

Detailed response to anonymous reviewer 2 comments

We would like to thank the reviewer for their critical but constructive review and for the helpful comments and suggestions to improve the quality and clarity of our manuscript. We are confident that we were able to satisfy all questions and concerns.

For reference, the original comments are always included in regular font with our response following in italic font.

General Comments

This manuscript describes the development of an ethylene-chemiluminescence (ET-CL) ozone (O₃) instrument for use on small drones (UAS), for the purpose of obtaining measurements from volcanic plumes. The authors provide a technical description of their instrument and results from an initial field test at Mt. Etna. Application of CL techniques to measure O₃ in volcanic plume studies is an excellent idea since volcanic SO₂ interferes with UV-absorption-based O₃ instruments, and miniaturizing a CL instrument for drone use is novel. .. The manuscript needs significant revision to be appropriate for publication. Please see below for more detailed comments.

Specific Comments

A significant omission in the manuscript is that the well-known and dangerous nature of ethylene is never mentioned. This was a primary reason the U.S. EPA moved away from the technique, as described in Long et al., 2014 (pg. 5):

“3.1.3. Disadvantages The method requires a constant supply of ethylene, which is a dangerous, flammable, and potentially explosive gas typically stored in high-pressure gas cylinders. The use of such gas cylinders may be inconvenient and is often restricted by building fire codes or other monitoring site limitations.”

Also in Spicer et al., 2010: “The chemiluminescence method has been currently replaced in the United States by a Federal Equivalent Method (FEM), UV absorption (UV). A switch to the UV method occurred to reduce operational costs and improve safety by eliminating the flammable compressed ethylene gas required by the FRM.”

The hazardous nature of ethylene should be discussed and recommendations for safe handling. As described, is the setup subject to hazardous materials rules (e.g. UN1950)? What limitations might the use of ethylene present for the practical application of this method? Were extra approvals needed to comply with aviation rules to carry ethylene on a UAS? If special steps were taken for permissions to operate a UAS carrying hazardous material, it would be useful to describe them to understand the practicality and potential broad applicability of the method.

Response:

We acknowledge the reviewer's safety concerns about handling ethylene in CL monitors. However, we also want to draw the attention to the fundamental differences between standardized and institutionalized air quality measurements and scientific field measurements at active volcanoes. Besides, the used gas amounts are far below limits for hazardous classification and the operation in the open atmosphere efficiently prevents accumulation of higher concentrations. We clarify these aspects in an added paragraph within the newly added Section 2.1:

“2.1 Selection of chemiluminescence technique.

The ethylene chemiluminescence (ET-CL) reaction was selected for ozone detection in UAV applications because it provides high photon yield in the visible range ($\lambda \approx 440$ nm) and operates stably without active drying. In contrast, the nitric oxide chemiluminescence (NO-CL) reaction produces electronically excited NO_2^ , emitting primarily in the red–near-infrared region with a broad maximum around 1200 nm (Clough, 1967). These long-wavelength photons have lower energy and are detected with markedly reduced quantum efficiency by standard photomultipliers, requiring cooled, red-sensitive detectors to suppress dark current noise. Such detector assemblies substantially increase mass and power consumption, which is critical in UAV applications.*

The effect of water vapour also differs fundamentally between the two chemiluminescence systems. For NO-CL, water acts as an efficient collisional quencher of NO_2^ emission, strongly reducing signal intensity and linearity (Matthews et al., 1977). For ET-CL, in contrast, water vapour slightly enhances the chemiluminescence signal through secondary excitation of formaldehyde and OH^* products, leading to a small positive bias rather than suppression (Kleindienst et al., 1993). Consequently, the humidity response of ET-CL can be accounted for in the measurement uncertainty, whereas NO-CL requires complete gas drying and thermal stabilisation to achieve reproducible sensitivity.*

Considering these differences in spectral emission, humidity response, and detector requirements, the ET-CL configuration provides the most practical balance between analytical performance, stability under ambient conditions, and compatibility with compact, low-power UAV payload operation.

Although ethylene is flammable, only a very small amount of gas was used, contained in a sealed aluminum minicylinder. The instrument was usually operated in the open atmosphere. The gas volume was far below limits typically relevant for hazardous classification. Consequently, the ET-CL setup did not represent a relevant safety risk during field deployment.”

- 28: re-word the sentence “Besides its prominent role and abundance in the stratosphere, smaller amounts of O_3 in the troposphere play an important role in the oxidation chemistry.” – perhaps “Besides its prominent role and abundance in the stratosphere, O_3 is an important oxidant in the troposphere.”

Response:

Done as suggested

- 32: “...measurements of the vertical profile with high spatial and temporal resolution are rare, yet highly desirable.”

UAS offer an interesting new platform to potentially obtain O_3 profiles, but it would be appropriate to mention existing global ozonesonde networks here, such as those organized by GAW/WMO, NDACC, NASA, NOAA, and SHADOZ (many of these efforts and related publications are summarized at <https://tropo.gsfc.nasa.gov/shadoz/index.html>). For example, Stauffer et al. (2022) summarized 42,042 sonde profiles from 60 global stations that tracked O_3 from the surface to 30 km altitude from the years 2004-2021, demonstrating that considerable effort has gone into obtaining high-resolution, global O_3 profile data. Perhaps “rare” should be qualified, or the type of vertical profile that is meant could be clarified. From a practical standpoint it is important to note that most countries restrict the altitudes at which UAS can operate without special permission, which presents a significant limitation for using

UAS to obtain vertical profiles. However, small UAS might have some advantages over other methods, such as tethered balloons, for low-altitude (i.e., boundary layer) studies.

Response:

We definitely agree with the reviewer that there are global ozone-sonde networks which have been operating for a long time already. However, we now notice that we were not very clear in our wording and our text might have been misinterpreted by the reviewer. Indeed, we mean sounding the O₃-profile in the lowest part of the atmosphere (up to around 1000m). We are sorry for this misunderstanding and thankful for the opportunity to clarify the sentence. We added the following text:

“measurements of the vertical profile with high spatial and temporal resolution in the lower troposphere (up to around 1000m), in particular the planetary boundary layer are rare.”

- 35-37: “In fact, nitric oxide and ethylene CL measurements of O₃ are still the standard method in the United States (USEPA, 2023) and are considered the most reliable O₃ measurement methods (e.g. Long et al., 2014, Long et al 2021).”

This is partially true, but needs to be edited to clarify that the Ethylene-chemiluminescence (ET-CL) technique has been superseded by the Nitric Oxide-chemiluminescence (NO-CL) method, as summarized in Long, 2021:

“The ET-CL method is no longer used nor produced commercially and has been replaced by the NO-CL method...The ET-CL method was promulgated as the Federal Reference Method (FRM) for measuring O₃ in the atmosphere in 1971, and the NO-CL method was promulgated as the FRM in 2015 (U.S. EPA, 2015).”

Further information on the EPA’s rationale to move from ET-CL to NO-CL as a reference method is found on pages 65428-65429 in the U.S. EPA (2015):

“The existing O₃ FRM specifies a measurement principle based on quantitative measurement of chemiluminescence from the reaction of ambient O₃ with ethylene (ET–CL). Ozone analyzers based on this FRM principle were once widely deployed in monitoring networks, but now they are no longer used for routine O₃ field monitoring... Although the existing O₃ FRM is still a technically sound methodology, the lack of commercially available FRM O₃ analyzers severely impedes the use of FRM analyzers...Therefore, the EPA proposed to establish a new FRM measurement technique for O₃ based on NO-chemiluminescence (NO–CL) methodology. This new chemiluminescence technique is very similar to the existing ET–CL methodology with respect to operating principle, so the EPA proposed to incorporate it into the existing O₃ FRM as a variation of the existing ET–CL methodology, coupled with the same existing FRM calibration procedure.”

Also, I could not find “USEPA, 2023” in the references, nor could I independently find updated rules on O₃ FRM after 2015. The U.S. EPA webpage states “In December 2020, EPA decided to retain the current ozone standards set in 2015” (<https://www.epa.gov/ground-level-ozone-pollution/setting-and-reviewing-standards-control-ozone-pollution>).

The information about ET-CL being superseded by NO-CL is elided in the present manuscript, and more background concerning the chosen measurement technique (ET-CL) should be included. I suggest reviewing these references, fixing the USEPA, 2023 reference

in the manuscript, and providing a more thorough background that explains why ET-CL was chosen for this application.

Response:

We thank the reviewer for this question, which again gives us the opportunity to clarify our point. The choice of the ethylene chemiluminescence (ET-CL) system was driven by the optical and operational constraints of UAV payload operation. While NO-CL can achieve very low detection limits in laboratory setups, the light it emits originates mainly from electronically excited NO₂ in the red to near-infrared spectral ranges (peak $\approx$ 1200 nm; Clough, 1967). Its detection requires red-sensitive photomultipliers which need to be cooled in order to suppress dark current noise. These detectors would add substantial mass and power consumption. In addition, the NO-CL emission is efficiently quenched by water vapour, which introduces interference to water vapour and causes loss of linearity and sensitivity (Matthews et al., 1977). ET-CL, by contrast, emits at shorter wavelengths ($\approx$ 440 nm) and shows a very small positive humidity bias that can be quantified and included in the uncertainty. We are convinced that this trade-off provides the best balance between analytical precision, ambient stability, and UAV compatibility.*

*These considerations are also explained in the new subsection (“**2.1 Selection of chemiluminescence technique**”, p. 4f1. 122-137) which we added to the revised manuscript. (See text above).*

We are also sorry that we forgot the USEPA, 2023 reference. It is now included in the list of references. Here ET and NO CL monitors are equally named as reference measurement principle

US Environmental Protection Agency (EPA): C.F.R., Appendix D to Part 50, Title 40, Reference Measurement Principle and Calibration Procedure for the Measurement of Ozone in the Atmosphere (Chemiluminescence Method), <https://www.ecfr.gov/current/title-40/part-50/appendix-Appendix D to Part 50> (last access: 8 Nov 2024), 2023.

- 52-54: “The correction of the data with simultaneously measured SO₂ (Kelly et al., 2013) or the application of selective SO₂ scrubbers (Surl et al., 2015; Vance et al., 2010), however, are difficult and – at best - introduce significant additional uncertainty.”

I agree that using filters like those described in Surl et al., 2015 and Vance et al., 2010 for proximal plume measurements with high SO₂ loadings is not ideal. However, it’s worth pointing out that both Vance et al. (2010) and Kelly et al. (2013) reported airborne measurements from dilute plumes where such interferences could be considered minor, and both studies found significant O₃ depletions in volcanic plumes that was much larger than any potential artifact:

In the case of Vance et al., several sets of measurements are included from a variety of techniques, but observations with the largest O₃ deficits come from airborne intercepts of the aged Eyjafjallajökull plume where co-measured SO₂ was less than 120 ppbv. This much SO₂ would result in a maximum of $\sim$ 1-2 ppbv positive interference in a UV O₃ instrument which is negligible compared to 10’s of ppbv of O₃ loss relative to ambient levels (Vance et al., 2010, Supplement, Table 2).

Kelly et al., 2013 reported airborne intercepts of plumes from Redoubt Volcano, with SO₂ peak levels reaching up to only 1.2 ppmv, and most levels were lower. Their discussion points out the strengths and weaknesses and errors associated with their approach: see Section 3.4, e.g.

“Use of an interference-free technique to measure O₃, such as chemiluminescence, would be preferable for making observations in volcanic plumes but unfortunately is not always practical. We acknowledge that the method we describe below has significant uncertainty but it has the advantage of using more common, inexpensive, and portable O₃ and SO₂ sensors to obtain information about O₃ in SO₂-rich volcanic plumes...”

However, Table 3 shows that the correction for SO₂ interference was generally quite small (a few ppbv O₃ – see O_{3(raw)} vs. O_{3(correct)}), and that in most cases even the uncorrected data showed lower in-plume O₃ levels than ambient O₃. In other words, the observed in-plume O₃ depletions in the presented measurements were generally larger than the artifacts introduced by SO₂ interference.

Thus, diminishing these previous studies does not seem justified. Instead, it could be noted that such approaches are best carefully applied in dilute plumes, and that another approach (ie, chemiluminescence, like that described in the present study) is generally advantageous and could be considered necessary for measuring O₃ in dense and/or young volcanic plumes.

Response:

It was never our intention to diminish the work of other authors and, and we fully agree that in very diluted plumes with SO₂ in the ppb range interferences are small or negligible. In our introduction we also specified that:

„Under most atmospheric conditions these interferences (especially due to SO₂) are negligible (Kleindienst et al., 1993; Williams et al., 2006) since ambient SO₂ levels are typically comparable to or lower than O₃ levels.

*Further we wrote: However, when probing volcanic emissions, SO₂ mixing ratios **may reach values up to several ten ppmv.**“*

However, to make this even more clear we added half a sentence in line 95 of our introduction: „ in particular during the first hour after the emission “

While we agree that there are cases where the SO₂ interference might be small and could be corrected we note that this is usually not known beforehand and bringing an instrument to the field that may or may not work under the given circumstances is not very useful. Therefore, we do not understand why the reviewer argues so strongly against the traditional ET-CL solution, as the reviewer confirms that this technique has been applied as a standard technique.

The strongest argument to not use ET-CL anymore as a reference technique is that this instrument is no longer commercially available. However, this does not speak against the actual technology, and there is no doubt that this technology was the standard technology in the US for many years.

We therefore don't see a necessity to change the sentence in lines 52-54 (numbering in the original manuscript).

- 60: As written, it's not clear what 'traditional' means here. This should be clarified with the expanded background that distinguishes between the CL-ET and CL-NO approaches.

Response:

Regarding the term „traditional“ we think we made the meaning of the term clear. Also, in the new section 2.1 (see above) we expanded the background and distinguish between CL-Ethylene and CL-NO as requested.

- 82-83: Kern et al., 2020 should be added here, as they found very low BrO/SO₂ ratios in the 2018 eruptive plume from Kilauea (see page 55), which corroborates with the low ozone depletion reported by Roberts (2018).

Response:

We thank the reviewer for this suggestion and added the above reference as suggested.

Changed text:

“... was explained by low concentration of halogens and is also supported by measurements of Kern et al., 2020”

- 79-88: I'm not sure if I understand the model, as described, that predicts minimal ozone destruction in volcanic plumes (and the URL link in the reference did not work for me). Does this model assume constant influx of O₃ into the plume? If so, it will not realistically capture the entrainment process during plume expansion. Furthermore, many “model studies with more evolved multiphase atmospheric chemistry mechanisms predict significant destruction of O₃ in volcanic plumes”, for example many well-known works by von Glasow (e.g. 2003, 2009, 2010), Bobrowski et al., 2007, Roberts (2009, 2014), and more recent works by their collaborators. While O₃ measurements in volcanic plumes remain rare - and many unknowns remain about in-plume halogen chemistry - most field measurements cited in the manuscript find significant O₃ destruction (e.g. Hobbs et al., 1982; Vance et al., 2010; Carn et al., 2011, Kelly et al., 2013, Surl et al., 2015, etc.). Thus, despite a paucity of in-plume O₃ measurements, existing field studies tend to agree in general with published plume chemistry models that include multi-phase reactive halogen chemistry that is kick-started by mixing of hot halogen-rich volcanic gases with ambient air. The purpose of this section should be clarified, and adequate information and supporting references are needed if the intended purpose is to draw distinctions between models that predict or don't predict ozone depletion in volcanic plumes.

Response:

Our point is that a simple model assuming typical figures for turbulent diffusion ($K=10^5$ cm²/s, see e.g. Brasseur & Solomon ...) in the free atmosphere will predict no significant O₃ depletion. Models making other assumptions (e.g. Glasow et al. 2003, 2009, 2010, Bobrowski et al., 2007, Roberts et al. 2009, 2014...) find O₃ depletion, however it is unclear whether the assumptions made in these models are realistic. Furthermore, when measurements of O₃ depletion in volcanic plumes were made, in most cases the halogen loading of the plume was

not measured. Therefore, in our opinion it is important to verify the model predictions by more measurements in the field together with halogen measurements in the future .

- 100: "...with C₂H₄ being the most commonly employed reactant and which is used also in this study..."

Again, this is no longer the case and C₂H₄ has been superseded by NO (e.g. U.S. EPA 2015, Long et al., 2021). Please amend here and throughout. The choice to build an ET-CL instrument rather than an ET-NO instrument needs to be explained.

Response:

We changed the quoted sentence and added - as described above - a new section 2.1 to motivate our choice for C₂H₄.

The new sentence read as follows: „In this study we used C₂H₄, which we motivate below in section 2.1”

- “The principle of CL O₃-Monitors” section: in addition to the theoretical description, this section should include practical information concerning the strengths and weaknesses of the technique. In addition to the problematic (flammable and explosive) nature of ethylene identified earlier, well-known positive interferences from water vapor in this type of instrument are not mentioned. This water vapor interference (which quenches the ET-O₃ reaction) is described in several references (e.g. U.S. EPA, 2015), including two already referenced by the authors (Kleindienst, 1993; Long et al., 2021). Example descriptions of the sense and magnitude of the water vapor interference are found in Kleindienst, 1993:

“The chemiluminescence-based monitors showed systematically higher readings than the UV monitors with added water vapor. The effect was found to be linear with water vapor concentration with an average positive deviation of 3.0 percent per percent H₂O at 25 degrees C. For these measurement, ozone concentrations ranged from 85 to 320 ppbv and water concentrations from 1 to 3 percent (i.e., dew point temperatures from 9 to 24 degrees C). These results are largely in agreement with previous studies conducted to measure this interference, although the present study extends the range of water concentrations tested.”

A more recent summary is given by Spicer et al., 2010:

“Historically two methods have been widely used for ambient air O₃ monitoring. The ethylene chemiluminescence Federal Reference Method (FRM) was dominant in the United States during the 1970s and 1980s. The only common documented interference to this method is water vapor. The extent of the positive bias is on the order of 3– 4% of the O₃ reading for each percent (10,000 parts per million [ppm]) of water vapor in the air.”

Note: Spicer et al. (2010) independently found positive interference of 3 to 10 ppbv O₃ per 10,000 ppmv H₂O at O₃ levels from 55-200 ppbv (3-9%) for a commercially available ethylene CL analyzer (Table 4).

Finally, the U.S. EPA commented on water vapor interference in ET-CL instruments when considering its rule change (U.S. EPA, 2015, pg. 65429):

“2. Comments on the FRM for O₃

Comments that were received from the public on the proposed new O₃ FRM technique are addressed in this section. Most commenters expressed general support for the proposed changes, although a few commenters expressed some concerns. The most significant issue discussed in comments was the relatively small but nevertheless potentially significant interference of water vapor observed in the ET–CL technique...However, in further response to these commenters' concerns, the EPA has modified Table B–3 to extend this water vapor mixing requirement to newly designated ET–CL analyzers, as well. These measures should insure that potential water vapor interference is minimized in all newly designated FRM analyzers."

Why is water vapor interference not included in the testing or error budget? In addition to describing the problem, simple solutions to the interference using simple commercially-available dryers are tested and analyzed (e.g. Long et al., 2021). According to a text search, the only mention of "water" in the manuscript is l. 70, where it is listed as the first (and presumably most abundant) component of primary volcanic gas emissions. This is potentially very important given how water-rich volcanic plumes are. Plumes routinely contain 1000's to 10,000's ppmv of water vapor (especially close to the source), which suggests that the reported ET-CL measurements could have potentially significant positive artifacts, unless this issue was mitigated somehow. Please describe any testing or mitigation tactics for dealing with water vapor during the development and field testing, how artifacts are dealt with in the results, and please clarify if water vapor was measured as part of the sensing package.

Response:

We appreciate the detailed references and suggestions, many of the named references are already cited in our original manuscript and therefore known to the authors. As mentioned above we have added an additional section regarding the choice of ET containing also a rough estimate on the water vapor influence (new section 2.1, see above).

We discussed the flammable (and potentially explosive) nature of ethylene before (see above). We also noted that a small, positive water vapour interference exists, (which is not due to quenching the excited product of the ethylene+O₃ reaction, since this would lead to negative water vapour interference). Under typical ambient conditions with 1% H₂O in the atmosphere this interference will amount to an additional O₃ signal of 3-4 ppb and less at higher altitudes where the low temperatures prevent such high H₂O levels. We also note that – while water vapour is the main constituent of most volcanic emissions – in a cold plume, where all these measurements are made the water vapour can not exceed saturation levels. Furthermore, the water vapour interference of the ET-CL method is an intrinsic feature of the method and there is no need to test it again and again.

- 124: Please include a photograph of the instrument to accompany the schematic shown in Fig. 1. For example, Figure 13 from Bräutigam, 2022 might be appropriate.

Response:

We included now a photograph from the instrument, see new Figure 1b

- 153: If I understand Figure 2 correctly, the dark current appears to vary from ~4-12 ppbv equivalent O₃ at temperatures from 15-35°C. How is the derived uncertainty of the fit so small ("1 ppb")?

Response: The reviewer understood correctly that the dark current varies from ~4-12 ppbv equivalent O₃ at temperatures from 15-35°C, but have probably overlooked our description in the text for the correction of the dark current which is done depending on the recorded temperature Equation 3, line 76 – 80. So 1 ppb is the uncertainty of this correction.

- 171: “To calibrate the monitor several calibration measurements with varying O₃ mixing ratios in different sequences are made.” – this is too vague. Please elaborate on the calibration conditions and procedures. Also indicate if the calibration procedure utilized dried or humid air.

Response:

We agree that the original description of the calibration procedure was too brief in this regard and have expanded this in the revised manuscript. The calibration description in the revised manuscript now reads as follows:

*“The CL O₃ monitor is calibrated using an O₃ generator, in our study primarily the Ozone Calibration Source Model 306 by 2B Technologies. It is a portable O₃ generator and can provide O₃ in the range of 0 to 1000 ppbv. Additionally, the O₃ generator ANYSCO type SYCOS KT-O₃/SO₂, which can provide 0 and 150 ppbv of O₃, was used. **In both instruments, ambient air is used as the feed gas and ozone is generated photolytically by UV irradiation of oxygen-containing air. Before entering the photolysis chamber, the incoming air is cleaned, and in the case of the O₃ generator ANYSCO type SYCOS KT-O₃/SO₂ it is additionally dried by passage through a silica-gel drying tube.***

For calibration the CL O₃ monitor is directly connected to the O₃ generator using a hose. We set the ozone mixing ratio at discrete steps (e.g. 0, ~10, ~50, ~100, ~150 ppbv) and held each step for several minutes to ensure sufficient statistical averaging. For each of these steps of constant O₃, the mean and the standard deviation of converted signals are calculated and plotted against the sampled O₃ mixing ratios as shown in **Errore. L'origine riferimento non è stata trovata.** A linear fit is performed; its fit parameters are then used for the calculation of the O₃ concentrations. Although VOLCANO3 demonstrated stable behaviour, it is advisable to perform a regular calibration check before each measurement campaign.

- 175: Change to “The detection limit...”

Response:

Unfortunately, it is not clear to us what we should change here.

- 180: here and throughout, make sure to include all equation variables and units, and be consistent (e.g. “ppm” appears 9 times in the manuscript, “ppmv” twice; “ppb” 20 times, ppbv once).

Response:

We read carefully through our manuscript again and made changes accordingly.

- 200: Was anything done to test and validate the instrument’s performance at different elevations? Was it compared to a reference instrument? If so, please include and explain how this was done. What was done to assure the instrument would work well in plume conditions (ie, high elevation, humid)?

Response:

We thank the reviewer for this suggestion and agree that it would be beneficial to validate our method with reference technology. However, as we clearly pointed out in our manuscript, there is no reference technology for O₃ measurements in volcanic plumes.

- 200: Was a vertical profile flown to evaluate atmospheric structure at altitudes relevant to the plume?

Response:

- *We agree that such and similar measurements would be interesting. However, detailed studies of the small-scale physicochemical structure of the atmosphere are beyond the scope of this technical manuscript. 221: please include more information on the “little-RAVEN”. What sensors were included? What were the ranges/resolution/etc. What was the weight? Was it flown simultaneously with the VOLCANO₃?*

Response:

A full description of the little-RAVEN system is given in Karbach et al., 2022, however we understand, that a short description of the most important components in the manuscript might help the reader.

Therefore, we revised the following part to the manuscript:

*– SO₂/CO₂ sensor “little-RAVEN” (Karbach et al., 2022) **with 868 MHz radio link (RFDesign, approx. 3 km range), GPS module for time and position (MTK3339 Adafruit), Alphasense electrochemical SO₂ sensor (calib. range: 0-16 ppm), CO₂ sensor (K30 FR Senseair, not used in this work), temperature, humidity & pressure sensor (BME280). Total weight: approx. 300 g.***

– Drone “Matrice 300 RTK”, DJI, <https://enterprise.dji.com/de/matrice-300/specs>

*The little-RAVEN sensor system, designed around an ESP microcontroller (**ESP32 from Espressif**), manages various sensors to determine SO₂, CO₂, temperature, humidity, pressure, and GPS location. It logs data onto internal memory and also transmits it to a ground station, allowing real-time localisation of the plume and confirming plume gas measurements. **For this work, Little-RAVEN was used as a stand-alone system which could be attached to the measurement drone to provide the aforementioned information simultaneously with the ozone measurements.***

- 230: Was the atmosphere stratified or compositionally heterogeneous with respect to the point of volcanic gas emission vs. the point of measurement in the buoyant plume? What was the difference in elevation from the vent to the altitude of the plume measurements? The manuscript only considers chemical ozone destruction and does not consider the impacts of mixing, entrainment, and transport of air from chemically dissimilar air parcels on measured O₃ (as described by Kelly et al. 2013).
 - Were any BrO measurements made coincident with the O₃ measurements? These would help to link O₃ depletion to BrO formation.

Response:

These are interesting questions, but they are all beyond the scope of this manuscript. The manuscript was prepared as an article for AMT with the scope to introduce newly developed instruments which will make such studies in future possible. Therefore, the focus of the article is the description of the instrument and to show the feasibility of such investigations which we do by presented first experiments carried out in a volcanic plume.

- 230-253: the results section is weak. Ozone depletion has been measured many times (relatively speaking) at Mt. Etna. How do these new results compare to previous measurements and models (e.g. Vance et al., 2010, Roberts et al., 2014, Surl et al., 2015)? Did the CL technique obtain different results than these previous studies?

The result of this paper is the proof that the newly developed O3 monitor is giving reasonable results. This is a paper for AMT and not for ACP and as mentioned in the response to the question just above, so we don't agree with the reviewer that our result section is weak.

*However, as mentioned below for another question of the reviewer we included the following words into the new version of our manuscript in line 334-336: "While our finding is consistent **with measurements by Surl et al., 2015 (15% - 45%) and Vance et al., 2010 (15% - 40 %)**,*

249: The SO₂ sensor range was only 16 ppm? Why? This seems like a serious limitation of the setup.

Response:

We chose a SO₂ sensor in the lower concentration range by design to maximize precision in the range that we initially targeted (this is within the ranges mentioned in Vance et al. (2010) and Kelly et al. (2013) for airborne plume measurements). A lower concentration sensor provides higher gain, lower noise, and finer resolution at 0–15 ppmv than that of an e.g. 0–200 ppmv sensor, which has a higher noise floor/lower sensitivity at low concentrations. Our sampling and measurement strategy targeted traverses farther away from the source that kept in-plume values mostly within this range. While the low concentration range is certainly a limitation, we chose this sensor nevertheless to optimize performance at the targeted range. We monitored for any approach to the upper limit; areas above 16 ppmv were excluded from quantitative analysis, so saturation does not affect reported results.

- 255: Improvements:

As noted above, C₂H₄ is flammable and problematic from a hazardous materials standpoint. Is cyclohexane (C₆H₁₂) also problematic from a safety/hazardous materials standpoint? What about other methods such as NO-CL or so-called 'scrubberless' methods where N₂O is converted to NO and used to titrate O₃ (described in Long et al., 2021)? Also, what would need to be done differently next time to better characterize the plume and its chemistry?

Response:

An evaluation of NO-CL is now given in the added section 2.1 to the new version of our manuscript, please see above to similar questions

- L294: "Today, our knowledge is mainly based on model studies. Such model studies show for instance a complete ozone depletion in the centre of halogen rich volcanic plume after a relatively short distance from the emission point (about 10 min

downwind, Roberts et al., 2014) but a solid experimental prove of those theoretical consideration is still missing.”

I disagree with this conclusion and suggest revisiting Roberts et al., 2014. They present several scenarios, some of which result in modest ozone depletion (see their figure 8).

Response:

Yes, we don't doubt that there are modest O₃ depletion possible. But what is not proven today if we can have a complete ozone destruction in the centre part of the plume. Such proof can be only gained by airborne measurements.

Further in the article Roberts et al, 2014 the authors write in the text : “ the single-box simulations presented here that predict the downwind trend do not simulate the ozone distribution across the plume cross section. Ozone loss is typically greater in the plume centre than near the edges”

Means the lines shown in Figure 8 are not spatially dissolved and don't exclude a heterogeneous distribution of O₃ in the plume.

The author further argue that O₃ could be a limiting factor for the formation of BrO, this still has to be proven, because this would be the case when O₃ would be reduced close to 0 in part of the plume. Spatially resolved measurements in the plume were difficult before the advent of drone based measurement, so they are becoming now possible with the instrument developed in this study.

It's true that only one study (thus far that I'm aware of) has coupled airborne measurements with model results (Kelly et al., 2013). In that case the model parameterization was constrained as best as possible by field measurements and did not predict complete ozone destruction in the plume. In fact, good overall measurement-model agreement was found, suggesting that the model captured the major pieces of the chemistry in that case. Unfortunately many of the most important species involved in the relevant chemistry are hard to measure, so models are critical for understanding these unique systematics. This comment should be reconsidered, although I agree that more measurements are needed.

Response:

We are not sure how we should understand this statement of the reviewer. Since we already state that measurements are needed we saw no necessity for further changes in the text.

L.303: Given the flammable and explosive nature of ethylene, is it reasonable to suggest flying such a payload over fires or cities? The conclusions need to reflect the limitations of the current approach.

Response:

See above - additional section 2.1

Table 1:

- Can a plume age be calculated for the listed measurements?

Response:

An estimate of the plume edge would have a very high error as plume speed was not measured during the campaign. So unfortunately we cannot calculate a meaningful plume age

- Why is the correlation coefficient and r^2 value listed? Isn't this redundant?

Response:

The reviewer is right but we would prefer to leave both values, although certainly R^2 is not strictly necessary

- How do the derived O₃/SO₂ ratios compare to other measurements from Etna (e.g. Surl et al. 2015)?

Response:

The O₃ depletion in Surl et al., 2015 (15-45%) and the one in Vance et al. 2010 (15-40%) are relatively similar to the one in our study where we determined a max. O₃ depletion of 15-59% during the various flights.

The O₃/SO₂ ratios are higher in our study as we measured in a more diluted plume compared to Surl et al. 2015

*We adapted the text of the revised manuscript in line 334-336: "While our finding is consistent **with measurements by Surl et al., 2015 (15% - 45%) and Vance et al., 2010 (15% - 40 %)**, which also indicate a strong anti-correlation between SO₂ and O₃, the observed O₃ depletion within the volcanic plume presents still an intriguing scientific puzzle."*

- What was the humidity inside the plume?

Response:

We revisited our data acquisition, and as expected the RH was highly variable between the days and the flights. The highest relative humidity was measured on June 13th and resulted up to 90 %. In all other flights the relative humidity was significantly lower, down to 10% The measurements were carried out at altitudes mostly above 3300 m in the volcanic plume, so at relatively low temperature, means a high water vapor content cannot be expected and as explained earlier would result in a very small additional error so not change significantly our results. Upon acceptance of the manuscript all measurement data including RH measurements will be available on Zenodo and in accordance with AMT data availability policies.

- At which altitudes was the plume measured?

Response:

The pressure displayed in color on the O₃ measurement plots is a good indicator for the elevation. The plume height was close to the summit crater height which is about 3300 m, we don't think that this is a relevant information for the table.

Figure 2:

- What are 'normal' measurements? Please clarify or refer the reader to the text where this is described.

Response:

We agree with the reviewer that 'normal' measurements is not a meaningful phrase and therefore rephrased the Figure caption:

“The black points display dark current measurements taken in the field by using an O₃ scrubber placed on the entrance, this was usually done before and after each measurement flight. ”