Detailed response to anonymous reviewer 3 comments

We would like to thank the reviewer for her/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.

Major Comments:

- There is no discussion of the effects of water vapour on the system, despite the listing of water vapour as the primary gas emission from volcanoes. This needs to be addressed, as there are % level biases reported for ethylene-CL with water vapour

Several authors (e.g. Kleindienst et al. 1993, Ollison et al. 2013, Spicer et al. 2012) agree that a positive interference to water vapour around 3-4 ppb O3 per 10,000 ppm of water vapour exists in ethylene CL instruments.

Response:

This appears to be an intrinsic feature of the method, so there is no need to measure it again with each implementation of an ethylene CL instrument. The revised manuscript includes a new section 2.1 which discusses the choice of the CL technique in this work and also includes a paragraph discussing the water vapour interference.

"Measurements with the VOLCANO3 instrument are typically performed in volcanic plumes that have cooled to ambient atmospheric temperature, so that atmospheric water vapour concentration cannot exceed local saturation level. Typical H_2O concentrations range from 1000 ppmv – 20000 ppmv and are lower at high altitudes and cold atmospheric temperatures. This adds an uncertainty of O_3 measurements of about ±4ppbv when assuming 10,000 ppmv water vapour as "standard". Note that even though water vapour is the most abundant component of volcanic emissions, its mixing ratio cannot exceed saturation level.

We also added the term to the uncertainty calculation in section 3.2.3:

"The fifth term in Eq. (7) accounts for the well-established positive interference of water vapour on ethylene chemiluminescence. This interference is approximately 3–4 ppbv O_3 per 10,000 ppmv H_2O (Kleindienst et al., 1993; Spicer et al., 2012; Ollison et al., 2013). As volcanic plume measurements are conducted at ambient atmospheric conditions, water vapour cannot exceed local saturation and typically ranges between 1,000 and 20,000 ppmv.

To include this effect in the instrument uncertainty, we assume a typical value of 10,000 ppmv and thus treat the humidity bias as a constant additive systematic uncertainty, ΔH_2O, given by:

$$\Delta_{\mathrm{H_2O}} \approx 4\ \mathrm{ppbv}\ .$$ "

- Section 3.2.1 describes how the PMT's dark current is corrected for based on a fit with cell temperature rather than maintaining a constant temperature. L150 states that the fit parameters "are determined at regular intervals" which is very vague. It is not clear to me if this is something that has been determined in the laboratory, or whether the instrument is capable of determining this during normal operation. If this is the latter, I don't see from the instrument description or figure 1 how this would be achieved.

Response:

The shown dark current measurements in Figure 2 are measurements partly taken during laboratory experiments but also measurements taken in the field. Usually we took dark current measurements before and after each flight by simply placing an O3 scrubber at the inlet. To this data the Richardson function is fitted, which is then used to determine the dark current for other measurements. In other words, the dark current correction is determined in the laboratory (and crosschecked with dark current datapoints from measurements not specifically done to determine the dark current) and then only applied to the measurements. So the fit is done only once.

We agree with the reviewer that the original text might sound somewhat unclear. We therefore rephrased it to better explain our entire procedure of the dark current correction:

„In order to subtract the dark current as a function of temperature from the data the Richardson function (see Eqn. 3) is fitted to the dark current data points (see Fig. 2):

The values of the fit are $a_1 = (9.9\pm0.3)\cdot10^{12}$ *mv/K*^{2}, $b_1 = (-1.2\pm0.001)\cdot10^4$ *K, and* $c_1 = (0.55\pm0.003)$ *mV.*

- Figure 3 shows the measured dark current, and within the relevant temperature range there is variation of +/- 5 ppbv of O3 from the fit. It needs to be more clearly demonstrated how the authors arrive at only 1 ppb of additional uncertainty from this.

Response:

As explained in section 3.2.1 we performed a dark current correction based on the measured temperature of the instrument. In this section we also – in our opinion clearly – explain how the error of the dark current correction propagates into the error of the final result.

- More broadly a better diagram of the instrument would substantially improve the readers understanding. For example, the authors note that the ethylene flow is controlled via capillary, but do not state how flow through the instrument is controlled or measured – though this is required for their correction factor Ccon. Without sufficient control would this not vary with altitude?

Response:

The measurement of the ethylene flow through the instrument is calculated from the pressure measured at the minican and the ambient pressure since the flow through a capillary is determined by the pressure difference at its ends. The relationship between the pressure difference at both ends of the capillary and the flow through the capillary was determined experimentally with specific experiments in the lab, where we used pneumatic trough measurements. As a sanity check we also used the volume loss in the minican during measurement to determine the mean flow of ethylene during the measurement. Both experiments are in good agreement and can be empirically fitted. This fit can then be used to correct the change in ethylene flowduring the measurements. The variations arise mainly from the decreasing fill level of the minican but also due to altitude as the reviewer correctly noted, and are accounted for by continuously measuring both the minican pressure and the ambient pressure.

The rate of the total flow (air plus ethylene) f_{tot} through the cell is controlled by the rotary vane pump. A step-down converter enables to change the supply voltage continuously between 0:5 - 4:8 V (for an input voltage of 5 V), changing the flow rate from 5 to 34 mL/s. During the measurement the pump voltage was set to a flow rate of 21 mL/s.

As the reviewer correctly notes the calibration depends on the temperature and pressure at which the instrument operates, this dependence is described in Eq. (2).

- No mention of the time resolution (data acquisition time or averaging intervals) of the instrument is mentioned. From figure 6 data is presented at what appears to be ~2 Hz? This is relevant broadly for the reader to understand the instrument's capabilities, but also for the context of performance statistics such as LOD. LODs reduce with averaging, and the reported LOD of 1.13 ppb appears low for a 2 Hz measurement, with the uncertainty from dark current alone presented as 1 ppb. Moreover the stated LOD assumes the standard deviation in the dark current to be 0.4 mV, which from figure 3 appears to be a favourable case? Do the authors have data that they could use to perform Allan variance to provide further information on the LOD?

Response:

We thank the reviewer for this insightful comment. The instrument is sampling rate is roughly 3.5 Hz, and all uncertainty and detection limit calculations in Section 5.4 are based on the unaveraged time series. For the final plots (e.g. Fig. 6), we applied a 6 s rolling mean (20 data points are averaged) to improve readability. For the 6 s averaged data shown in the figures, the noise and thus the effective LOD are reduced.

- Section 3.2.4 Instrument response time describes the experiment as “swiftly connecting the hose to the monitor”. More details are required on how this was conducted – was the process automated using a fast acting valve? If this was performed manually, I would expect this response time to be biased high. A good understanding of the time response is relevant to the previous point surrounding data acquisition and averaging, and should be put into context with how those data are presented.

Response:

The connection and disconnection of the hose were performed manually. We acknowledge that this could slightly bias the estimated response time toward higher values. However, since the response time was obtained from exponential fits to the monitor’s signal ($R^2 > 0.9$), a small delay during manual switching would mainly shift the response curve horizontally rather than affect its exponential shape. Therefore, the derived value represents a slightly conservative estimate of the true instrument response time. We have clarified this point in Section 3.2.4 and discussed the potential influence of manual switching in the text.

Technical Comments:

- Reference need to be checked, for example: L36 USEPA 2023 does not appear in the reference list, the DOI for Kleindienst 1993 returns “not found”, the 2B Technologies manual is not referenced in the text.

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.

DOI for Kleindienst et al. 1993 corrected (DOI was correct, just the website apparently disappeared). We added the reference to the 2B Technologies manual. We replace the reference to: ‚L36 USEPA 2023' by ‚EPA 2020':

EPA 2020 - Integrated Science Assessment (ISA) for Ozone and Related Photochemical Oxidants (Final Report, Apr 2020), EPA/600/R-20/012, see: https://cfpub.epa.gov/ncea/isa/recordisplay.cfm?deid=348522

- Figures in the SI are referenced out of order to that in which they are presented e.g S4 is referenced on L88, S1 is not referenced until L234.

Thanks the reviewer for noting this error. We corrected the order of the Figures accordingly.

- Data availability – I see no reason why this data cannot be archived (along with processing code?) and referenced in this section, as per the AMT data policy?

Response: We agree with the reviewer and upon acceptance of the manuscript the data will be available on Zenodo.

L37 "nevertheless, nowadays and since many decades" needs rewording

Response: We reworded the sentence.

- L127 includes text from the figure caption for Figure 1.

Response: We deleted the additional text.

- L128 / 130 / 131 – the labels that this text is referring to do not appear on the figure, and instead seem to refer to Figure 13 of Bräutigam 2022.

Response: We added a new Figure 1b (a photo of the instrument as requested by other reviewers) and this includes also the before missing labels

- L128 t(h)rough

Response: Corrected

- L 211 "0.6 million years" should this read "0.6 million years ago"?

Response: No we didn't mean "0.6 million years ago" - the activity is still ongoing since then, therefore the text is not changed.

- L233 "Fig Figure 5"

Response: Done

- L266 The chemspider reference does not appear in the reference list, and I suspect provides a reference to the data where this is determined?

Response: We added the URL to chemspider (https://www.chemspider.com) to the reference list.