Author response to RC1 of Karu, E., Li, M., Ernle, L., Brenninkmeijer, C. A. M., Lelieveld, J., and Williams, J.: Atomic emission detector with gas chromatographic separation and cryogenic preconcentration (CryoTrap-GC-AED) for atmospheric trace gas measurements.

Here present an in-depth analysis of a potentially useful new instrument for atmospheric research, namely the CryoTrap-GC-AED system. The instrument was purchased to replace an ageing FID system, the aim being to simplify calibrations with the equimolar response ideally offered by this technique and to use the element specific signals with low associated noise to search for new species of atmospheric interest. In this paper we report that in fact the species measurable by this instrument do exhibit compound specific responses due to the sampling preparation steps, and that no exotic heteroatom containing species were discovered in the samples analyzed. Although apparently disappointing it is nonetheless important to report these findings. The initial manuscript submitted included the instrument description and several examples of how selected data was used to derive new atmospheric information (for example on the upper atmosphere budget of OCS). At the request of the editor this was split into this instrumental paper (here) and a separate data analysis paper. We agree with the reviewer that since no new species (containing of iodine, bromine, nitrogen, silicon, mercury, selenium and arsenic) were revealed in any of the sampled environments to date that a GC-MS targeting the compounds in the calibration gas would have served the same purpose. Although it should be noted the GC-MS could exhibit a much greater range of sensitivities to individual compounds. For transparency we state this point now clearly in the discussion as "L249: For the work presented here, a pre-concentrating GC-MS could have served as the same or better alternative for monitoring targeted species present in a calibration gas. Nevertheless, the AED system has advantages for searching exotic heteroatom molecules in the atmosphere, for the non-carbon elements which are in the detector wavelength range.". We take the view that it is important to document the instrument performance "warts and all".

Compound specific response – all compounds measured in the atmosphere were calibrated against a multi-component gas mixture, thus all the losses were accounted for.

Added to the manuscript at L190.

Identify unknowns by determining composition of a mixed halocarbon compound – Unfortunately, chlorine and fluorine do not land in the quantifiable 161 – 211 nm wavelength range (AED III HR has a restricted wavelength range, but all the wavelengths can be recorded simultaneously. AED II has a mechanically turning grating for measuring different wavelength groups in the range of 171 to 837 nm, thus nevertheless the simultaneous measurement of the whole range is not possible).

Added to the manuscript at L44.

Throughout my PhD, I was always on a search for new compounds in the group of iodine, bromine, nitrogen, silicon, mercury, selenium and arsenic but these elements were mostly under the quantifiable detection limit with the method developed, and in the regions measured.

Added to the manuscript at L251.

Might have been done more easily with a GC/FID or GC/MS – We agree that for the presented case these instruments would have been a better option, but as we were also searching for new heteroatom containing species in the samples, where AED detector has an advantage.

Added to the manuscript at L249.

AED capability to measure oxygen – not suitable for trace atmospheric measurements as the requirement is to use 10% methane 90% nitrogen reagent gas mixture. As this reagent gas produces a very high background signal it was not feasible to use it for trace gas measurements which was the aim of this project. This AED capability is suitable for oxygen measurements in oil and gas industry.

Added to the manuscript at L245.

L33 Even though "great care" was taken to minimize compound specific effects, such effects are later reported. Here the authors claim that a single RF could be applied to an unknown compound, but they don't indicate how they choose this RF, or if they use some average.

Compound specific RFs could be applied for a similar compound groups (pseudo-unknown compounds) within the uncertainty range. Even better approach would be to average similar compound group RFs to quantify the pseudo-unknown or a compound missing in the calibration standard.

Added to the manuscript at L35.

L41 The authors show a range of 161 – 211 nm for the range of the JAS AEDIII HR instrument. It seems from the literature of JAS that higher wavelengths are also accessible. Earlier AED models did have a much wider range. Can the authors clarify if this limited range is all that is available? Improved responses for some elements might be found at higher wavelengths. If the instrument is limited in wavelength range, perhaps the authors could comment on the advantages or disadvantages of a limited range versus an extended range instrument.

With the AEDIII HR wavelength range of only 161 – 211 nm can be measured simultaneously (light is focused in a horizontal plane onto two back-thinned CCDs). Due to a physical hardware gap between the two CCDs, there is a 7 nm gap in the wavelength spectra between 183 – 190 nm range). Therefore, e.g. chlorine and fluorine cannot be measured with the AEDIII HR version. For example, AEDII (previously developed by HP -> Agilent -> JAS GmbH) was able to measure in the range of 171 to 837 nm with a turning grating as mentioned above, therefore not all wavelengths simultaneously. Unfortunately, chlorine (sensitive at 479 nm) and fluorine (sensitive at 690 nm) are not in the measurement range of AEDIII HR. The advantage of the limited wavelength range is the simultaneous recording of the whole spectra with 0.01 nm step resolution.

Added to the manuscript at L44 and L108.

The newer development by the JAS company AED III Wide Range (WR) measures much wider range with movable optics. Thus, simultaneous recording of the whole spectral range is once again not possible (different elements must be recorded in different wavelength range groups). Therefore, also the resolution is lower and likely also the sensitivity (they do not state the sensitivity yet).

https://www.jas.de/en/products/jas/aed/aed-iii-wr-wide-range-spectrometer/

L47 The authors state that the performance of atomic emission lines for multiple compounds is discussed. However, no information is provided if the authors characterized different potential atomic emission lines for each atom. Why were these particular lines chosen? Or if different ratios of combustion gases were tested to evaluate the impact of plasma conditions on the results.

The most sensitive atomic emission lines in this setup and in the range of this detector were chosen. Iodine (163 nm), sulfur (181 nm), carbon (193 nm), bromine (163 nm) and nitrogen (174 nm). No secondary atomic emission lines for each element were used. The optimal ratio of hydrogen at 12 psi (0.83 bar) and oxygen (15 psi (1.03 bar) supply pressure was used throughout the measurements.

Added to the manuscript at L49 and L101.

L56 Are the sample inlet lines temperature controlled? Is an internal standard used? Did you determine the maximum sample size possible before the most volatile measured compound breaks through the trap?

All the sample inlet lines entering the CryoTrap instrument were at constant lab temperature and same length inlet lines were used for calibration standards and the sample lines, thus any losses here would be accounted for. No internal standard was used for these measurements. As the liquid nitrogen based trapping at -60°C to the main Tenax trap retains the analytes well, no breakthrough of the most volatile measured compounds was noticed with the maximum sample size of 1 800 mL tested.

Added to the manuscript at L120.

L64 Could you specify the sample and other flows used during sample collection/transfer?

Nominal sample trapping flow of 200 mL min^{-1} was used and recorded. Helium flush flow rate was set to 100 mL min^{-1}. Trap module 1 to trap module 2 transfer flow of 10 mL min^{-1} was used.

Added to the manuscript at L69, L71 and L72.

L96 Perhaps also specify purity requirements for the H_2 and O_2.

For the reagent gases extra ultra-high purity H_2 (EUHP purity > 99.99999% by a Parker Balston Hydrogen Generator, model H2-300, Parker Hannifin Corporation, USA) and ultra-high purity O_2 (UHP, purity 99.9999%, Westfalen, Germany) were used.

Added to the manuscript at L57.

L114 Could you specify what backflush and bakeout times were required based on the carryover experiments? What level of carryover is observed from ppb level to zero level samples?

With the 15 min bakeout step after the injection the modules 1 and 2 are heated to 150°C and 210°C respectively and back-flushed with He flow (75 ml min^{-1}), whereas the bulkhead heaters are kept at 150°C. After this bakeout no carryover was measured.

Added to the manuscript at L122.

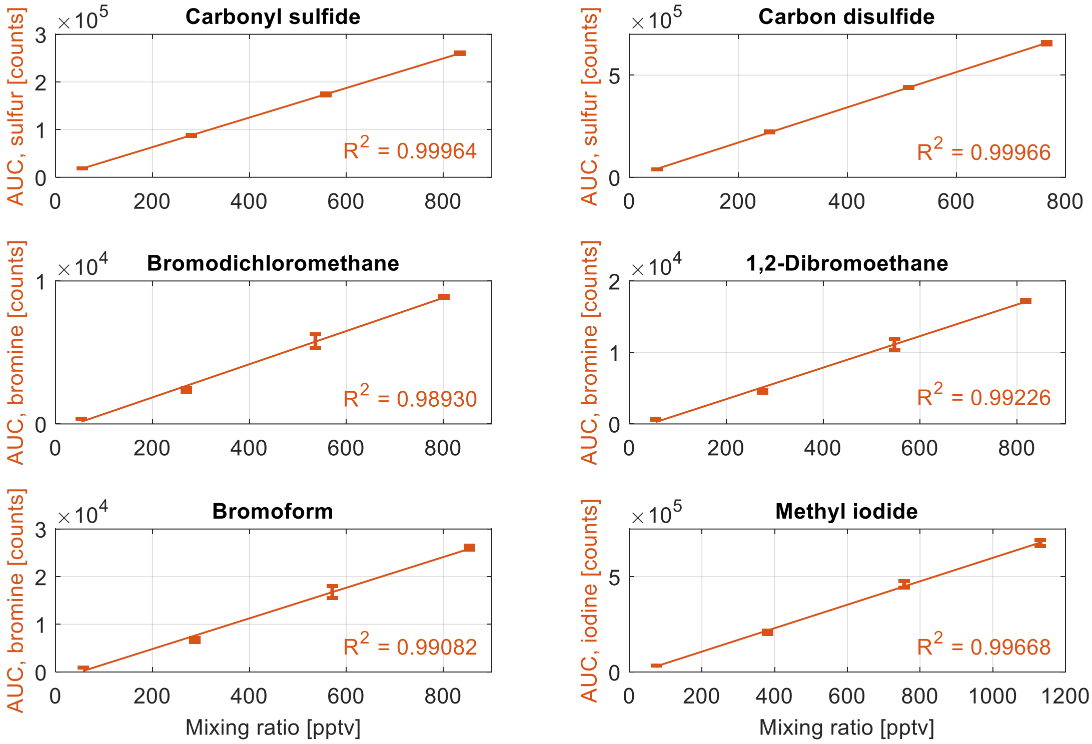
L116 Only two standards are described, but it says that three were used. Please clarify. Later a NOAA ambient air calibration standard was mentioned. Is this number 3? If so, how does this compare with dilutions of the Riemer or NPL standards?

Sorry for the typo. Two standards were used for characterization experiments. For the IAGOS-CARIBIC sample measurement procedure, the National Oceanic and Atmospheric Administration (NOAA) ambient air calibration standard was used for calibrating carbonyl sulfide to the NOAA-scale.

L131 Not really sure what linear up to 4 orders of magnitude means? Could you please provide a table of response factors determined for a range of different classes of compounds over the 4 orders of magnitude that were tested. Can you also do a similar table for the calibration levels used for the characterization experiments (e.g. 50 – 1000 pptv).

With this sentence it is meant that linear calibration can be used at least from 1 pptv to 10 ppbv. It was a conservative measurement range, probably the linear range is even larger.

An example calibration curve for 6 species below:



L137 I am curious how the instrument drifted under normal use. Is there a significant drift in system response over time?

The most significant drift comes from discharge tube wear, but this was accounted for with frequent calibration standard measurement. Between different discharge tubes and the discharge fitting quality the background signal varied significantly.

L144 The LOD determination can be done in a variety of ways. In a system that is free of adsorption or other artifacts, the equation 1 might be a reasonable extrapolation to determine detection limit. However, the system described does have some compound specific characteristics, so it would be helpful to verify the reported LODs with actual measurements near that LOD (e.g., within a factor of 3).

For the LOD calculations the lowest practically achievable calibration points were used. As the compounds of interest in the unknown samples were almost always in the real calibration range, thus should not have a large effect.

L152 It is not clear how the average RF that is calculated was actually used for quantitation.

The average RF was used for unknown analyte determination derived from a linear calibration graph (area under curve [counts] vs. MR [pptv]).

L154 Were other carbon emission lines tested? If so, what were the different characteristics? Section 3.1 This section describes results that begs further investigation and discussion. The range of reported response for carbon in different compounds is very troubling. What is reported is not the equimolar response that is claimed for the system, and it suggests big problems somewhere. A factor of >2 between benzyl chloride and butyl nitrate seems to me to be a big problem that needs to be evaluated further. To me, the differences suggest issues of stability or standard drift, though system artifacts can't be ruled out. The observed differences could be checked with independent standards, or at least compare calculations of mixing ratios based on both carbon and heteroatoms in the molecule. Further, the large variability within each response factor also seems to be a problem (36% for butyl nitrate, 43% for benzyl chloride). It is not clear to me how these variations are useful for quantitative analysis.

Overall, the response factor uncertainty (to 1 sigma) is quite variable, from reasonable few percent to much higher values depending on compounds. The authors also note that the standard deviations from the Apel-Riemer standard is about 2 x that of the NPL standard. The authors speculate that this may result from changing discharge tubes, though one could also speculate that the dilution system used for the Apel-Riemer tests had some stability problems. If the problem is from discharge tubes, wouldn't this suggest a significant problem for routine application?

Only the carbon emission line at 193 nm as the most sensitive atomic emission line in the range was tested. The big RF differences could arise from different loss and trapping efficiencies in the whole analytical pathway as well as plasma atomization efficiency. Furthermore, the extra step of diluting the nominal 50 ppbv Apel-Riemer-2015 standard is an extra point for higher uncertainty compared to the direct trapping of the nominally 4 ppbv NPL-2017 calibration standard. Also, the stability differences within the calibration standards bottles could also play a role.

Added to the manuscript at L189 and L198.

Paragraph beginning L178. This paragraph describes the crux of the problem with this paper and with the proposed method. The nominal advantage of the equimolar response of an AED is not found in this system, presumably because of sample preparation/separation issues. I don't think it lies with the AED, but this could be checked by additional testing. My suggestion would be to locate the source of the problems and determine what needs to be fixed to improve the accuracy and precisions of the whole instrument. As presented, the analytical system described has some basic flaws. It can, as the authors point out, be used if one calibrates each compound. But this is essentially no different from use of an FID, which is substantially less complicated. (I would be interested to know if the cryo-enrichment unit was tested using an FID detector, and how this might compare.) The average RF is precise to about 10% (only 1 SD), and this offers no advantage over other common analytical systems.

Correct. Unfortunately, until now the CryoTrap system was not tested with an FID instrument. I agree, this would give significantly more insight to both, the CryoTrap preconcentration and thus indirectly also to the AED detector. Some comparison measurements were made between the CryoTrap-GC-AED and the GC-FID instrument where same sample air was analyzed. The results agreed within 10%. Nevertheless once again, as all the reported compounds were analyzed against calibration gas with the same parameters as unknown samples, thus all the losses were accounted for.

Added to the manuscript at L190.

Section 3.2 Why is chlorine not included in this section? Was this not measured due to wavelength limitations? If available, please add Cl atom responses to this Table 2, and discuss in this section. It would have been great to also have Cl responses for the Apel Riemer standard to help diagnose the system. Also, I was trying to compare relative C and halogen, N, or S responses, but couldn't match all compounds between Table 1 and Table 2. For example, bromodichloromethane and acrylonitrile are in Table 2, but not listed in Table 1. Why?

Yes, unfortunately chlorine is not in the range of this AED detector. The reason some compounds are missing from the carbon emission line determined response (Table 1) is mostly due to the co-eluting of the compounds on the C193 nm chromatogram, but clearly separated e.g. on the bromine chromatogram. In the case of the missing compounds, they will be added to Table 1.

L204. This sentence further explains the fundamental problem with the proposed method. "The different element count scales were non-related to each other." It seems to me that this negates the advantages of AED over other methods. Note for example CS2 and OCS. Ratio of C response between compounds (OCS/CS2): C ratio = 637/696 = 0.915; S ratio=342/476 = 0.718. How these differences are *handled in practice needs clarification. It is not specified in the later examples, for example, if C or S emission lines are both used for the CS2 and OCS measurements, or one or the other. The authors might also wish to check on influence of CO2 on the response factors. I found a 1994 reference (Swan and Ivey, DOI: 10.1002/jhrc.1240171203) that discuss use of AED for ambient S compound analysis. Interestingly, their S ratio response between OCS and CS2 was 2932/1745 = 1.68, something quite different from that reported here (note: should add this reference to Introduction).*

All element emission lines were used independently and only one element's wavelength (the most sensitive for every specific compound) was used for calibration and quantification of the analytes of interest.

Added to the manuscript at L220.

Thank you for this reference, this is added to the manuscript.

Added to the manuscript at L27.

Section 3.3 The authors compare the advantages/disadvantages of the AED system to other common analytical systems. Given the problems outlined, the main advantage seemed to be the detection of compounds with low FID response, particularly COS. This is not particularly compelling, as other (simpler) options are available. The calculated detection limits are useful for ambient measurement of the NMHC, OCS, and perhaps several oxygenated species. LODs of halogenated species is too low for ambient measurement in most environments. The authors further argue that the multielement capabilities of the system are useful for screening gas samples. I would agree, but the selective transmission of compounds through their system would make quantitative estimations problematic, especially for exotic compounds. It would have been much more interesting to see how this system might be used to measure volatile arsenic, selenium or silicon compounds, which are not routinely done by other methods. Furthermore, the issue of the deterioration of the plasma tube and potential effects on atomic emission would also seem to be a big disadvantage for routine analysis. Given that the instrument has been in use for several years, the authors may be able to comment on that in more detail.

Agreed. During the measurement campaigns, we were always on the search for more exotic arsenic, selenium and silicon compounds but unluckily they were not detectable in the regions we measured and within the sensitivity of these elements for the system. CryoTrap-GC-MS is a better alternative for tasks monitoring targeted species. For example, the AED measurements could reveal exotic species from volcanic emission environments. This is now stated in the discussion section.

Added to the manuscript at L250.

Section 4 Case Studies. The case studies presented show that the AED system can produce data that appears reasonable. It would be important to help validate the analytical system if it was compared to currently validated techniques, or if the instrument was used in some sort of multi-lab comparison study. The forest study was mostly for terpenes and sulfur species. Were any new S species (or other heteroatom) species found in this environment? For the CARIBIC flights, one might get a better sense of sample to sample reproducibility if the data were presented in a graphical time series that also included flight altitude and perhaps ozone as a secondary tracer. Or, if the samples were measured in more than one lab, a comparison of the data for OCS would be of interest.

Until now, multi-lab comparison study has not been conducted but it would help to further characterize the instrument. In the boreal forest study, no new sulfur or other heteroatom species were detected with the method used. For the IAGOS-CARIBIC OCS, currently the CryoTrap-GC-AED is the only instrument measuring this species.

Author response to RC2 of Karu, E., Li, M., Ernle, L., Brenninkmeijer, C. A. M., Lelieveld, J., and Williams, J.: Atomic emission detector with gas chromatographic separation and cryogenic preconcentration (CryoTrap-GC-AED) for atmospheric trace gas measurements.

Line 62: Is there any data to show that the adsorption to the Silonite-D layer to de-active surfaces is very low?

Reference added:

Cardin, D.: Improving the Performance of Time Integrated Sampling of TO14 Compounds into Stainless Steel Canisters. Application Note: A-3725-02, 1999.

Added to the manuscript at L67.

Figure 1: please say what part of the cycle this configuration is in, it took me a while to work out the flow regime in the valves. In the module 3, pre-concentration trap, does this contain packing or is it just a coated empty tube?

The figure indicates the main sample trapping configuration through trap 1 and 2. The colors help to follow the flow path. The green color indicates the GC-AED column He flow and the blue color indicates the sample preconcentration flow pathway, starting from sample 1 inlet. Module 3 is just a part of 1/32" coated empty tube, no packing material inside.

To help clarify this we have inserted at line 371 the sentence "Blue color indicates the CryoTrap sample pre-concentration flow pathway through tarp 1 and 2, starting from sample 1 inlet position. Green color indicates the GC-AED He flow through to the column and leading to the He plasma.".

To include the information on module 3 a further sentence was also added at line 76.

Line 98: Can you be sure 100 % conversion to elements in the AED? Could this also be part of the reason for compound RF variability?

Good point, the conversion to atoms in the He plasma may not be 100%. This can also play a role in the compound RF variability.

RF variability may stem from less than 100% conversion of molecules to atoms in the plasma. Added to the manuscript at L189.

Line 105: What is element installation?

This is an automatic process of calibrating CCD diode numbers to wavelengths according to the calibration table.

Element installation is an automated process of calibrating CCD diode numbers to wavelengths.

Added to the manuscript at L110.

Line 113: This sentence is not very clear. Please consider rewording.

Done. "Furthermore, at the beginning of the experimental design the highest calibration standard MR level carryover and retention potentials were tested for all of the compounds of interest with the zero-air measurement directly after as the sample measurement."

Added to the manuscript at L119.

Line 121: give details of the MFC

Information added. “MFC, EL-Flow, Bronkhorst, the Netherlands”

Added to the manuscript at L129.

Line 147: Why are the RFs for heteroatom containing species given as a per C RF? Does Table 1 consider solely the C signal and not the other wavelengths? I can see when reading further that this is the case. Perhaps just include a sentence to describe that you will first look at C only and then consider the other elements separately.

Mistake corrected. The equation was written for the case of carbon emission line, but now written correctly in the general form. Table 1 is solely RF for per carbon atom, but Table 2 is RF per heteroatom.

Corrected in the manuscript at L156.

Figure 1: Are all 84 species chromatographically separated in the C wavelength signal? This is essential if the C wavelength response is used. Also, how was the retention order determined? Was a GC-MS /retention indices used to determine the retention times prior to this detector being added?

Most but not all of the 84 species are chromatographically separated in the carbon wavelength chromatogram. Co-eluting species that are detectable only in the carbon wavelength spectra are not reported. Retention times were determined with single species headspace “sniffing” tests and calibration gas mixtures.

Table 2: Is there a trend in RF or RF variability based on whether a compound is a hydrocarbon or hetero-VOC?

No clear trend was detected.

Figure 4: I would like to see more discussion of the reproducibility for each compound. In some cases the standard deviation seem high and there is a significant discrepancy between the two standards.

The discrepancy between two standards could have arisen from the extra dilution requirement of the 84 component nominal 50 ppbv Apel-Riemer-2015 calibration standard, which adds extra uncertainty. The nominal 4 ppbv NPL-2017 calibration standard needed no extra dilution.

The standard deviations of some compounds were higher than others, the Apel-Riemer standard being more variable. This was possibly the result of the extra dilution step required to dilute this standard to measurement level mixing ratios.

“In addition to the pre-concentration losses, the RF variability may also stem from less than 100% conversion of molecules to atoms in the plasma. As the per atom response factors determined to be compound specific, all the analytes of interest were always calibrated and quantified against a calibration standard, which was pre-concentrated and analyzed with exactly the same parameters as the samples. Therefore, all the losses and other effects in the analytical system leading to the variation in the RFs were accounted for.”

“The discrepancy between the two calibration standard determined RFs seen in Table 1 and 2 could rise from the point that the compounds in the NPL-2017 calibration standard are at nominal 4 ppbv and could be pre-concentrated directly, but the Apel-Riemer-2015 compounds are nominally at 50 ppbv, thus requiring extra dilution before the trapping. The dilution with zero-air introduces further uncertainty for the RFs determined from the Apel-Riemer-2015 calibration standard.”

Added to the manuscript at L189 and L198.

Line 196, Figure 2: It might be worth pointing out here that the high background is responsible for the higher LOD. The hetero-atom chromatograms show very useful selectivity and removal of the complex *background signal. This is not really discussed here but seems like it would be useful in ambient samples, although only if the reduction in LOD is not an issue. Could you identify any other heteroatom containing species in the ambient samples, rather than just the targeted ones shown? It would be good to see the chromatograms for the other elements for a real sample, rather than just a gas standard. I can see this is where the technique could have advantages over an FID. As presented, the case studies don't really provide exciting new data that couldn't be achieved with more standard instrumentation.*

Great point. "Nevertheless, bromine emission line provides great selectivity, where the high background removes the complex background signal"

Added to the manuscript at L214.

Although we were always on the lookout for new heteroatom containing species in the ambient samples, we did not find any new compounds which were at a higher concentration than the LOD of the methods used.

"Unfortunately, no new exotic species (containing of iodine, bromine, nitrogen, silicon, mercury, selenium and arsenic) were revealed in any of the sampled environments to date."

Added to the manuscript at L252.

"For the work presented here, a pre-concentrating GC-MS could have served as the same or better alternative for monitoring targeted species present in a calibration gas. Nevertheless, the AED system has advantages for searching exotic heteroatom molecules in the atmosphere, for the non-carbon elements which are in the detector wavelength range. For example, to analyze volcanic emissions."

Added to the manuscript at L249.

Line 236: perhaps direct reader that this information is about to be presented. When I first read this, I wondered why this information was given here.

Done. "and will be presented in Chapter 4.1"

Added to the manuscript at L267.

Line 258: extra space in 1400

Done.

Line 301: why was the NPL standard only used at 50 mL? This seems odd considering the Apel-Riemer is at much higher concentrations

For routine measurements only one calibration MR was used for NPL-2017 standard (measured after every 5 unknown samples) for better statistics and time management.

Line 325: should this say "marine OR volcanically"?

You are correct, changed.

Atomic emission detector with gas chromatographic separation and cryogenic pre-concentration (CryoTrap-GC-AED) for atmospheric trace gas measurements

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Abstract. A gas detection system has been developed, characterized and deployed for pressurized gas phase sample analyses and near real-time online measurements. It consists of a cryogenic pre-concentrator (CryoTrap), a gas chromatograph (GC), and a new high-resolution atomic emission detector (AED III). Here the CryoTrap–GC–AED instrumental setup is presented and the performance for iodine (1635 ± 135 counts I-atom^{-1} pptv^{-1}), sulfur (409 ± 57 counts S-atom^{-1} pptv^{-1}), carbon (636 ± 69 counts C-atom^{-1} pptv^{-1}), bromine (9.1 ± 1.8 counts Br-atom^{-1} pptv^{-1}) and nitrogen (28 ± 2 counts N-atom^{-1} pptv^{-1}) emission lines is reported and discussed. The limits of detection (LODs) are in the low pptv range (0.5 – 9.7 pptv) and the signal is linear to at least 4 orders of magnitude, which makes it a suitable method for diverse volatile organic compound (VOC) measurements in the atmosphere, even in remote, unpolluted regions. The new system was utilized in a field study in a boreal forest at Hyytiälä, Finland in late summer 2016 which made monoterpene measurements possible among the other VOCs. Furthermore, pressurized global whole-air sample measurement collected onboard the Lufthansa Airbus A340-600 IAGOS-CARIBIC aircraft in the upper troposphere and lower stratosphere region was carried out with the new setup, providing the observational data of many VOCs, including the long-lived organosulfur compound carbonyl sulfide.

1 Introduction

Atomic spectrometric analysis provides highly sensitive, equimolar, linear response at least over 5 orders of magnitude (> 10^5) and accurate elemental composition data of samples. If detection is preceded by analyte separation using gas chromatography (GC), compound specific data is obtainable. The first atomic emission detector (AED) with a plasma as an excitation source coupled with a GC was introduced in 1965 (McCormack et al., 1965). This group was the first to recognize the analytic potential of combining a GC separation with microwave induced plasma excitation and an electronic emission spectra detector. Early AEDs, using microwave induced plasmas, were operated at reduced pressures (Risby et al., 1983), until an atmospheric pressure version was developed in 1977 (Beenaker, 1977). The first commercial AED based on a microwave induced plasma and photodiode array detector coupled to a GC was released by Hewlett Packard in 1990 (Quimby and Sullivan, 1990). First AED to measure atmospheric organosulfur species was reported in 1994 (Swan and Ivey, 1994). These systems also provided speciated element specific chromatograms and were used in a variety of applications including the analysis of oils for sulfur containing compounds (Link et al., 2002). In contrast with the alternative analytical approach of gas chromatography coupled to mass spectrometry (GC–MS), the AED has the advantage of being equimolar and linear in detector response. That said it is important to keep in mind that a detector is often the last step in the whole analytical instrumental setup, therefore the response factor (RF) reflects the entire analyte pathway from the sample inlet up to the detector signal recording. This means that analyte losses by adsorption and absorption effects taking place in the transfer lines, pre-concentration stages, GC column and in the detector flow paths etc. contribute to the final RF. In this study, great care was taken to minimize the loss factors. Hence, the RF for a particular compound group can be derived for one element (e.g. carbon) from the similar single compound specific RFs and then applied to all carbon containing compounds within the group in the chromatogram. This greatly simplifies the calibration and allows quantification of pseudo-unknown compounds not present in a calibration standard. For this reason, the AED has been used for the quantification of species that have been identified by GC-MS (Apel et al., 1998; Greenberg et al., 1999). Recently, further technical developments in the AED have led to improvements in sensitivity that allow trace gases in air to be quantified directly, making such systems of interest to atmospheric scientists. The simultaneous high-resolution wavelength recording capability of the new AED III detector (161 – 211 nm) in the CryoTrap–GC–AED system allows for reliable screening for elements present in the speciated compounds, thus simplifying the identification of unknown compounds. In contrast, AED II has a mechanically turning grating for measuring different wavelength groups in the range of 171 to 837 nm, nevertheless due to the turning grating the simultaneous measurement of the whole range is not possible. Furthermore, the newly developed system in principle allows for pseudo-unknown compound quantification in a chromatogram within the uncertainty range when a broad range of compound specific RFs are used for the determination of the single element RF.

In this study, the instrumental setup and performance of the CryoTrap–GC–AED system are examined. The performance for iodine (163 nm), sulfur (181 nm), carbon (193 nm), bromine (163 nm) and nitrogen (174 nm) emission lines is examined. The most sensitive atomic emission lines for the five elements in the range of the detector were chosen. The calibration linearities, limits of detection and compound specific response factors are reported for 64 compounds.

2 Experimental

The CryoTrap–GC–AED system consists of three stages: a liquid nitrogen based pre-concentration system (Entech model 7200, USA); a gas chromatographic separation (Agilent GC 7890B, USA); and a helium plasma based third generation atomic emission detector (Joint Analytical Systems AED III High Resolution, Germany). The schematic of the instrumental setup is shown in Fig. 1. Ultra-high purity helium (UHP, purity 99.9999%, Westfalen, Germany) flowing through a heated purifying catalyst (Valco Instruments VICI, USA) is used throughout the system as the carrier and purging gas. For the reagent gases extra ultra-high purity H_2 (EUHP purity > 99.99999% by a Parker Balston Hydrogen Generator, model H2-300, Parker Hannifin Corporation, USA) and ultra-high purity O_2 (UHP, purity 99.9999%, Westfalen, Germany) were used.

2.1 Cryogenic pre-concentration (CryoTrap)

The sample is introduced to the pre-concentration unit (CryoTrap) via an eight port multi position valve, consisting of the helium supply gas, four sample introduction inlets, an internal standard, a calibration standard and a blind port (Fig. 1, upper panel). The four sample introduction lines are each 2.0 m long (Restek Corp. Silcosteel, USA) with outer diameter 1/16″ (1.59 mm), inner diameter 0.040″ (1.02 mm). The sample is drawn onto the two enrichment traps via an evacuated volumetric reservoir, where the sample introduction volume is accurately determined by measuring the pressure at given temperature. All the CryoTrap internal flow path surfaces are coated with a thin high density ceramic Silonite-D layer to provide extremely inert surfaces, which nearly eliminates the adsorption of the analytes to the surfaces (Cardin, 1999).

The CryoTrap internal flow path is flushed with the sample gas before each pre-concentration step. After that the sample air is drawn (200 mL min^{-1}) through the first stage of pre-concentration, called the dehydration module (Fig. 1, middle panel), where H_2O is selectively removed on an empty Silonite-D coated stainless-steel trap (outer diameter 1/8″ (3.18 mm), 31 cm long) held at -50°C. After collecting the required volume of sample, the trap is flushed with 75.0 mL of helium (100 mL min^{-1}) to remove any remaining air. Then module 1 is heated to 10°C and forward purged with 50.0 mL (10 mL min^{-1}) helium flow onto the main Tenax packed and Silonite-D coated volatile organic compound (VOC) enrichment trap (module 2, the second step of pre-concentration; outer diameter 1/8″ (1.02 mm), 31 cm long) held at -60°C. The forward helium purge helps to successfully transfer heavy, polar and semi-volatile organic compounds (SVOCs) onto the main module 2 VOC trap. The last pre-concentration step is pre-cooling of the cryo-focusing trap (module 3, unpacked ~4 cm long part of Silonite-D coated 1/32″ (0.79 mm) transfer line) to -180°C and thereafter kept at -160°C during module 2 back flushing at 230°C for 2.5 min, which will refocus the volatiles to a much smaller dead volume for splitless injection onto a GC column. The module 3 1/32″ (0.79 mm) transfer line is rapidly heated to 60°C for 2 min inside a sheathing 1/8″ (3.18 mm) perfluoroalkoxy alkane (PFA) tube with hot air supplied through the rotary plate kept at 100°C. This ensures rapid and splitless injection of analyte molecules to the GC column through a transfer line heated to 110°C. The pre-concentration unit is equipped with two bulkhead heaters in between the heated rotary plate and the traps for better water condensation management.

2.2 Gas chromatograph (GC)

Gas chromatography is a common choice for analytical separation of VOCs for measurement with various detectors (Bourtsoukidis et al., 2017; Apel et al., 1998). We use an Agilent 7890B GC for the compound separation. The GC was fitted with a Supelco SPB-624 capillary column (length × inner diameter: 60 m × 250 µm; film thickness 1.40 µm), which is an intermediate polar, proprietary phase bonded fused silica GC column. The SPB-624 type columns are widely used for volatile non-halogenated, halogenated, and aromatic compounds analysis.

Helium is used as the column carrier gas, of which the flow rate is controlled over the GC electronic pneumatic control (EPC) valve number 3. First, helium flows from the GC EPC valve into a 1/16″ (1.59 mm) stainless steel line connected to the CryoTrap rotary valve number 2 (Fig. 1). After the pre-concentration procedure the helium flow with the remobilized analytes is guided back to the GC oven through a heated (110°C) Silonite-D coated 1/32″ (0.79 mm) transferline. Then, in the GC oven a Swagelok T-split union guides the flow to the analytical column for splitless injection. The other end of the GC capillary column was led directly to the AED cavity through a heated transferline (250°C).

2.3 Atomic emission detector, third generation (AED III)

AED measures the energy emitted at characteristic wavelengths by sample atoms present in the helium (200 - 250 mL min^{-1}) plasma cavity to quantify their number in a chromatographic peak. Combining this data with GC analyte separation, the amount of the substance can be quantitatively determined.

The helium carrier gas (3.5 mL min^{-1}) eluting from the GC is led to the AED cavity through the capillary column that is housed in the heated transfer line (250°C). The helium plasma discharge cavity is also kept at constant 250°C temperature. The mixture of the carrier (helium) and reagent gases hydrogen (at 12 psi (0.83 bar) supply pressure) and oxygen (15 psi (1.03 bar) supply pressure) flow through a fused silica discharge tube where the gases are ionized into a plasma state by microwave energy. In the high-energy plasma the eluted sample compounds from the GC are broken down into free radicals, ions and atoms. As they return from their excited state to ground state configuration, light radiation is emitted in their element specific characteristic wavelengths. The emitted ultraviolet radiation passes through a fused silica lens and a narrow slit, and then is reflected onto a reflective holographic grating by a fixed mirror. The grating disperses the light into discrete vertical bandwidths along a plane-concave polychromatic grating. Thereafter, the grating reflects and focuses the light in the wavelength range 161 – 211 nm in a horizontal plane onto two back-thinned charge-coupled devices (CCDs). Due to the physical gap between the two CCDs there is a 7 nm gap in the range of 183 – 190 nm of the spectra. The CCDs convert light intensities across the given spectrum into electrical currents which are recorded by the "AED III Instrument Control Software". The software automatically calibrates the received light intensity signal from the CCD diode numbers into wavelengths intensity data according to a calibration table. This process (called element installation in the software) takes place automatically before every sample measurement. After each measurement, all the wavelength dependent emission data are stored with 0.01 nm resolution. An example of a 5 element simultaneously recorded chromatogram of the 84 component Apel-Riemer-2015 gas calibration standard is shown in Fig. 2.

2.4 Characterization experiments

All the characterization experiments started with a zero-air (hydrocarbon free synthetic air with 20.5% oxygen and nitrogen rest (Westfalen, Germany), which flows through an extra catalyst kept at 500°C to remove the trace amounts of hydrocarbons) measurement for determining the instrumental background. Furthermore, at the beginning of the experimental design the highest calibration standard MR level carryover and retention potentials were tested for all of the compounds of interest with the zero-air measurement directly after as the sample measurement. The trap back-flushing and bakeout times were adapted accordingly. With the 15 min bakeout step after the injection the modules 1 and 2 are heated to 150°C and 210°C respectively and back-flushed with He flow (75 ml min^{-1}), whereas the bulkhead heaters are kept at 150°C.

Two independent gas calibration standards were used for the characterization experiments: the 84 component (each nominally at 50 ppbv mixing ratio (MR) in UHP nitrogen rest) Apel-Riemer-2015 gas calibration standard (Table S1) and the 30 component (each nominally at 4 ppbv MR in UHP nitrogen rest) non-methane hydrocarbon (NMHC) ozone precursor National Physical Laboratory 2017 (NPL-2017) primary calibration standard gas cylinders (Table S2).

The Apel-Riemer-2015 standard used for the characterization measurements was diluted with the same zero-air as described above with two mass flow controllers (MFC, EL-Flow, Bronkhorst, the Netherlands). The MFC for the calibration gas had a range up to 20 mL min^{-1} and the MFC for zero-air a range up to 5 L min^{-1}. For these experiments a constant 1 L min^{-1} zero-air flow was used and five steps (1, 5, 10, 15, 20 mL min^{-1}) of calibration gas were used, to produce nominal MRs of 50, 250, 500, 750 and 1 000 pptv. This MR range is relevant for many ambient VOC measurements. With each sample pre-concentration a 1 400 ml aliquot of the diluted sample flow was trapped and the rest of the flow was led to lab exhaust. Calibration level measurements were repeated four times. No dilution for the NPL primary calibration standard was used and thus trapped directly in the amounts of 40, 60, 80 and 250 mL (producing MR in the range of 114, 171, 229 and 714 pptv for 1.4 L unknown sample relevance). The NPL calibration step measurements were also repeated four times.

With separate tests the maximum linearity range of the CryoTrap-GC-AED was tested with the undiluted Apel-Riemer-2015 calibration gas measurement (~ 50 ppbv per compound). For higher MR samples also a smaller sample volume can be trapped, making it possible to measure even higher MR samples. The system was tested to be linear to at least 4 orders of magnitude.

3 Instrument performance

The AED system was always recalibrated immediately prior to and during the measurement of the samples with unknown MRs, using the independent gas calibration standards: the Apel-Riemer-2015 and the NPL-2017 gas cylinders. In addition, during the regular automated IAGOS-CARIBIC pressurized sample measurement procedure, the National Oceanic and Atmospheric Administration (NOAA) ambient air calibration standard and the NMHC NPL standards were periodically measured after every five samples. From the calibration standard measurements, the linearities (R-squared), limits of detection (LOD), response factors per atom and measurement uncertainty were determined for all quantifiable compounds in the standard and listed in Table 1 and 2.

The LODs were calculated from the average height of the lowest calibration levels and the average height of the noise signals corresponding to the same chromatogram for each separable and measurable compound of the calibration standards. Three times signal-to-noise ratio (by peak height) was maintained to define the LOD, representing the ~99.7% confidence interval. The LOD calculation is represented by Eq. (1):

$$LOD = 3 \times \frac{\overline{noise} \times \overline{MR}}{\overline{peak\ height}}, \qquad (1)$$

where $\overline{noise}$ is the average height of the noise signal, $\overline{MR}$ is the average mixing ratio of the lowest level calibration level and $\overline{peak\ height}$ is the average peak height of that calibration level of the corresponding compound.

The average per atom RFs were calculated separately for each species using the average area under the peak curve ($\overline{AUC}$), the corresponding average MRs ($\overline{MR}$) and the number of atoms (NOA) present in the compound of interest as show by Eq. (2):

$$\overline{RF} = \frac{\overline{AUC}}{\overline{MR} \times \mathrm{NOA}} \, . \qquad (2)$$

The RFs were calculated separately for all compounds and their individual calibration MR levels and thereafter all the individual RFs over the whole calibration range were averaged to a single RF per compound.

3.1 Carbon emission line performance

The performance of the carbon emission line (193 nm) derived from measurements of three calibration standard gases is listed in Table 1. For Apel-Riemer-2015, the derived LODs are in the range 0.8 – 9.7 pptv. Each compound's RF is the average of 18 independent data points in the whole 50 – 1 000 pptv calibration range. The RFs for these compounds lie between 343 ± 147 counts C-atom^{-1} pptv^{-1} (benzyl chloride) to 800 ± 291 counts C-atom^{-1} pptv^{-1} (isobutyl nitrate) and on average 587 ± 91 counts C-atom^{-1} pptv^{-1} (47 compound mean). For NPL-2017, the LODs are in a smaller range of 0.5 – 1.1 pptv (more similar compounds) and the RFs per carbon atom range from 581 ± 23 counts C-atom^{-1} pptv^{-1} (1,2,4-trimethylbenzene) to 913 ± 77 counts C-atom^{-1} pptv^{-1} (toluene). The measured 22 compound NPL-2017 gas standard average RF was 684 ± 46 counts C-atom^{-1} pptv^{-1} (about 17% higher compared to Apel-Riemer-2015 measurements and with about half the standard deviation). The both experiment average per carbon atom RF was determined 636 ± 69 counts C-atom^{-1} pptv^{-1}.

The CryoTrap-GC-AED system sensitivity and precision are also dependent on the discharge tube, as the two experiments were conducted with different discharge tubes (as the old one broke). Nevertheless, sample gas was always directly determined against calibration standards with the same discharge tube. If a discharge tube breakage took place, a complete new calibration was carried out. The same 10 compounds (isobutene, 1,3-butadiene, pentane, isoprene, hexane, benzene, toluene, ethylbenzene, 1,3,5-trimethylbenzene and 1,2,4-trimethylbenzene) which were measured from both calibration standards are compared in Fig. 3. Three compounds: pentane, ethylbenzene and especially toluene do not adhere to the 1σ confidence interval on the one to one RF comparison between these two experiments. The reason remains unknown as there are other similar compounds to these in the comparison which stick to the correlation.

Like the RFs, also the compound specific LODs depend on the CryoTrap pre-concentration efficiency, compound transmission efficiency through the gas transfer lines, GC separation and carry through efficiency and AED helium plasma atomization and excitation efficiency. Throughout the whole instrument development process, best efforts were undertaken to use suitable transfer lines and gas union (Swagelok, USA) materials like Silcosteel (fused silica coated stainless steel), stainless steel, PFA and Teflon for minimizing analyte flow path losses, i.e. through wall losses (absorption and adsorption effects), condensation etc. Furthermore, high purity stainless steel pressure regulators were used for calibration standard gas bottles with analyte free degassing O-rings.

The compound specific per carbon atom RFs from the NPL-2017 NMHC calibration standard are summarized in Fig. 4. The AED detector should have an equimolar response, but nevertheless a spread for the carbon 193 nm emission line intensity between around 550 to 900 counts pptv^{-1} C-atom^{-1} was observed depending on the compound. Thus, the CryoTrap-GC-AED detected response must be considered as a whole for the entire instrument where the trapping and transmission efficiency is compound specific and directly influence the final detected signal. In addition to the pre-concentration losses, the RF variability may also stem from less than 100% conversion of molecules to atoms in the plasma. As the per atom response factors determined to be compound specific, all the analytes of interest were always calibrated and quantified against a calibration standard, which was pre-concentrated and analyzed with exactly the same parameters as the samples. Therefore, all the losses and other effects in the analytical system leading to the variation in the RFs were accounted for. The same applies also to the other elements measured. The average of the compound specific median RFs is 663 ± 66 counts pptv^{-1} C-atom^{-1}. Therefore, within the uncertainty range the compound independent calibration could be applied. It is possible to lower the uncertainty if a similar compound group's average RF is used for the target species. Nevertheless, for higher accuracy a direct calibration method is recommended. Throughout this study the direct calibration method was used.

The discrepancy between the two calibration standard determined RFs seen in Table 1 and 2 could rise from the point that the compounds in the NPL-2017 calibration standard are at nominal 4 ppbv and could be pre-concentrated directly, but the Apel-Riemer-2015 compounds are nominally at 50 ppbv, thus requiring extra dilution before the trapping. The dilution with zero-air introduces further uncertainty for the RFs determined from the Apel-Riemer-2015 calibration standard.

3.2 Iodine, sulfur, bromine and nitrogen emission line performances

The Apel-Riemer-2015 gas phase calibration standard was used to evaluate the performance of other available and relevant atomic emission lines for atmospheric chemistry (Table 2).

Methyl iodide (iodine wavelength measured at 178 nm) has LOD of 0.7 pptv, and RF of 1635 ± 135 counts I-atom^{-1} pptv^{-1}. The LOD of methyl iodide on iodine emission line was 9.6 times more sensitive compared to carbon emission line. Carbonyl sulfide (OCS) and carbon disulfide (CS_2) had LODs of 1.9 and 1.8 pptv, respectively. OCS had RF of 342 ± 34 counts S-atom^{-1} pptv^{-1}, and CS_2 had RF of 476 ± 79 counts S-atom^{-1} pptv^{-1}. The sulfur emission line at 181 nm was determined to be on average 3.1 times more sensitive compared to the carbon 193 nm emission line, calculated from OCS and CS_2 LOD values. The average sulfur response factor determined from the two latter compounds is 409 ± 57 counts S-atom^{-1} pptv^{-1}. Bromodichloromethane (9.9 ± 1.5 counts Br-atom^{-1} pptv^{-1}), 1,2-dibromoethane (9.0 ± 1.8 counts Br-atom^{-1} pptv^{-1}) and bromoform (8.3 ± 2.0 counts Br-atom^{-1} pptv^{-1}) at bromine emission line at 163 nm had significantly higher LODs of 115.7, 61.9 and 64.2 pptv, respectively compared to iodine, sulfur and carbon emission lines due to significantly higher background. The average per bromine atom response factor was determined 9.1 ± 1.8 counts Br-atom^{-1} pptv^{-1}. Nevertheless, bromine emission line provides great selectivity, where the high background removes the complex background signal. Nitrogen at 174 nm proved to be the least sensitive element for AED III detector. Nitrogen containing compounds: acetonitrile, acrylonitrile, isopropyl nitrate, propyl nitrate and isobutyl nitrate varied significantly with their LODs (see Table 2), despite all containing a single nitrogen atom. The different transmission efficiency of each of the five nitrogen compounds through the system's flow paths could cause such differences. The average per nitrogen atom response factor determined from the five nitrogen compounds was 28 ± 2 counts N-atom^{-1} pptv^{-1}. The different element count scales are non-related to each other. All the measured element's emission wavelength spectra were used independently, where the most sensitive emission line was chosen for each compound of interest. For example, in the case of OCS molecule the sulfur emission line was used.

3.3 Advantages and disadvantages of the CryoTrap-GC-AED

Considering all the species measured with the CryoTrap-GC-AED, the system proved to be very sensitive detecting iodine, sulfur and carbon elements with RFs 1635 ± 135 counts pptv^{-1} I-atom^{-1}, 409 ± 57 counts pptv^{-1} S-atom^{-1} and 636 ± 69 counts C-atom^{-1} pptv^{-1}, respectively. The different elemental emission wavelength intensity count scales are not directly comparable due to different elemental background noise levels. From these three elements the lowest background noise level was measured for iodine, followed by sulfur and then by carbon. The element background noise level determines the LODs for these elements in the same increasing order, also seen in the Table 1 and 2.

The great advantage of the AED system is that compounds which are insensitive to the flame ionization detector (FID) and other detectors, e.g. carbonyl sulfide, can be measured by exploiting other emission lines such as sulfur. Generally, the CryoTrap-GC-AED system is in the same sensitivity range as an FID detector (Baker et al., 2010). The electron capture detector (ECD) remains more sensitive and sometimes no pre-concentration of the air sample is necessary (e.g. Schuck et al., 2009) however, an ECD is limited only to the electron capturing compounds. The GC-MS systems generally have high sensitivity and good selectivity but require separate calibration gases for all species to be quantified since response factors vary considerably. Modern online mass spectrometry (MS) detectors, especially the proton transfer reaction time-of-flight mass spectrometry (PTR-TOF-MS) provide high sensitivity (sub pptv) and highly time resolved (< 1 s) measurement techniques without the need for pre-concentration, e.g. the new Tofwerk / Aerodyne Research Vocus PTR-TOF (Krechmer et al. 2018). However, without pre-separation with gas chromatography the chemical identity of signals can be ambiguous.

The specific emission wavelength range of the high-resolution AED III enables the measurement capability to accurately detect at least 11 elements (e.g. bromine at atomic emission wavelength of 163 nm is not mentioned in their list, but could be accurately measured): antimony, arsenic, carbon, germanium, iodine, nitrogen, oxygen (requires 5% methane in 95% nitrogen reactant gas), phosphorus, selenium, silicon and sulfur, of which a maximum of 8 can be simultaneously saved from the raw data (JAS product description from their webpage, 2020). This makes the first screening of an unknown gas phase sample for compounds with various elements much easier and faster compared to more complex mass spectra. The AED capability to measure oxygen is not suitable for trace atmospheric measurements due to the requirement of 10% methane reagent mixture. As this high concentration of methane produces a very high background signal. This capability is suitable for oxygen measurements in oil and gas industry.

For the work presented here, a pre-concentrating GC-MS could have served as the same or better alternative for monitoring targeted species present in a calibration gas. Nevertheless, the AED system has advantages for searching exotic heteroatom molecules in the atmosphere, for the non-carbon elements which are in the detector wavelength range. For example, to analyze volcanic emissions. Unfortunately, no new exotic species (containing of iodine, bromine, nitrogen, silicon, mercury, selenium and arsenic) were revealed in any of the sampled environments to date.

Some disadvantages of the current AED III detector are the short lifetime of the fused silica tube where the plasma is being maintained and the early software / electronic issues inhibiting the proper acquisition of the data. The helium plasma is sustained in a small quartz tube (47 mm long, 1.0 mm inner diameter, 1.25 mm outer diameter) with a polyimide coating (27 mm long) in the middle part of the outer surface. The tube is positioned in a water-cooled cavity, maintained at 80°C. The lifetime of the discharge tube was around 5 to 30 days, sometimes up to 3-4 months, depending on the sample throughput and quality of the replacement of the fragile discharge tube. The discharge tube could break at any moment without a warning during a measurement sequence, leading to the loss of a sample.

The high consumption of helium to maintain the plasma is expensive and of an environmental concern as helium is escaping from our atmosphere to the space. Furthermore, the large consumption of liquid nitrogen (around 2 – 3 L sample^{-1}) for the sample cryogenic pre-concentration makes it demanding on operator time, logistical field support, and somewhat expensive to operate. The use of liquid nitrogen makes it difficult to operate this instrument at remote areas. Nevertheless, the CryoTrap-GC-AED instrument was taken to a field measurement campaign at Finnish boreal forest in 2016 where among the other species it contributed to the quantification of monoterpene compounds, when accounting for the directly measured NO_3 radical reactivity in the boreal forest (Liebman et al., 2018) and will be presented in Chapter 4.1.

4 CryoTrap-GC-AED case studies

The newly developed instrument has been deployed in near real-time field measurements and in lab based pressurized canister measurements. In the following we demonstrate two case studies, one based in the forest in Hyytiala, Finland and the other in the home laboratory in Mainz, Germany.

4.1 Finnish boreal forest field measurements at Hyytiälä site

Boreal forest (taiga) makes up around 33% of Earth's forest cover, making it the largest terrestrial biome in the world. Even in the epoch of the Anthropocene about ¾ of the boreal forest remains natural (Brandt et al., 2013). The field campaign took place in a boreal forest measurement site SMEAR II (Station for Measuring Forest Ecosystem-Atmosphere Relations II) at Hyytiälä, Finland in September 2016 (Hari and Kulmala, 2005). The site is situated approximately 50 km away from the first more densely populated location, thus anthropogenic influence is relatively low, particularly when the wind masses originate from the north with low human activity and pollution.

The instrumentation was installed in an air-conditioned measurement container maintained at 25°C temperature. The CryoTrap-GC-AED system measured ambient air which was pulled from the center of a shared 8.5 m tall high-flow inlet (15 cm diameter, flowrate ~ 10 m^3 min^{-1}). From the 8.5 m inlet the air was drawn to the container through a 15 m long ½″ (1.27 cm diameter) PFA tubing at a flowrate of ~ 20 L min^{-1} (transmission time 3.3 s). The inlet line was insulated and heated (10°C above ambient) to avoid sunlight interactions and condensation. Membrane filters (polytetrafluoroethylene with pore size 5.0 µm, 47 mm diameter by Sartorius AG, Germany) were used to avoid particles entering the tubing at the connection from the high-flow inlet and replaced every 5 days. From the 15 m long sampling line inside the container the cryogenic sample trapping phase took place with a flowrate of 200 mL min^{-1} and a total of 1 400 mL air was trapped for each sample. After the injection of a pre-concentrated sample from the last focusing trap to the GC, the traps were baked out and the pre-concentration of a next sample started in parallel with the previous GC run. This enabled mean sample throughput time intervals of 1 h 22 min. The average liquid nitrogen consumption rate was 2.5 L h^{-1}. The CryoTrap and AED parameters presented in Section 2 and GC program listed in Table 3a were used.

The diel cycles of isoprene and 5 monoterpene species (α-pinene, Δ-3-carene, β-pinene, camphene, d-limonene and isoprene) are presented in Fig. 5. All monoterpene species show daytime minima and night-time maxima. This is unexpected as the emissions of monoterpenes are primarily temperature dependent and ambient temperatures were higher by day (Tarvainen et al., 2005). Here the recurring night-time MR maxima can be explained with the shallow, nocturnal boundary layer, typically accompanied by a temperature inversion in the lower troposphere, effectively trapping the ground-level emissions (Liebmann et al., 2018). The measured monoterpene species and isoprene on average accounted for about 70% of the directly measured NO_3 reactivity at night-time and about 40% during daytime, published in a separate research article (Liebmann et al., 2018).

The diel cycles of carbonyl sulfide and carbon disulfide are shown in Fig. 6. OCS showed daytime maxima between 9:00 and 15:00 UTC (12:00 and 18:00 local time), which is unexpected as daytime uptake by vegetation is generally regarded as the dominant sink for OCS (Sandoval-Soto et al., 2005). Again, the previously discussed shallow nocturnal boundary layer plays a role, as much less in-mixing of higher concentration OCS from the free troposphere takes place during night-time. Furthermore, it confirms the recently published finding at the same measurement location that OCS uptake is light independent and controlled by stomatal opening, and therefore stomatal conductance and OCS uptake can continue during night-time under these conditions (Kooijmans et al., 2017). The night-time uptake of OCS by vegetation should be further characterized and parameterized for 3D global chemistry-transport model applications. CS_2 did not show any significant diel cycle and MRs significantly varied between 0.5 and 5 pptv.

4.2 IAGOS-CARIBIC whole-air sample measurement with CryoTrap-GC-AED

The IAGOS-CARIBIC (In-service Aircraft for a Global Observing System – Civil Aircraft for the Regular Investigation of the Atmosphere Based on an Instrument Container) (Brenninkmeijer et al., 2007) is a regular observation project with scientific instruments on board commercial aircraft (Lufthansa Airbus A340-600 in cooperation with Lufthansa AG) which carries out atmospheric monitoring on a global scale, especially in the upper troposphere / lower stratosphere (UT/LS, ~ 10 – 12 km) region. Since December 2015, a new CryoTrap–GC–AED system has been applied to measure whole-air pressurized gas samples that were taken as part of this project. Many VOCs such as NMHCs (Baker et al., 2010), sulfur containing species, oxygenated and halogenated trace gases can be measured in the C3 – C14 range. These species are important to tropospheric ozone production, stratospheric ozone depletion and radiative forcing.

The whole-air samples (WAS) were pressurized at about 4 bar absolute pressure with two triggered retrospective air collectors (TRACs) each consisting of 14 specially manufactured glass vessels (2.74 L), and a high-resolution sampler (HIRES) which consists of 88 stainless steel canisters (1.0 L). Every time after the flights took place and the samplers were delivered to the lab, the measurement procedure began with the initial pressure measurement of all the 116 individual samples. CryoTrap-GC-AED was applied to measure the IAGOS-CARIBIC TRAC and HIRES whole-air samples. At the beginning of each measurement sequence, a 2.0 m long sample line was connected to a TRAC or HIRES sampler port, and a leak check is conducted by evacuating the connected sample line to ~3.0 psi (0.21 bar) absolute pressure with the CryoTrap instrument pump. After the pressure stabilization in the line, a leak check was carried out for 3 min. If the pressure reading was less than ±0.5 psi (0.03 bar) different, which is within the precision range of the pressure gauge, the line is considered leak tight. The CryoTrap traps Module 1 and Module 2 (Fig. 1) are heated at 150ºC and 220ºC, respectively for 20 min for conditioning. The GC oven program is summarized in the Table 3 below. Again, the three independent gas phase calibration standards (Apel-Riemer-2015, NPL-2017, NOAA-2017) were used for calibrating the system (Table S1 and S2). A 1 400 mL aliquot of an IAGOS-CARIBIC air sample was pre-concentrated. Exactly the same conditions were used for the calibration standards (except NPL standard where 50 mL were pre-concentrated) in order to have the same conditions and to thereby minimize the instrumental uncertainty. The IAGOS-CARIBIC WAS measurement sequence with the CryoTrap-GC-AED starts with a calibration. The measurement of zero-air (produced the same way as described in Section 2) is followed by the certified ambient air standard (NOAA-2017) measurement. The latter is followed by diluted Apel-Riemer-2015 gas phase standard measurement (as described in Section 2). After that the continuous measurement of the WAS samples started. The NOAA-2017 certified ambient air reference calibration standard and the NPL 30 component ozone precursor NMHC reference calibration standard were measured after every five WAS sample measurement to compensate for instrumental sensitivity drift throughout the analysis.

An example dataset of OCS MRs measured in the UT/LS region from two flights (Munich to Los Angeles and Munich to Shanghai in February 2019) are depicted in Fig. 7. The OCS data combined with the other VOC species from the same samples was used to determine the global atmospheric and lower stratospheric lifetime, troposphere to stratosphere flux of OCS and the stratospheric sink using the linear relationship between the long-lived species MRs (and their variability) to their known atmospheric lifetimes. This will be discussed in detail in a separate research article (article under review).

5 Conclusions

The newly developed CryoTrap-GC-AED analytical instrument enables the measurement of gas phase samples in minute concentrations (low pptv level) suitable for ambient air VOC species measurements in the troposphere and lower stratosphere. With this instrument it is possible to measure samples from canisters (e.g. IAGOS-CARIBIC whole-air samples) and also directly with circa 1-hour sampling frequency at a measurement station (e.g. Hyytiälä Finnish boreal forest measurement campaign in 2016) (Karu, 2019; Liebmann et al., 2018). The instrument proved to be sensitive and linear over more than 4 orders of magnitude (> 10^4), however, the application of the equimolarity feature of the detector is limited by pre-concentration and transmission losses. The RFs variability can accounted for with direct calibration methods, which lead to more accurate results as were found out in this study. Nevertheless, known compounds present in a chromatogram and not present in the calibration standard can be still quantified with an accuracy of around 30-40%. Thus, for more accurate results direct calibration against certified gas phase calibration standards with exactly the same measurement conditions and volumes is recommended. The possibility to measure 11 elements and 8 of them simultaneously might allow discovery of new atmospheric species of interest, e.g. containing selenium or silicon atoms, particularly in marine or volcanically influence environments. The instrument would become significantly more reliable if longer lasting helium discharge tubes were developed and the commercial software and electronics were improved. For further developments of the detector the possibility to measure a wider spectral range would allow detection of even more elements simultaneously.

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

Author contribution: EK and JW developed the idea. EK established the new measurement technique. EK, ML and LE carried out the experiments. CAMB developed the CARIBIC air sampling systems. EK wrote the manuscript with support from ML and JW. All authors discussed the results, commented and helped to improve the manuscript.

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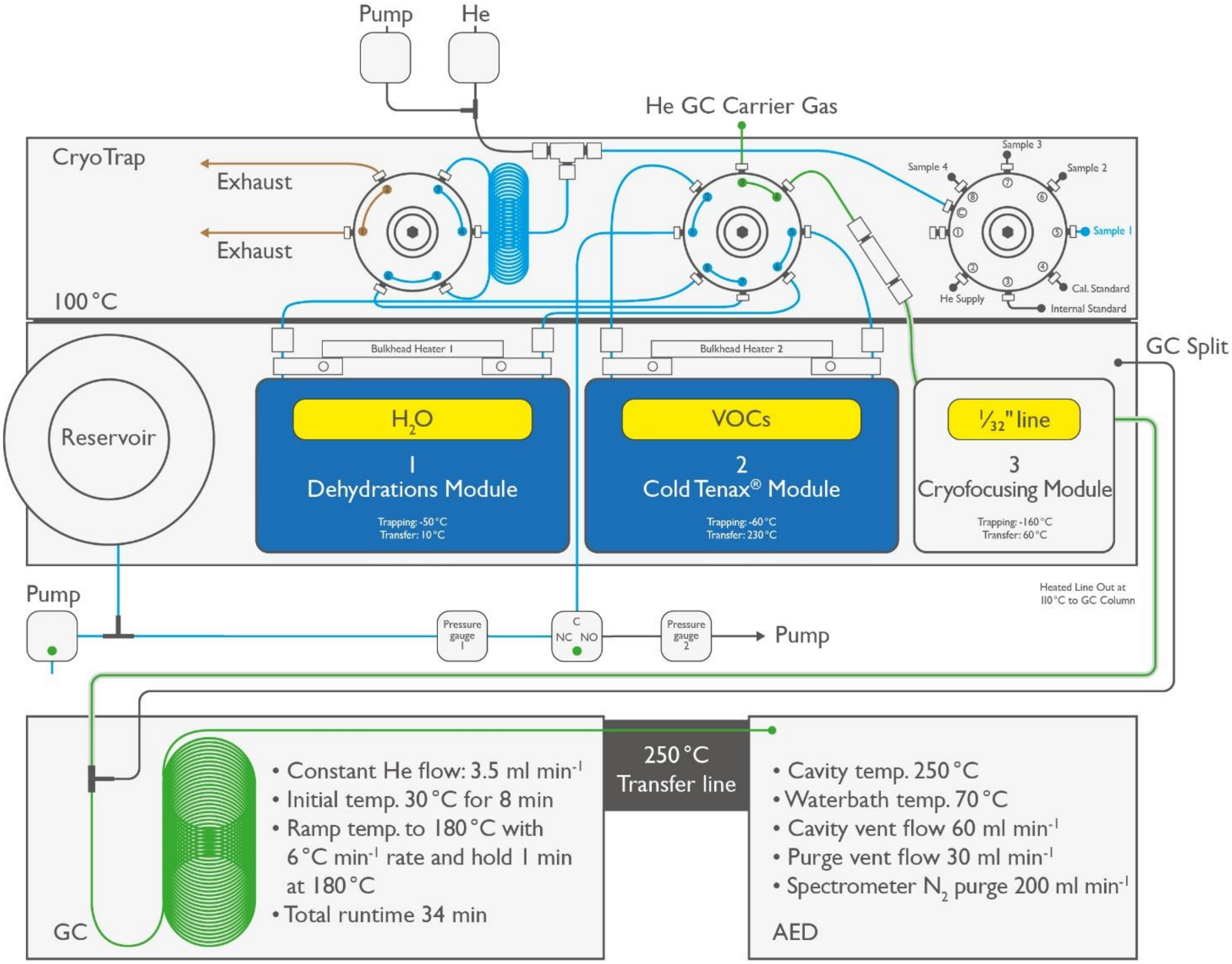


Figure 1: Schematic overview of instrumental setup, CryoTrap–GC–AED. **Blue color indicates the CryoTrap sample pre-concentration flow pathway through tarp 1 and 2, starting from sample 1 inlet position. Green color indicates the GC-AED He flow through to the column and leading to the He plasma.**

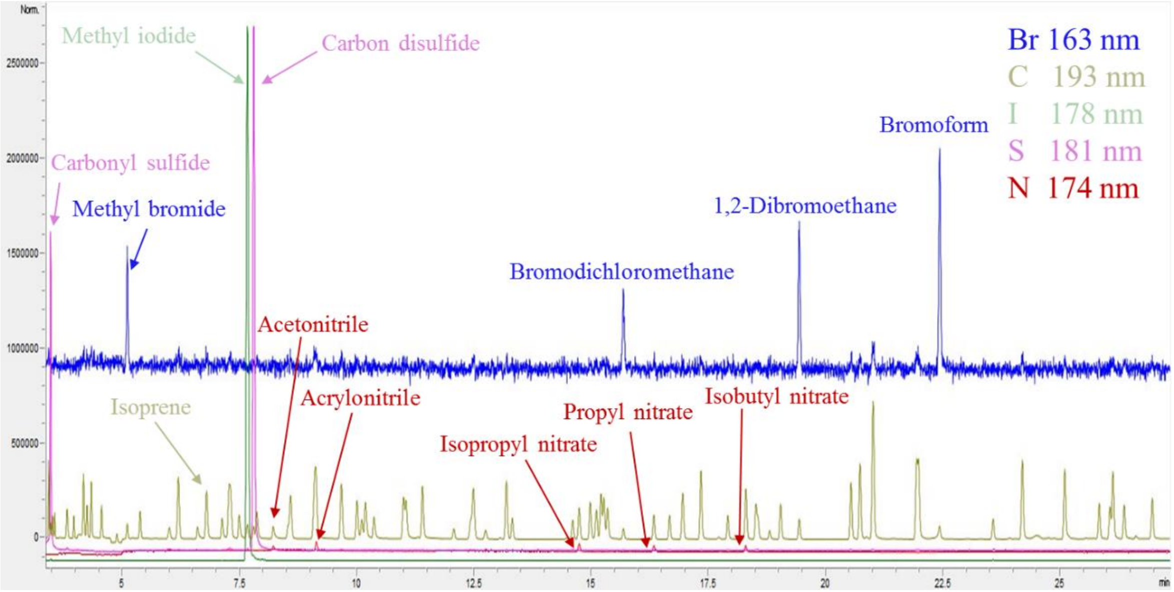


Figure 2: Example CryoTrap-GC-AED normalized multi-element overlay chromatogram of ~250 pptv 84 component Apel-Riemer-2015 gas calibration standard.

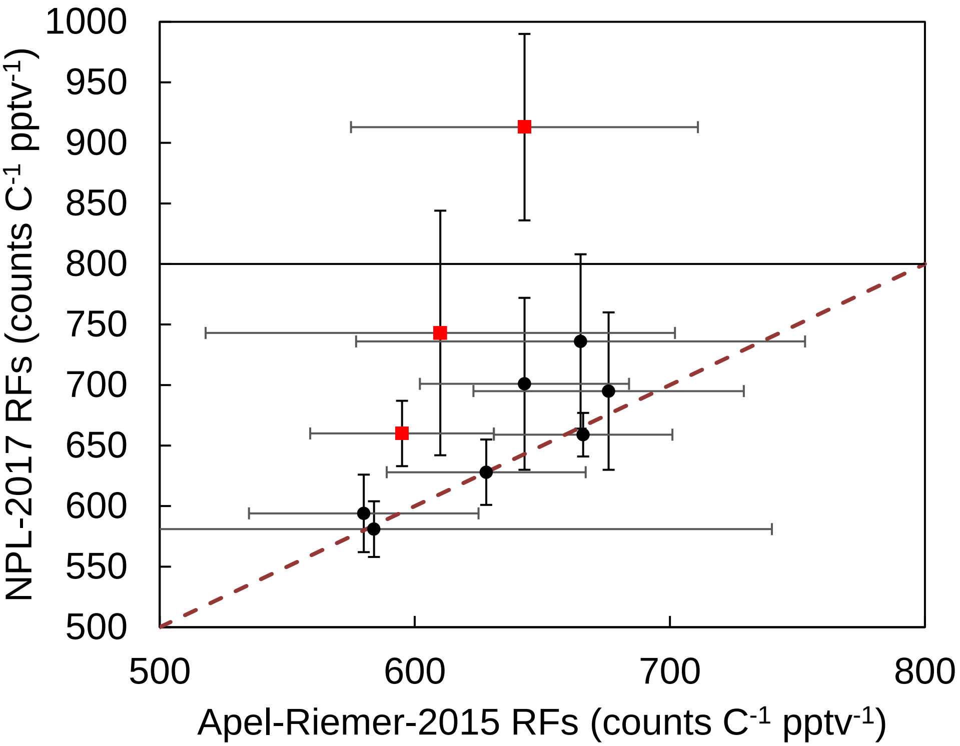


Figure 3: Response factor comparison between the 10 common compounds measured from both Apel-Riemer-2015 and NPL-2017 gas calibration standards. The black circles show the average of all the calibration level data points for the according compounds measured in the Apel-Riemer-2015 and NPL-2017 gas calibration standards. The x and y-axis whiskers represent the standard

deviation of all the measured data points for the according compound in the Apel-Riemer-2015 and NPL-2017 standards, respectively. The brown dashed line shows the one to one RF correlation between the two measurement experiments. The red squares with black whiskers show the pentane, ethylbenzene and toluene 1σ outliers (from bottom of the graph to top, respectively).

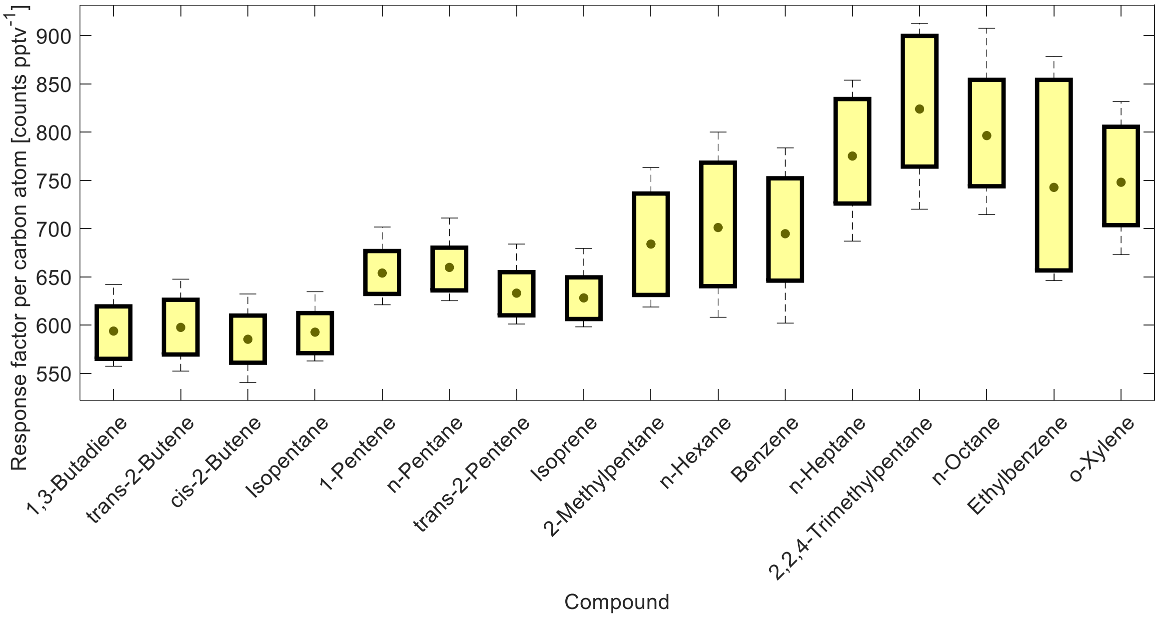


Figure 4: Boxplot graph from a selection of compound-specific per carbon atom RFs determined from the NPL-2017 NMHC primary calibration gas standard. The compound carbon emission line (193 nm) response factors as counts C-atom^{-1} pptv^{-1} are ordered by a growing number of carbon atoms on the x-axis. Central gray circles indicate the means, top and bottom edges of the box represent the 75th and 25th percentiles respectively, the whiskers show the single highest and lowest data point spread, N=176.

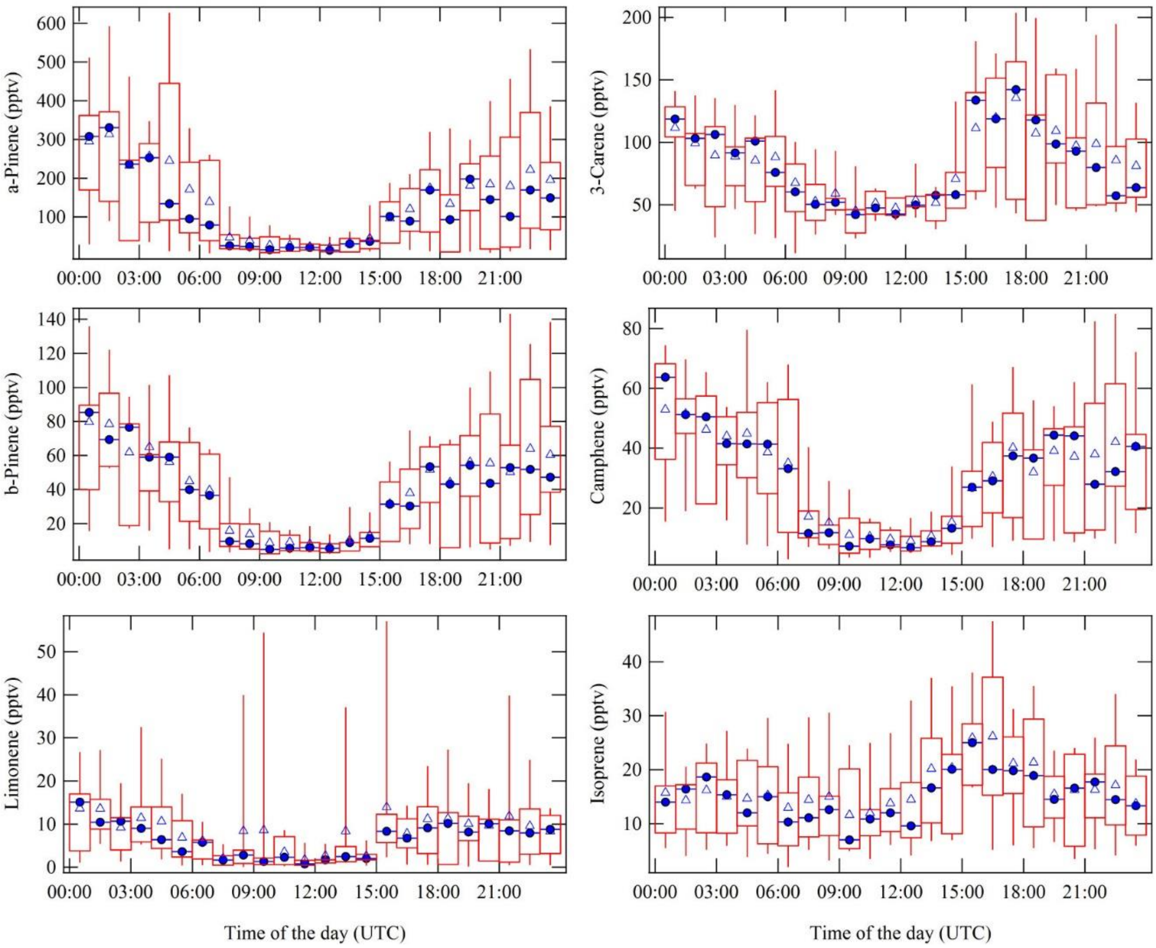
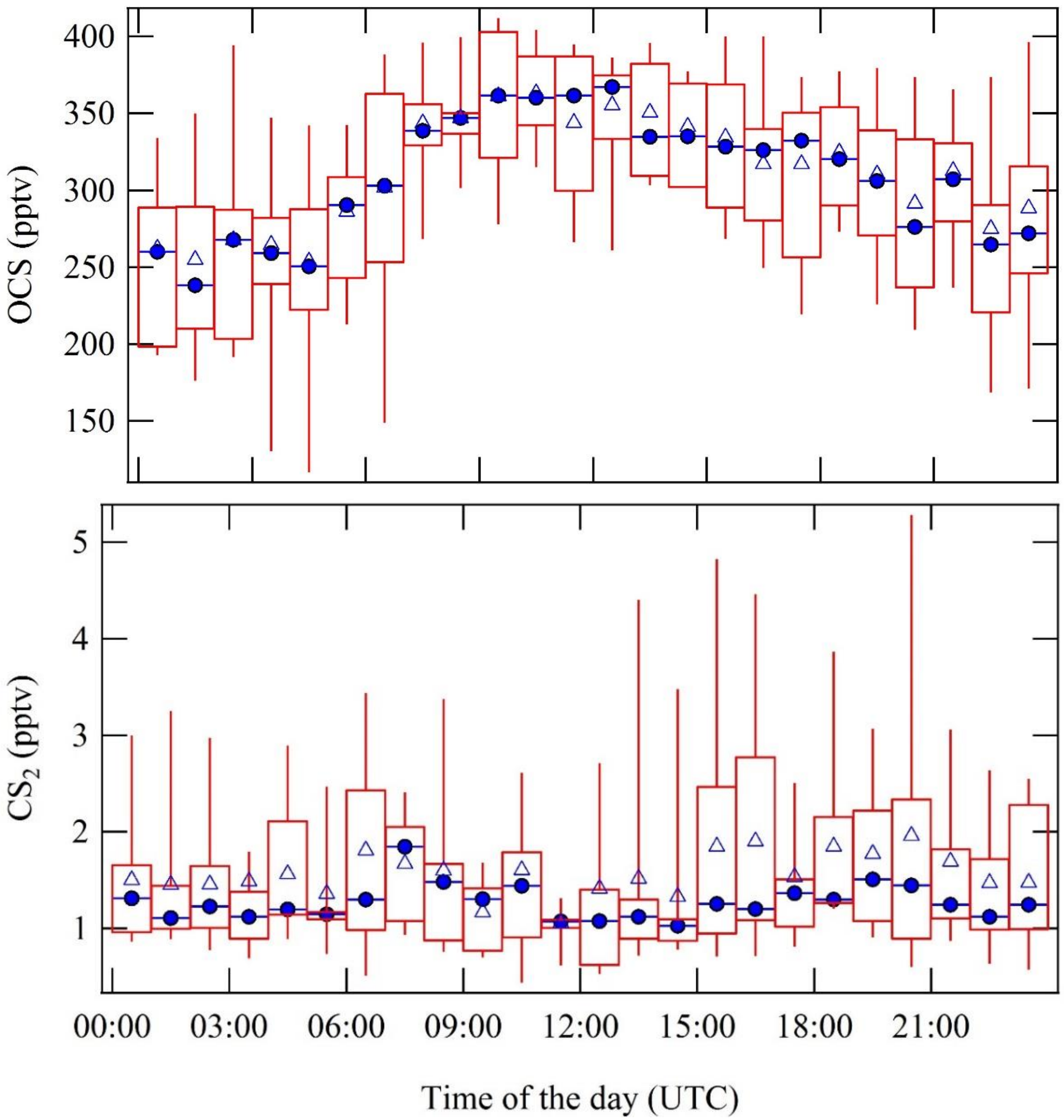
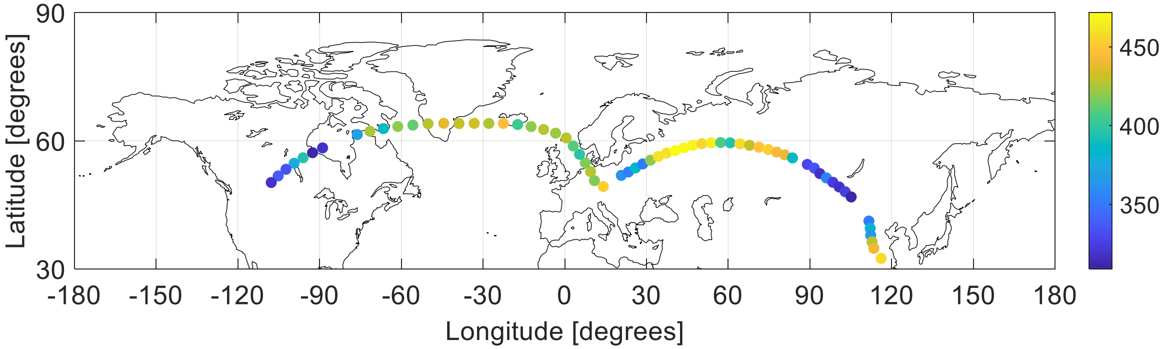


Figure 5: Complete measurement period average diel cycles of α-pinene, Δ-3-carene, β-pinene, camphene, d-limonene and isoprene. For excluding the nearby sawmill (5 km in southeast direction) monoterpene emission transport event, the data from September 9 until 11 6:30 UTC were not included in the diel cycles. Blue triangles resemble the campaign overall hourly average and blue circles
395 **represent the hourly median values. The red rectangles with the whiskers show the data spread, where 50% of the data falls into the rectangles. The upper whiskers signify the upper 75-percentile data spread and the lower whiskers indicate the lower 25-percentile of the data variation. Substantially higher MRs were observed at night-time compared to day.**



400 **Figure 6: Diel cycles of OCS MRs (upper) and CS2 MRs (bottom) based on all AED measured data points throughout the measurement campaign. Blue triangles show the overall hourly mean and blue circles show the hourly median values. The red rectangles with the whiskers show the data spread, where 50% of the data falls into the rectangles. The upper whiskers represent the upper 75-percentile data spread and the lower whiskers denote the lower 25-percentile data variation.**



405 **Figure 7: Two IAGOS-CARIBIC example flights from Munich to Los Angeles and from Munich to Shanghai (in February 2019) with OCS MRs according to the color scale [pptv].**

Table 1: CryoTrap-GC-AED system limits of detection (LODs) on 3σ level, R^2 linearity and average response factors (RFs) per
410 **carbon atom values derived from (a) Apel-Riemer-2015 and (b) NPL-2017 gas calibration standard measurements.**

(a) Apel-Riemer-2015

Compound	**LOD (pptv)**	**R^2**	**No. of C atoms**	**Average RF per C atom ± standard deviation (counts C-atom^{-1} pptv^{-1})**
Carbonyl sulfide	6.1	0.99832	1	637 ± 37
Dichlorodifluoromethane (R-12)	2.7	0.99189	1	589 ± 39
Chlorodifluoromethane (HCFC-22)	2.4	0.99589	1	745 ± 32
Chloromethane	2.9	0.99581	1	661 ± 43
Methanol	3.7	0.92247	1	529 ± 172
Methyl bromide	5.1	0.99429	1	553 ± 64
Trichlorofluoromethane	5.6	0.99431	1	652 ± 34
Methyl iodide	6.7	0.99668	1	552 ± 68
Carbon disulfide	5.4	0.99015	1	696 ± 109
Chloroform	5.7	0.99474	1	652 ± 55
Tetrachloromethane	7.0	0.99447	1	637 ± 69
Bromoform	5.8	0.99384	1	737 ± 57
Vinyl chloride	2.0	0.99492	2	549 ± 46
Acetaldehyde	1.8	0.99402	2	636 ± 35
Chloroethane	2.6	0.99469	2	550 ± 46
Acetonitrile	4.8	0.96653	2	523 ± 133
1,1-Dichloroethane	3.9	0.97800	2	430 ± 35

1,2-Dichloroethane	3.3	0.99494	2	563 ± 46
Trichloroethylene	9.7	0.95093	2	457 ± 280
1,1,2-Trichloroethane	3.3	0.99287	2	715 ± 99
1,2-Dibromoethane	3.4	0.99489	2	638 ± 98
1,1,2,2-Tetrachloroethane	3.2	0.99468	2	654 ± 100
Propene	0.8	0.99478	3	620 ± 33
2-Propanol	1.7	0.99457	3	698 ± 37
Isopropyl nitrate	2.2	0.99886	3	742 ± 137
Propyl nitrate	9.6	0.99813	3	439 ± 232
cis-1,3-Dichloropropene	2.8	0.99452	3	512 ± 84
Isobutene	0.9	0.99532	4	666 ± 35
1,3-Butadiene	1.0	0.99492	4	580 ± 45
Methacrolein	1.5	0.99458	4	728 ± 79
Butanol	2.5	0.99537	4	384 ± 42
Isobutyl nitrate	2.0	0.99878	4	800 ± 291
Pentane	1.1	0.98933	5	595 ± 36
Isoprene	1.2	0.99494	5	628 ± 39
Hexane	1.0	0.99496	6	643 ± 41
Benzene	0.9	0.99451	6	676 ± 53
4-Methyl-2-pentanone (MIBK)	1.9	0.99513	6	566 ± 150
2-Hexanone	2.7	0.99284	6	357 ± 129
Hexanal	6.1	0.98819	6	386 ± 182
Chlorobenzene	1.4	0.99540	6	573 ± 107
1,3-Dichlorobenzene	2.8	0.98789	6	399 ± 133
Benzyl chloride	4.7	0.97921	6	343 ± 147
1,2-Dichlorobenzene	2.6	0.99017	6	412 ± 125
Toluene	0.9	0.99502	7	643 ± 68
Ethylbenzene	0.9	0.99536	8	610 ± 92
1,3,5-Trimethylbenzene	0.9	0.99470	9	665 ± 88
1,2,4-Trimethylbenzene	1.1	0.99135	9	584 ± 156

(b) NPL-2017

Compound	LOD (pptv)	R^2	No. of C atoms	Average RF per C atom ± standard deviation (counts C-atom^{-1} pptv^{-1})
Propene & Propane	0.8	0.99444	3	627 ± 18
Isobutane	0.8	0.99164	4	659 ± 18
1,3-Butadiene	0.8	0.99432	4	594 ± 32
trans-2-Butene	0.8	0.99083	4	598 ± 33
cis-2-Butene	1.0	0.99129	4	585 ± 30
Isopentane	1.1	0.99598	5	593 ± 26
1-Pentene	0.9	0.99263	5	654 ± 26
n-Pentane	0.9	0.99263	5	660 ± 27
trans-2-Pentene	0.9	0.99026	5	633 ± 27
Isoprene	1.0	0.99181	5	628 ± 27
2-Methylpentane	0.9	0.97498	6	684 ± 54
n-Hexane	0.8	0.96687	6	701 ± 71
Benzene	0.7	0.96992	6	695 ± 65
n-Heptane	0.6	0.99386	7	775 ± 62
Toluene	0.5	0.99127	7	913 ± 77
2,2,4-Trimethylpentane	0.6	0.99205	8	824 ± 76
n-Octane	0.5	0.98977	8	796 ± 68
Ethylbenzene	0.5	0.92709	8	743 ± 101
o-Xylene	0.5	0.99552	8	748 ± 60
1,3,5-Trimethylbenzene	0.5	0.96353	9	736 ± 72
1,2,4-Trimethylbenzene	0.6	0.99727	9	581 ± 23
1,2,3-Trimethylbenzene	0.6	0.99681	9	619 ± 26

415 **Table 2: CryoTrap-GC-AED system limits of detection (LODs) on 3σ level, R^2 linearity and response factors (RFs) per iodine, sulfur, bromine and nitrogen atom values derived from Apel-Riemer-2015 calibration standard measurements.**

Compound	LOD (pptv)	R^2	Element	Average RF per atom ± standard deviation (counts atom^{-1} pptv^{-1})
Methyl iodide (iodine)	0.7	0.99668	I	1635 ± 135
Carbonyl sulfide (sulfur)	1.9	0.99964	S	342 ± 34

Carbon disulfide (sulfur)	1.8	0.99966	S	476 ± 79
Bromodichloromethane (bromine)	115.7	0.98930	Br	9.9 ± 1.5
1,2-Dibromoethane (bromine)	61.9	0.99226	Br	9.0 ± 1.8
Bromoform (bromine)	64.2	0.99082	Br	8.3 ± 2.0
Acetonitrile (nitrogen)	265.1	0.98281	N	19.8 ± 2.7
Acrylonitrile (nitrogen)	139.4	0.99657	N	28.2 ± 0.8
Isopropyl nitrate (nitrogen)	64.6	0.98954	N	35.8 ± 2.9
Propyl nitrate (nitrogen)	82.0	0.99180	N	25.8 ± 2.2
Isobutyl nitrate (nitrogen)	57.1	0.99060	N	28.2 ± 2.1

Table 3: The GC oven programs for (a) Finish boreal forest and (b) IAGOS-CARIBIC measurements.

(a) Finnish boreal forest

Rate (°C min^{-1})	**Temperature (°C)**	**Hold time (min)**
	35	5
6	180	5
Total runtime: 34.0 min		
Pressure (psi)	**Average velocity (cm sec^{-1})**	**Holdup time (min)**
44.25 (3.05 bar)	44.02	2.27

(b) IAGOS-CARIBIC

Rate (°C min^{-1})	**Temperature (°C)**	**Hold time (min)**
	30	8
6	180	1
Total runtime: 34.2 min		
Pressure (psi)	**Average velocity (cm sec^{-1})**	**Holdup time (min)**
45.02 (3.10 bar)	44.23	2.26

References

Apel, E.C., Calvert, J.G., Greenberg, J.P., Riemer, D., Zika, R., Kleindienst, T.E., Lonneman, W.A., Fung, K., and Fujita, E.: Generation and validation of oxygenated volatile organic carbon standards for the 1995 Southern Oxidants Study Nashville Intensive. Journal of Geophysical Research: Atmospheres, 103, 22281-22294, 1998.

Baker, A. K., Slemr, F., and Brenninkmeijer, C. A. M.: Analysis of non-methane hydrocarbons in air samples collected aboard the CARIBIC passenger aircraft. Atmospheric Measurement Techniques, 3, 311-321, 2010.

Barkley, M. P., Palmer, P. I., Boone, C. D., Bernath, P. F., and Suntharalingam, P.: Global distributions of carbonyl sulfide in the upper troposphere and stratosphere. Geophysical Research Letters, 35, 2008.

Beenaker, C.: Evaluation of a microwave-induced plasma in helium at atmospheric pressure as an element-selective detector for gas chromatography. Spectrochimica Acta Part B: Atomic Spectroscopy, 32, 173-187, 1977.

Bourtsoukidis, E., Helleis, F., Tomsche L., Fischer, H., Hofmann, R., Lelieveld, J., and Williams, J.: An aircraft gas chromatograph–mass spectrometer System for Organic Fast Identification Analysis (SOFIA): design, performance and a case study of Asian monsoon pollution outflow. Atmospheric Measurement Techniques, 10, 5089-5105, 2017.

Brandt, J.P., Flannigan, M., Maynard, D.G., Thompson, I., and Volney, W.J.A: An introduction to Canada’s boreal zone: Ecosystem processes, health, sustainability, and environmental issues. Environmental Reviews, 21, 207-226, 2013.

Brenninkmeijer, C. A. M., Crutzen, P., Boumard, F., Dauer, T., Dix, B., Ebinghaus, R., Filippi, D., Fischer, H., Franke, H., Frieβ, U., Heintzenberg, J., Helleis, F., Hermann, M., Kock, H. H., Koeppel, C., Lelieveld, J., Leuenberger, M., Martinsson, B. G., Miemczyk, S., Moret, H. P., Nguyen, H. N., Nyfeler, P., Oram, D., O'Sullivan, D., Penkett, S., Platt, U., Pupek, M., Ramonet, M., Randa, B., Reichelt, M., Rhee, T. S., Rohwer, J., Rosenfeld, K., Scharffe, D., Schlager, H., Schumann, U., Slemr, F., Sprung, D., Stock, P., Thaler, R., Valentino, F., van Velthoven, P., Waibel, A., Wandel, A., Waschitschek, K., Wiedensohler, A., Xueref-Remy, I., Zahn, A., Zech, U., and Ziereis, H.: Civil Aircraft for the regular investigation of the atmosphere based on an instrumented container: The new CARIBIC system. Atmospheric Chemistry and Physics, 7, 4953-4976, 2007.

Brühl, C., Lelieveld, J., Crutzen, P. J., and Tost, H.: The role of carbonyl sulphide as a source of stratospheric sulphate aerosol and its impact on climate. Atmospheric Chemistry and Physics, 12, 1239-1253, 2012.

Cardin, D.: Improving the Performance of Time Integrated Sampling of TO14 Compounds into Stainless Steel Canisters. Application Note: A-3725-02, 1999.

Crutzen, P. J.: The possible importance of CSO for the sulfate layer of the stratosphere. Geophysical Research Letters, 3, 73-76, 1976.

Hari, P., and Kulmala, M.: Station for measuring ecosystem-atmosphere relations (SMEAR II). Boreal Environment Research, 10, 315-322, 2005.

Greenberg, J.P., Guenther, A., Zimmerman, P., Baugh, W., Geron, C., Davis, K., Helmig, D., and Klinger, L.F.: Tethered balloon measurements of biogenic VOCs in the atmospheric boundary layer. Atmospheric Environment, 33, 855-867, 1999.

JAS product description: https://www.jas.de/en/products/jas/aed/AED%20III%20High%20Resolution%20(HR)/, last access: 26 May 2020.

Jobson, B. T., Parrish, D. D., Goldan, P., Kuster, W., Fehsenfeld, F. C., Blake, D. R., Blake, N. J., and Niki, H.: Spatial and temporal variability of nonmethane hydrocarbon mixing ratios and their relation to photochemical lifetime. Journal of Geophysical Research: Atmospheres, 103, 13557-13567, 1998.

Junge, C. E.: Residence time and variability of tropospheric trace gases. Tellus, 26, 477-488, 1974.

Karu, E.: Atmospheric sulfur compounds in the troposphere and stratosphere measured with an atomic emission detector. PhD Dissertation, Max Plank Institute for Chemistry & Johannes Gutenberg University Mainz, 1-164, 2019.

Kjellström, E.: A Three-Dimensional Global Model Study of Carbonyl Sulfide in the Troposphere and the Lower Stratosphere. Journal of Atmospheric Chemistry, 29, 151-177, 1998.

Kooijmans, L.M.J., Maseyk, K., Seibt, U., Sun, W., Vesala, T., Mammarella, I., Kolari, P., Aalto, J., Franchin, A., Vecchi, R., Valli, G., and Chen, H.: Canopy uptake dominates nighttime carbonyl sulfide fluxes in a boreal forest, Atmospheric Chemistry and Physics, 17, 11453–11465, 2017.

Krechmer, J., Lopez-Hilfiker, F., Koss, A., Hutterli, M., Stoermer, C., Deming, B., Kimmel J., Warneke C., Holzinger, R., Jayne J., Worsnop, D., Fuhrer K., Gonin M., and de Gouw, J.: Evaluation of a New Reagent-Ion Source and Focusing Ion−Molecule Reactor for Use in Proton-Transfer-Reaction Mass Spectrometry. Analytical Chemistry, 90, 12011-12018, 2018.

Liebmann, J., Karu, E., Sobanski, N., Schuladen J., Ehn, M.3, Schallhart, S., Quéléver L., Hellen H., Hakola H., Hoffmann T., Williams J., Fischer H., Lelieveld J., and Crowley, J.N.: Direct measurement of NO_3 radical reactivity in a boreal forest. Atmospheric Chemistry and Physics, 18, 3799–3815, 2018.

Link, D.D., Baltrus, J.P., Rothenberger, K.S., Zandhuis, P., Minus, D., and Striebich, R.C.: Rapid Determination of Total Sulfur in Fuels Using Gas Chromatography with Atomic Emission Detection. Journal of Chromatographic Science, 40, 500-504, 2002.

McCormack, A., Tong, S., and Cooke, W.: Sensitive Selective Gas Chromatography Detector Based on Emission Spectrometry of Organic Compounds. Analytical Chemistry, 37, 1470-1476, 1965.

Montzka, S., Calvert, P., Hall, B., Elkins, J., Conway, T., Tans, P., and Sweeney, C.: On the global distribution, seasonality, and budget of atmospheric carbonyl sulfide (COS) and some similarities to CO_2. Journal of Geophysical Research: Atmospheres, 112, 2007.

Murphy, D. and Fahey, D.: An estimate of the flux of stratospheric reactive nitrogen and ozone into the troposphere. Journal of Geophysical Research: Atmospheres, 99, 5325-5332, 1994.

Plumb, R. A. and Ko, M. K.: Interrelationships between mixing ratios of long-lived stratospheric constituents. Journal of Geophysical Research: Atmospheres, 97, 10145-10156, 1992.

Risby, T. H., Talmi, Y., and Uden, P. C.: Microwave induced electrical discharge detectors for gas chromatography. Critical Reviews in Analytical Chemistry, 14, 231-265, 1983.

Sandoval-Soto, L., Stanimirov, M., von Hobe, M., Schmitt, V., Valdes, J., Wild, A, and Kesselmeier, J.: Global uptake of carbonyl sulfide (COS) by terrestrial vegetation: Estimates corrected by deposition velocities normalized to the uptake of carbon dioxide (CO2). Biogeosciences Discussions, 2, 125-132, 2005.

Schuck, T. J., Brenninkmeijer, C. A. M., Slemr, F., Xueref-Remy, I., and Zahn, A.: Greenhouse gas analysis of air samples collected onboard the CARIBIC passenger aircraft. Atmospheric Measurement Techniques, 2, 449–464, 2009.

Swan, H. B., and Ivey, J. P.: Analysis of Atmospheric Sulfur Gases by Capillary Gas Chromatography with Atomic Emission Detection. Journal of High Resolution Chromatography, 17, 814-820, 1994.

Williams, J., Gros, V., Bonsang, B., and Kazan, V.: HO cycle in 1997 and 1998 over the southern Indian Ocean derived from CO, radon, and hydrocarbon measurements made at Amsterdam Island. Journal of Geophysical Research: Atmospheres, 106, 12719-12725, 2001.

Quimby, B.D., and Sullivan, J.J.: Evaluation of a microwave cavity, discharge tube, and gas flow system for combined gas chromatography-atomic emission detection. Analytical Chemistry, 62, 1027-1034, 1990.

Prather, M.J., Hsu, J., DeLuca, N.M., Jackman, C.H., Oman, L.D., Douglass, A.R., Fleming, E.L., Strahan, S.E., Steenrod, S.D., Søvde, O.A., Isaksen, I.S.A., Froidevaux, L., and Funke, B.: Measuring and modeling the lifetime of nitrous oxide including its variability. Journal of Geophysical Research: Atmospheres, 120, 5693-5705, 2015.

Plumb, R.A., and Ko, M.K.W.: Interrelationships between mixing ratios of long-lived stratospheric constituents. Journal of Geophysical Research: Atmospheres, 97, 10145-10156, 1992.

Cantrell, C.A.: Technical Note: Review of methods for linear least-squares fitting of data and application to atmospheric chemistry problems. Atmospheric Chemistry and Physics Discussions, 8, 6409-6436, 2008.

Barkley, M.P., Palmer, P.I., Boone, C.D., Bernath, P.F., and Suntharalingam, P.: Global distributions of carbonyl sulfide in the upper troposphere and stratosphere. Geophysical Research Letters, 35, 2008.

Krysztofiak, G., Té, Y.V., Catoire, V., Berthet, G., Toon, G.C., Jégou, F., Jeseck, P., and Robert, C.: Carbonyl Sulphide (OCS) Variability with Latitude in the Atmosphere. Atmosphere-Ocean, 53, 89-101, 2015.

Trenberth, K.E., and Smith, L., The mass of the atmosphere: A constraint on global analyses. Journal of Climate, 18, 864-875, 2005.

Tarvainen, V., Hakola, H., Hellén, H., Bäck, J., Hari, P., and Kulmala, M.: Temperature and light dependence of the VOC emissions of Scots pine, Atmospheric Chemistry and Physics, 5, 989–998, 2005.

Thomason, L., and Peter, T.: Assessment of stratospheric aerosol properties (ASAP), Report on the SPARC Assessment Kick-Off Workshop, Paris, France, 4-6 November 2001. Stratospheric Processes and Their Role in Climate Newsletter, 18, 2002.

Kremser, S., Thomason, L.W., von Hobe, M., Hermann, M., Deshler, T., Timmreck, C., Toohey, M., Stenke, A., Schwarz, J.P., Weigel, R., Fueglistaler, S., Prata, F.J., Vernier, J., Schlager, H., Barnes, J.E., Antuña-Marrero, J., Fairlie, D., Palm, M., Mahieu, E., Notholt, J, Rex, M., Bingen, C., Vanhellemont, F., Bourassa, A., Plane, J.M.C., Klocke, D., Carn, S.A., Clarisse, L., Trickl, T., Neely, R., James, A.D., Rieger, L., Wilson, J.C., and Meland, B.: Stratospheric aerosol—Observations, processes, and impact on climate. Reviews of Geophysics, 54, 278-335, 2016.