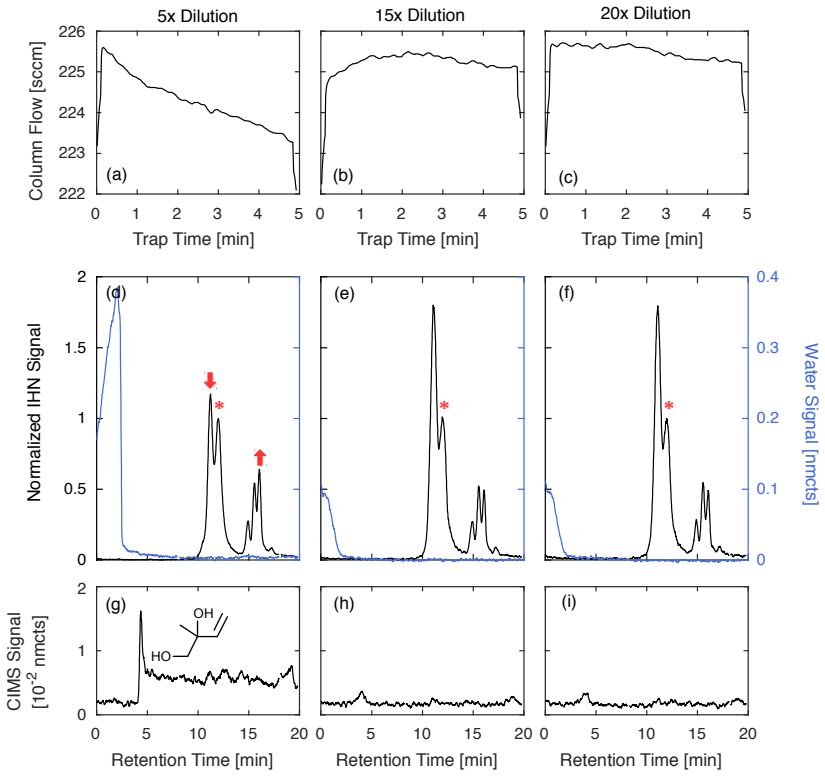


Figure 7. Comparison of ~~hydroxy nitrates formed during chamber experiments~~ GC column flow (~~A-B~~A-C) ~~from propene~~ and three chromatograms (~~left~~D-F) of IHN (*m/z* 232, black) and water (*m/z* 104, blue) at three ~~structural isomers~~ different dilutions from a high RH chamber experiment. The beginning of ~~butene~~ a chromatogram is marked when the temperature program initiates. When water is trapped during the lowest dilution (~~right; 1-butene (orange~~5x), ~~2-butene~~ column flow decreases (~~teal~~indicating an ice blockage) and the isomer distribution of IHN is dramatically altered as noted by a loss in the first peak (1,2-IHN) and ~~2-methyl-propene~~ increase in the last peak (~~red~~*E* 1,4-IHN)~~; dominant hydroxynitrate structures shown~~. These peak changes are marked by arrows and described relative to 4,3-IHN (*)~~with the corresponding~~ . The 1,2-isoprene diol (*m/z* ~~signal~~ 187, G), an expected product of 1,2-IHN hydrolysis, is also observed ~~during a 2017 field study~~ in ~~Pasadena~~this scenario. However, ~~CA (C-D)~~when the sample is sufficiently diluted prior to trapping, the water signal quickly falls to background levels and isomer distribution is preserved with minimal diol formation. ~~Data shown here has undergone a 10 second average~~Column flow also remains relatively stable throughout the trapping period when minimal water is retained.

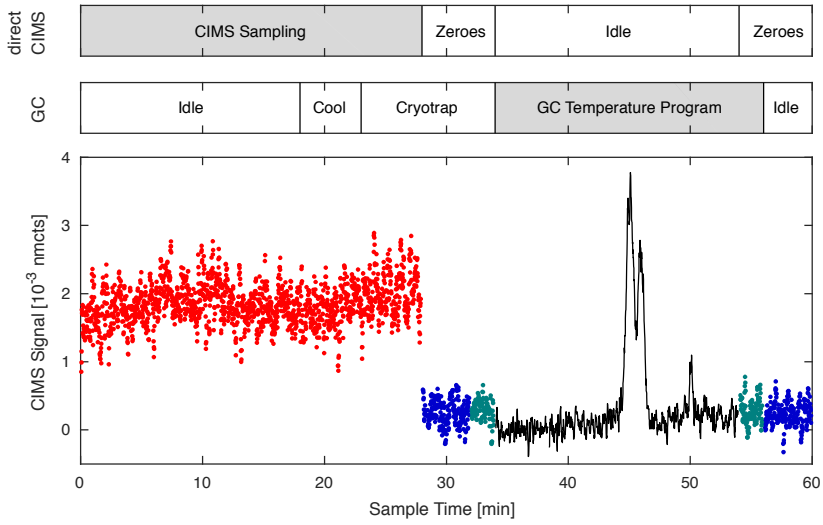


Figure 8. Typical GC-CIMS sampling cycle during the 2017 field study in Pasadena, CA. Data ~~is~~ shown for *m/z* 232. Cycle has a period of 1 hour in which the first half is dedicated to direct CIMS measurements (red), the latter half measures compound signals that have undergone chromatographic separation (black). The two sampling modes are separated by a zeroing periods comprised of a four minute ambient zero (blue) and a two minute dry zero (green). Most GC processes occur in the background during direct sampling, as to not interrupt data collection. Data shown here is a two second average. Changes in the amount of flow entering the ion source during direct CIMS and GC-CIMS sampling directly correlate with the signal to noise seen during each operating mode. The increased flow rate through the ion source during the GC sampling mode results in higher ion counts and increased signal to noise.

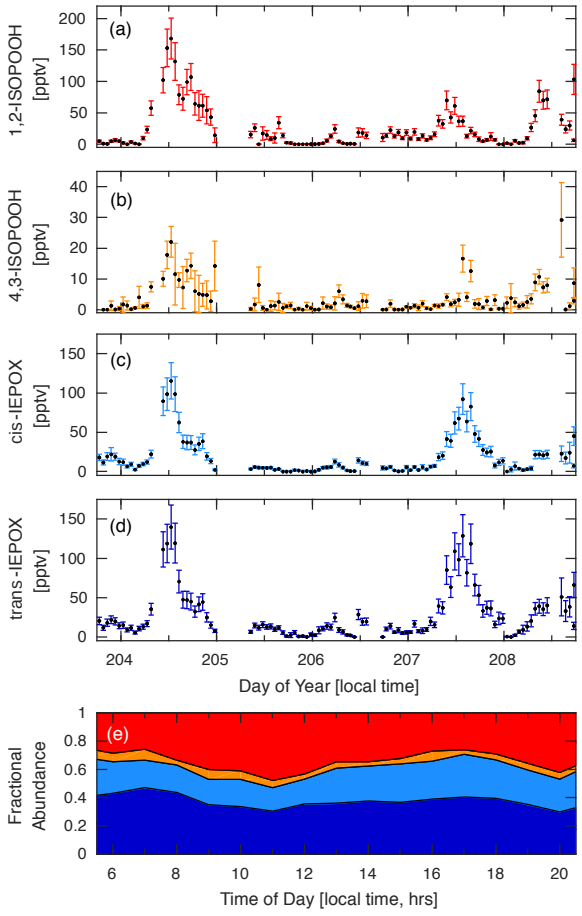


Figure 9. ~~Average~~ Time series for the four isobaric species: ~~(mean) diurnal profiles obtained from *n* number of chromatograms (~~A) ~~collected during the PROPHET campaign for (B)~~ 1,2-ISOPOOH, (~~C~~B) 4,3-ISOPOOH, (~~D~~C) *cis*-IEPOX, and (~~E~~D) *trans*-IEPOX~~(marked by colored squares)~~. Data was collected during the PROPHET campaign between ~~23~~ 22 - ~~28~~ 27 July, 2016. ~~For each box surrounding these average values, the central lines mark the median, the top and bottom edges represent the 25th and 75th percentiles, respectively, and the whiskers mark the maximum and minimum values observed that are not considered outliers (marked separately by a red '+' symbol~~E) ~~. (F) Average diurnal~~ Diurnal profile of the fractional abundance of each of these four isomers based on their hourly mean values calculated from the time series data shown here. Shaded areas correspond to 1,2-ISOPOOH (red), 4,3-ISOPOOH (orange), *cis*-IEPOX (light blue) and *trans*-IEPOX (dark blue).

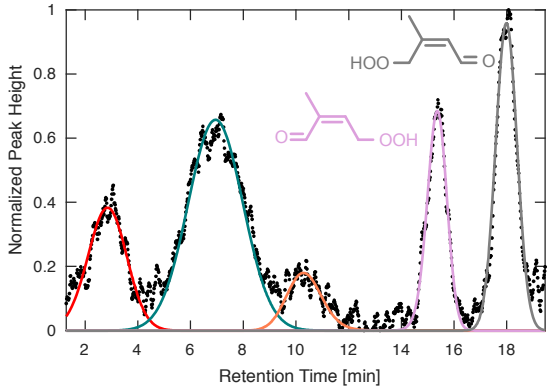


Figure 10. Chromatogram obtained during the PROPHET campaign for *m/z* 201. The latter two peaks have been identified previously as the two HPALD isomers ~~providing evidence of isomerization in that environment~~(Teng et al., 2017). The three peaks early remain unidentified. GC signal has been normalized to the largest peak height.

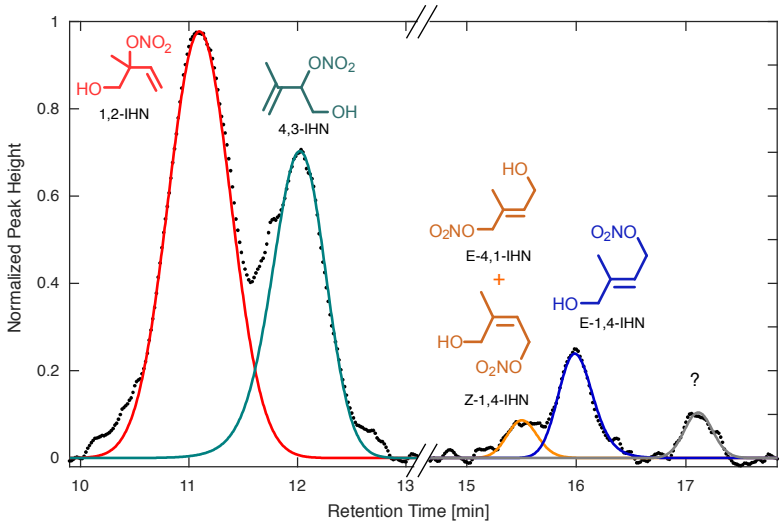


Figure 11. Chromatogram obtained during the Caltech field study for *m/z* 232, attributed to the IHN isomers, normalized to largest peak height. At least four isomers of IHN were observed: 1,2-IHN (red), 4,3-IHN (green), *E*-4,1- and *Z*-1,4-IHN (coelute, orange), and *E*-1,4-IHN (blue). *Z*-4,1-IHN was not present above the instrument detection limit. An unidentified component, which likely corresponds to a species observed in laboratory isoprene oxidation studies, is present near the end of the chromatogram (grey, see Teng et al. (2017)).

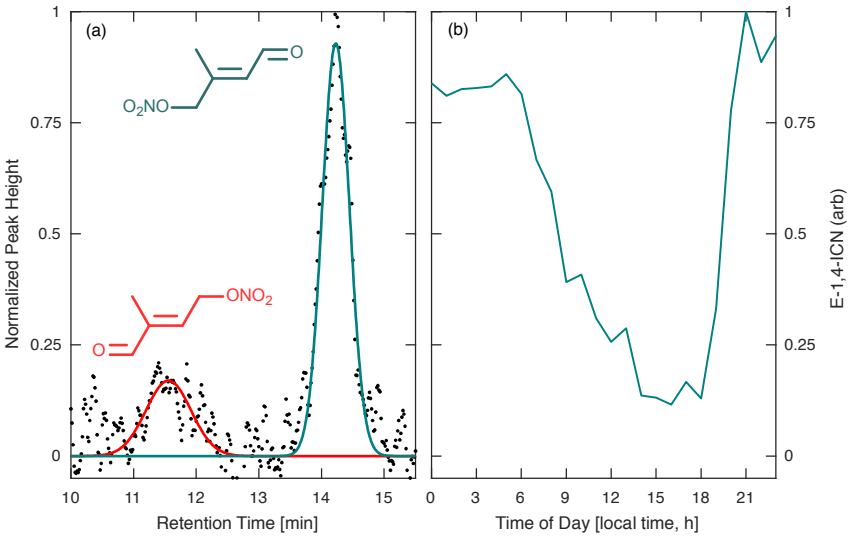


Figure 12. (A) Chromatogram obtained during the Caltech field study for the two isoprene carbonyl nitrate isomers (4,1-ICN in red and 1,4-ICN in green, *m/z* 230) produced by isoprene + NO_3 chemistry, normalized to the largest peak height. Peak assignment is based on results from Schwantes et al. (2015). (B) Average diurnal profile of most abundant ICN isomer, 1,4-ICN, obtained from chromatograms collected between 01-16 Aug, 2017 during the Caltech field study. This profile appears to correspond with the expected formation of ICN from NO_3 oxidation of isoprene in dark/dim conditions and the rapid loss in light periods.

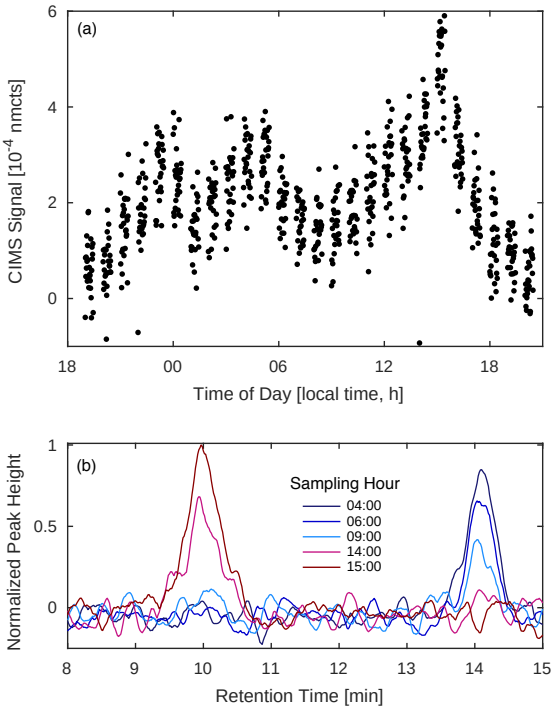


Figure 13. (A) Diurnal profile of unidentified compounds observed at *m/z* 236 (MW 151) from 11-12 Aug~~.~~, 2017 during the Caltech field study and (B) select field chromatograms from the same sampling period. The GC shows at least two compounds contribute to the signal, one more abundant at night (~~C~~blue) and the other more abundant in the late afternoon (~~D~~red).

Table 1. Examples of OVOCs measured in this study.

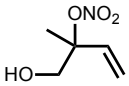
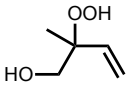
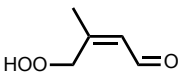
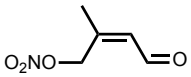
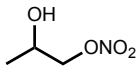
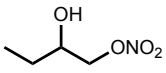
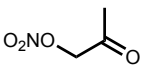
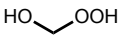
Compound	Abbreviation	Example Structure
isoprene hydroxy nitrate	IHN	
isoprene hydroxy hydroperoxide	ISOPOOH	
isoprene epoxydiol	IEPOX	
isoprene hydroperoxy aldehyde	HPALD	(cis) 
isoprene carbonyl nitrate	ICN	
propene hydroxy nitrate	Propene HN	
butene hydroxy nitrate	Butene HN	
propanone nitrate	PROPNN	
hydroxymethyl hydroperoxide	HMHP	

Table 2. Comparison of elution temperature (°C) and retention time (minutes, in parenthesis) for isoprene nitrates.

Study	Column	1-OH 2-N	4-OH 3-N	*Z* 4-OH 1-N	*E* 4-OH 1-N	*Z* 1-OH 4-N	*E* 1-OH 4-N
Mills et al. (2016)	Rtx-1701[a]	N/A	110 (26.1)	119.2 (36.5)	133.7 (39.3)	133.2 (39.4)	142.7 (41.2)
Mills et al. (2016)	Rtx-200[a]	N/A	101.1 (16.7)	110 (22.4)	110 (25.1)	110 (23.3)	110 (26.5)
This Study	Rtx-1701[b]	42.4 (10.5)	45.1 (11.4)	63.2 (14.5)	71.3 (15.3)	71.3 (15.3)	76.4 (15.8)

[a] Column is 30 m, 0.32 mm ID, 1 µm phase thickness

[b] Column is 1 m, 0.53 mm ID, 3 µm phase thickness