Detailed response to Luke Surl comments

We would like to thank Luke Surl for his positive review and for his helpful comments and suggestions to improve the quality and clarity of our manuscript.

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

1. Introduction

The introduction provides a reasonable background to the field. I would suggest that the following are additionally addressed:

• Prior studies such as Rüdiger et al. (2018) and Karbach et al. (2022) have deployed drone based in-plume measurements for other gases, notably SO2. Such drone based systems should be briefly referenced.

Response:
We believe that this would distract too much from the actual topic of presenting a new developed miniaturised CL-O3 monitor. It would only unnecessarily lengthen the introduction, and we therefore prefer not to make any changes to the text in this regard.

• So as to highlight the advantages of the VOLCANO3 being drone-deployed, the introduction should overview the settings for prior O3 measurements within plumes (i.e. aircraft based or ground-based and relying on grounding plumes)

Response:
In our opinion this topic is already well covered in our introduction, citing most of the previous volcanic plume studies for O3. Nevertheless, we added a small clarification in line 95 emphasizing the logistical challenges accessing volcanic plumes for O3 measurements in previous efforts.

So far the following O3 measurements within plumes have been referred to, including the overview article of Vance et al., 2010:

"Consequently, SO_2 typically dominates UV absorption in volcanic plumes and prohibits an accurate quantification of the O_3 UV absorption signal (Kleindienst et al., l993; Leston et al., 2005; Williams et al., 2006). The correction of the data with simultaneously measured SO_2 (Kelly et al., 2013) or the application of selective SO_2 scrubbers (Surl et al., 20l5; Vance et al., 20l0), however, are difficult and – at best - introduce significant additional uncertainty. "

"Field studies (using CL as well as short-path UV absorption instruments) have shown varying degrees of O_3 depletion across different volcanoes, in some cases up to 90% O_3 loss compared to ambient levels were reported (e.g. at Mount St. Helens, USA, see Hobbs et al., l982). In other cases, no O_3 depletion was found (e.g. at Kilauea, Hawaii, USA, see Roberts, 20l8) which was explained by low concentrations of halogens ***and is supported by measurements by Kern et al, 2018****. "*

"Measuring O_3 levels in volcanic plumes is challenging and often relies ***on substantial logistical efforts such as aircrafts or requires specific meteorological or topographical conditions to access the plume with ground-based instruments.*** *The aim of this study is to provide a technique for reliable O_3 measurements in volcanic plumes. Building upon previous studies, this work focuses on employing gas-phase chemiluminescence (CL)-based O_3 monitors for volcanic plume measurements (Hobbs et al., 1982; Vance et al., 2010; Carn et al., 2011)."*

2. The principle of CL-O3 monitors

This section describes, technically, the theory of chemiluminescence and reports the overall calculations that produce mixing ratio numbers as equation 1 and 2. This is useful and generally well described. The assignment of units to the parameters here needs to be consistent, with explicit units for pressure and temperature.

Response:
We have carefully reviewed the section again and added the requested information in line 115/116

*"p is the ambient pressure **in Pa**, T the ambient temperature **in K**, "*

We didn't find any further disagreement

3. A compact CL ozone monitor

This section would be improved by a photograph of the system, in addition to the schematic shown in Figure 1.

Response:
We now added a photograph of the system as Figure 1 b.

There is a mismatch between the text and Figure 1 – there are references to labels A-D in the text but no such labels on the Figure.

Response:
Sorry indeed this might have read misleading. With the new added Figure 1b we adapted the text accordingly.

The section on CL-Monitor Characterization is useful for replicability. Some minor comments regarding this:
• It would be helpful to know if such correction/calibration is required for each deployment.

Response:
The monitor showed quite stable behaviour, however a regular calibration is advised. We added a sentence:

"Although VOLCANO3 demonstrated stable behaviour, it is advisable to perform a regular calibration check before each measurement campaign."

• The parameter acal should be defined immediately after its use.

Response:
You are right we shifted the sentence "a_{cal} is the calibration constant" two lines above.

• The O3 generators for calibration are external to the main devoice. The specific O3 generators used in this study could be replaced with alternative model. Therefore, the wording should clearly state that "In this study [these devices] were used".

Response:

We agree and change accordingly. In line 168/169 it reads now: "The CL O_3 monitor is calibrated using an O_3 generator, ***in our study*** *primarily the Ozone Calibration Source Model 306 by 2B Technologies."*

• I assume the constant O3 periods discussed on line 180 are during calibration. This should be explicitly stated.

Response:
We are a bit confused by this comment. Former line 180 is indeed in the calibration section describing how the measured O_3 values during the calibration are gained.
We copy here the lines the reviewer is referring to and don't see a point for further clarification.

"The CL O_3 monitor is calibrated using an O_3 generator, in our study primarily the Ozone Calibration Source Model 306 by 2B Technologies. It is a portable O_3 generator and can provide O_3 in the range of 0 to 1000 ppb. Additionally, the O_3 generator ANYSCO type SYCOS KT-O_3/SO_2, which can provide 0 and 150 ppb of O_3, was used. To calibrate the monitor several calibration measurements with varying O_3 mixing ratios in different sequences are made. For the periods of constant O_3, the converted signals are averaged and plotted against the sampled O_3 mixing ratios as shown in Fig. 3. "

• As written the text in lines 190-193 describes only generating a step-up in O3. If a step-down was also tested, as implied on line 194, this should be explicitly noted.

Response:
Accordingly, to the suggestion of the reviewer we added few words in former line 192, now213ff:

"Once a stable mixing ratio is achieved, the hose can be swiftly connected and disconnected to and from the monitor, respectively."

4. Field measurements

This section describes a field campaign at Etna where the VOLCANO3 instrument was deployed and produced promising results.
Section 4.1 and Figure 4 demonstrate that VOLCANO3 can produce typical vertical O3 profiles.
Section 4.2.2. describes the instrumentation used in the campaign. VOLCANO3 is paired with "little RAVEN" as described in Karbach et al. (2022) for various measurements including SO2. This is a critical element of the system, as without these volcanic plumes could not be identified in the signal. The weight of little-RAVEN should be given in this section, as it is useful for the reader to know the combined payload of the two instruments.

Response:
We added the weight and a little description of little RAVEN in the text
"SO_2/CO_2 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 SO_2 sensor (calib. range: 0-16 ppm), CO_2 sensor (K30 FR Senseair, not used in this work), temperature, humidity & pressure sensor (BME280). Total weight: approx. 300 g"

"little-RAVEN" has an SO2 saturation point of 16 ppm. This is a significant limitation and the current presentation at line 250 is too late. I suggest presenting this information within section 4.2.2.
Section 4.2.3. discusses the four flights of the campaign.

Response:
The calibration range of little RAVEN is now mentioned in section 4.2.2 of the revised manuscript. Further the text is adapted in line 335-339 and the limiting factor of the SO2 sensor range is pointed out again as a future improvement for plume studies:
"For instance, to fully answer the question on O_3 distributions in volcanic plumes and if O_3 might be a limiting factor on the bromine transformation in volcanic plumes, more comprehensive measurement campaigns are essential ***and care should be taken to complement the O_3 measurements by applying an SO_2 sensor which covers the entire range of SO_2 mixing ratios in the plume under investigation.*** *"*

These flights are mapped on Figure 5. This map should clearly indicate the launch and return points for the flights. I also suggest adding arrows to the flight path so the reader can see the direction of flight.

Response:
We followed the suggestions and adapted Figure 5 as suggested.

Figure 6 shows clear anti-correlation of SO2 and O3 for one of the flight data sets. This is a very interesting result. Data for all flights are tabulated in Table 1. It is unclear how results where SO2 was above the saturation level were treated in the calculation of summary statistics, this should be made clear to the reader

Response:
Values where SO_2 was above the saturation level or equal were not considered for the calculation of summary statistics. Formally this had been stated already in the Figure caption:

"In-plume datapoints are defined according to the SO2 mixing ratio for values larger than 1.5 ppm and smaller than the saturation value of 16 ppm."

However, we added this information also to the table caption:

"The mean O_3 inside the plume is obtained by averaging over periods for which xSO2 > 1.5 ppmv and below 16 ppmv"

5. Future developments

This section makes some reasonable suggestions as to how the VOLCANO3 system could be developed, particularly in terms of reducing weight.
I would like to see discussion here that relate to the 16 ppm saturation point for SO2 measurements. This is currently a significant limitation, as it prevents identification of the most dense parts of the plume where near total ozone loss may be expected. Could VOLCANO3 be paired with alternative SO2 monitors?

Response:
Certainly, SO2 sensors with a larger range are commercially available and often applied and have been even used by part of the authors of this article in earlier works as referred to already by the reviewer himself - for instance Ruediger et al used an SO2 sensor up to 200 ppm. Our article is rather a proof of concept paper for the newly developed O3 monitor. But certainly, in future investigations of volcanic plumes SO2 sensors with a larger range should be used. As this is not part of a needed development we added this point to our discussion and conclusion section:

Line 296-298

"and care should be taken to complement the O3 measurements by applying an SO2 sensor which covers the entire range of SO2 mixing ratios in the plume under investigation"

6. Discussion and conclusion

At line 286 "ambient measurements in Heidelberg" are mentioned, but these are not mentioned in the paper.

Response:
We thank the reviewer for this notification. In an earlier draft of the manuscript we had also included vertical profile measurements from Heidelberg which were later excluded for easier comprehension and to avoid redundancy as we have included a vertical profile taken during the campaign at Mt Etna (Figure 4)
But overlooked this remaining half sentence noted by Luke Surl. The sentence has been changed now.

"Calibration measurements in Heidelberg, as well as measurements in the field, ..."

At line 289 the measurement accuracy is reported to be around 7% for 40 ppb O3.
The final sentence of this section appears to be incomplete.

Response:
We don't find the incomplete sentence, mentioned by the reviewer.

Other comments, mostly technical

• Throughout: Some numerical values use commas rather than dots for decimal markers. These should be dots throughout

Response:
Thanks for noting that we revised accordingly.

• Throughout: The format of mixing ratios (ppmv, ppbv vs. ppm, ppb) should be consistent Throughout.

Response:
We revised the manuscript accordingly.

• Line 13: Add "tropospheric" before volcanic plumes

Response:
We don't agree here with the reviewer as O3 depletion can also take place in volcanic plumes located in the stratosphere.

• Line 14. Suggest the statement "the underlying chemical mechanisms are still poorly understood" be changed. There exists now a reasonable theoretical understanding of the associated chemistry, albeit with some unknowns.

Response:
We changed to: "The underlying chemical mechanisms are still incompletely understood"

• Line 57: “in use since decades” change is “have been used for several decades”.

We revised the manuscript accordingly.

• Line 77: change “assumption” to “result” or similar. This phenomenon has been repeatedly observed and can be described in stronger terms than an “assumption”.

Response:
We don’t agree with the reviewer as most of the O3 measurements in volcanic plumes have been carried out without or very incomplete investigation of reactive halogens in volcanic plumes. Therefore, scientifically spoken it is still rather an assumption than a confirmed result.

• Line 120: Change format of reference.
Response:
The reference format has been adapted to match the style of the manuscript.

• Line 127: the presence of “(:” suggests some text or label is missing here.

Response:
There is nothing missing it is the start of an enumeration : 1)

• Line 150: change “in” to “at”

Response:
Changed as suggested.

• Line 211: suggest “Geological evidence suggsts volcanic activity since 0.6 million years” changes to “Geological evidence suggests it has been active for approximately 0.6 million year”. Alternatively, this sentence could be removed entirely.

Response:
Changed as suggested.

• Line 212-213: suggest removing “is undergoing significant morphological changes over time”, and changing “currently hosting” to “currently has”.

Response:
Done as suggested.

• Line 247: remove “basically”

Response:
Changed as suggested.

• Line 301-302: change “prove” to “proof”, change “those theoretical considerations” to “these model predictions”.

Response:
Changed as suggested.

• Line 418-419: Check URL format

Response:
Done.

- Line 480: Change “Tabel” to “Table”

Response:
Done.