

Referee #1

We thank the reviewer for reading the manuscript very carefully, and providing detailed and interesting comments. Some of the comments, especially those regarding the figures had already been corrected for the AMTD publication. Our responses are typed below the respective reviewer comment for ease of reading, and refer to the line numbers in the revised manuscript.

C1) “This paper was an interesting read and the results of this study are certainly of interest to the atmospheric chemistry community. I recommend that this work be accepted after the following points have been addressed.”

“(1) The claim is made in the title and repeated several times over within the manuscript (e.g., lines 487-493) that this work constitutes a well calibrated measurement technique. However, this claim is not substantiated convincingly within the paper, at least not for the trace gases. While I would like to believe that the authors’ measurements and data treatment are accurate, what is missing from this manuscript is a comparison with independent validated measurements of NO₂, glyoxal and/or methyl glyoxal abundances. For example, there are concentrations given on lines 489 and 490 and in Figures 8 and 9. How did the authors verify that these numbers are indeed correct, given that there was so much drift in the mixing ratios? Just as was done for the aerosol, it should have been possible (and easy) to generate a calibrated gas stream containing NO₂, for example.”

R1) While we agree that using a calibrated gas stream of NO₂ may provide alternative means to demonstrate control over calibration, we respectfully disagree with the notion that any necessary information is missing from this manuscript. O₄ and H₂O also are trace gases, and the advantage of these particular gases over NO₂ is that we do not need to rely on making a calibrated sample, but rather know a-priori the O₄ abundance from a simple pressure measurement; for H₂O from measurement of RH and temperature. Rather than varying the concentration of the calibration gas, we have chosen to vary the effective path length, which is a less common, but equally valid approach that is fully sufficient to demonstrate control over calibration.

We feel that this approach also lies closer to the core of ‘uncertainty’ with CEAS calibrations when using highly reflective mirrors where factors like aerosols become much more important.

C2) “(2) The authors use both an open and closed cavity, and state that they made “the first well-calibrated CEAS measurements in open air.” It would therefore have been nice to see a discussion why the use of an open cavity would be preferred. Sure, there are obvious advantages because there are no inlet losses. However, not all surfaces are eliminated. There is, for example, the optical table, where gases could absorb to or evaporate from. Also, it seems to me that lower detection limits are achievable when aerosols are removed (e.g., via a filter) – see Table 3. Another potential problem with the open cavity design is that the purge gas could slowly fill the space between the mirrors when there is little air movement. Thus, it’s not at all obvious why the open cavity would be advantageous.”

R2) Conclusion section: We have expanded our discussion on the advantages of open cavity measurements. The ‘other losses’ mentioned by the reviewer seem to us rather indirectly related to the focus of the manuscript. We agree that there could be potential for such losses, but these

are not specific to our CE-DOAS instrument, and greatly reduced by eliminating the sampling lines and enclosure in the first place.

The reviewer is correct that sensitivity increases if aerosols are removed. However, for gases like glyoxal or methyl glyoxal, which associate with aqueous interfaces, eliminating any amount of surface area is advantageous. Further, despite the fact that the attainable path length with our instrument is limited to ‘one extinction length’, the attainable path length is for all practical scenarios still larger as that attainable for comparable base-path length White or Herriott cells, enabling more sensitive measurements also in the presence of aerosols. We follow the suggestion in another reviewer comment to discuss this benefit on the basis of absolute path lengths in the conclusion section.

C3) “The various “first” and “novelty” claims were distracting from the otherwise good work and sometimes unjustified. For example, cavity-enhanced absorption spectroscopy with light emitting diodes has already been demonstrated by several groups, and “calibration” of optical path length using O4 is hardly new in the DOAS community.”

R3) We have reworked the manuscript to synergize and reduce such claims, which we feel are justified in the blue spectral range (title, lines 33, 126, conclusion section). The application of O4 indeed represents a transfer of know-how from the MAX-DOAS technique. To our knowledge it is demonstrated for the first time at atmospheric conditions for a CEAS measurement. This is not a straightforward accomplishment, but required identification of the stronger LED, matching it with the highly reflective mirror. The application of the approach we developed is not limited to the blue spectral range, and we have included this mentioning in the manuscript (conclusion section).

Specific points:

C4) “line 31. 30 - 70 Mm⁻¹ seems like a narrow range for aerosol extinction values. Is there a reason for this?”

R4) Supplementary material Figure S1, and Section 3.8: The following text was added: “The dynamic range over which aerosol extinction was varied does not limit our conclusions. The range of aerosol produced was limited by the atomizer output, and needs to be regarded in relation to the aerosol free cavity loss. Indeed the lower value of aerosol extinction exceeds the extinction due to Rayleigh scattering in our cavity. The upper end value of aerosol extinction is the dominating over the combined Rayleigh and mirror loss. Our experiments vary the overall extinction loss by a significant factor of 2.2. See also Figure S1 in the supplementary material.”

C5) “line 50: As far as I know, the cells are known as Herriott-type, not Harriet-type. While both are widely used, they have been surpassed by astigmatic type cells (e.g., J. B. McManus, P. L. Kebabian, W. S. Zahniser, Appl. Optics (1995) 34, 3336). It would also be good to simply state the path lengths that can be achieved with the various types of cells rather than giving the difference as a factor.”

R5) line 50, conclusion section: We have corrected the spelling. We have included the reference to astigmatic cells, and now list attainable path lengths for a comparable base-path.

C6) “lines 54-66. This sentence is awkward to read (mainly because of the way papers are cited in ACPD). Consider consolidating the references in the form of a table, or add to Table 1.”

R6) line 56: We have modified the sentence to help readability. Indeed we had considered compiling the information into a table when writing the paper, but felt that a Table with the ambition for completeness was well beyond the scope of this paper. The compromise in the AMTD paper is that all efforts in the blue spectral range are compiled in a Table, and other work is cited in the text.

C7) “lines 76-78 “This potential had as of yet not been developed.” It sounds like this would be as simple as placing a (Teflon) filter on the inlet. This has really not been tried with CE-DOAS? I’d have thought someone would have done this by now.”

R7) line 84: The idea is to retrieve aerosol information and trace gas absorption simultaneously without loss of path length calibration (not just remove all aerosol information by filtering the inlet). We have modified language to avoid the possibility of confusion.

C8) “lines 149 - 140 – The reference Volkamer et al 2010 was incomplete; hence, I am not sure how IO and glyoxal are relevant to climate – are they?”

R8) The reference has been updated. We do not say that both gases are climate relevant, but that they are ‘potentially climate relevant’ for reasons described in the reference.

C9) “line 150 “the first well calibrated CEAS measurement” – were other CEAS instruments used that were not well calibrated (e.g., Washenfelder et al.)? Or are these the first measurements of a well-calibrated instrument? Consider rephrasing as to avoid the confusion.”

R9) line 167: We do not mean to imply that other CEAS instruments have not been ‘well calibrated’, and have now speak of our technique being ‘inherently calibrated’. Traditional CEAS instruments suffer from changes in the alignment of mirrors, mirror reflectivity, and or fluctuations in lamp intensity. Our approach is inherently insensitive to the latter, and alerts and characterizes changes in extinction that are due to the other factors as part of each individual spectrum.

C10) “line 154. Consider rephrasing the sentence as Figure 2 also shows a DMA and aerosol generation equipment. For a fraction of a second I wondered if a DMA was needed to run a LED-CE-DOAS....”

R10) line 173: Done.

C11) “line 160, line 173. Please state what constitutes a “good” match of LED and mirror reflectivity (wavelength? output power? beam size?)”

R11) line 185: We have added text to describe this: A good match of LED and R consists in suitable optical power output of the LED, limited out of band light from single pass transmission through the cavity, with the overall effect that the intensity past the cavity is reasonably constant (balanced) over the dynamic range of the detector.

C12) “line 184 reflectivity of 99.996% - is this measured or stated by the manufacturer? At what wavelength?”

R12) line 210, 223 ff: This is the measured R at the center wavelength of 455nm, this information has been added to the paper.

C13) “line 354-356. “We can account for the distortion in L by applying a correction factor $F(\lambda)$ to $L(\lambda)$.” This is perhaps the most interesting aspect of this paper. Couple of questions: 1) If the distortion is really in L, why not scale L instead of the cross-section (eqn 6)? 2) What values does F typically take? Since this method is applied in Figure 5, consider showing F as a function of wavelength in 5B.”

R13) Section 3.2: We now make a plot of $F(\lambda)$ available as Figure S1 as part of the ‘supplementary information’. Our approach decouples the wavelength dependence of L_{eff} (captured by F) from the absolute value of pathlength, which is determined from O4 or water. The choice to scale the cross-section is the most convenient scaling method to use, as F makes L_{eff} constant over the fitted wavelength range.

C14) “lines 365-377. The ratio of $ds/d\lambda$ can, potentially, vary for different trace gases, and may be shorter for IO than for NO₂. Please comment on the analytical uncertainty that this may introduce.”

R14) Experimentally we can say that the precision at which ds can be quantified is 1 cm, or 1% of the cavity length for water. This error is dominated by the accuracy of the relative humidity sensor. From diffusion theory the length scale for gas-diffusion against the direction of our purge flow can be shown to be much smaller, even for the more diffusive gases with low molecular weight, like oxygen. Assuming plug flow, a 50 cm³/min purge flow corresponds to a flux of 4.2 10¹⁸ molec/cm²/s over a 5cm² area (cross section of our mirror mounts); with a typical diffusivity of oxygen (0.22 cm²/sec) we apply Fick’s law to calculate that our purge sustains a concentration gradient of 1.9 10¹⁹ molec/cm⁴. For a realistic scenario (purge: pure N₂; cavity gas: air, STP) our purge flow sustains an oxygen concentration gradient of 5 10¹⁸ molec/cm³ over 0.26cm distance. For trace-gases the concentration gradient will be many orders of magnitude smaller, and gives rise to a correspondingly smaller length scale for back diffusion (10⁻⁷ cm for NO₂ @ 10 ppb). Any heavier gases would be less diffusive, and hence the error is even smaller. The analytical uncertainty from back diffusion is not significant. The manuscript was not modified.

C15) “line 455. Please define PSL.”

R15) line 267: PSL are ‘Poly Styrene Latex’ spheres. This had been defined already in the AMTD version of the paper.

C16) “line 478. Subscript missing for NO₂.”

R16) Correction already included in AMTD

C17) “line 488. Strike the word “room”. “between the mirrors” already defines the space and is more accurate.”

R17) We adopt the suggestion by the reviewer.

C18) “lines 496 – 497. “the first CE-DOAS detection of glyoxal and iodine oxide are accomplished.” Didn’t Washenfelder et al detect glyoxal using cavity-enhanced differential optical absorption?”

R18) We quote the Washenfelder work extensively in our paper, and do not feel that our language takes away from the value of their work. We refer to the first LED-CE-DOAS detection of glyoxal and IO. Notably, DOAS is strongly affected in the blue spectral range by the variable Xe-emission peaks used by Washenfelder. Our LED overcomes this limitation, and hence we consider the use of DOAS worth highlighting. We acknowledge that the technological advances from the bright LED identified in this work will benefit IBBCEAS retrievals as well.

C19) line 498. “The innovative use...” The use of diodes in CEAS is not new – see Ball et al., CPL (2004) 398, 68-74, and Kasyutich et al. Appl Phys B (2003) 76, 691-97 – so it’s not clear to me what was innovative here. Consider striking the word “innovative”.

R19) We did not say that use of LEDs is new, neither did we mean to imply this. We have modified the language in this section. Notably, the high power LED identified and characterized as part of this work, however, enables the coupling of high R with LEDs, lower noise, and balance light intensity, all of which are pre-requisites to realizing the ‘inherent calibration’ from O₄ and/or water. This is also more apparent now from the new Table 4 that compares detection sensitivity on a common basis. The conclusion section has been synergized and shortened.

C20) “Lines 492-531. The conclusion section is somewhat unusual in length and contains a lot of things that better belong in a discussion section. For example, lines 502-504: While LEDs are likely longer-lived and have an unstructured and constant in time emission spectrum, these are not conclusions of these study but rather discussion points. Consider reorganizing this part of the manuscript.”

R20) The conclusion section has been shortened.

C21) “Table 1 – it would be informative here to have a column with detection limits and integration time.”

R21) Table 1: We have added mentioning of detection limits, where available.

C22) “Table 3 – define detection limit (3 sigma, 2 sigma) as a courtesy to the reader – I know it’s stated on line 408-409 but it took me 1 hour to find it there.”

R22) Done.

C23) “Figures – general comments. It was sometimes not clear what was plotted and why, and too many traces were on the same graph (e.g., Fig. 1, Fig 7b, Fig 3 etc) making the Figures unnecessarily confusing. Furthermore, the fonts and sizing of labels were inconsistent from Figure to Figure.”

R23) Figure fonts and labels have been standardized and clarified.

C24) “Figure 1 – I am not sure I fully understand this Figure as the caption is inconsistent with the graph. The caption says that are 2 scenarios plotted: free tropospheric conditions ($AOD = 1 \times 10^{-7} \text{ cm}^{-1}$ at 450 nm, thin dashed line); and polluted urban conditions ($2.5 \times 10^{-6} \text{ cm}^{-1}$ at 450 nm, thick dashed line). The thick dashed line appears at 10^{-3} cm^{-1} , while the thin line appears at 10^{-5} cm^{-1} . The latter two seem a bit high. Also, it would have been helpful if all quantities were explained. What is “mirror loss” and how was it determined? What was the equation used to calculate the path length? What Rayleigh scattering cross-sections were used etc.”

R24) Figure 1: The units for the left side of the graph were indeed incorrect- the proper label should read ‘Cavity extinction loss per traverse’. Thus the aerosol loss would then be divided by 100 to get the cm^{-1} extinction. The mirror loss term, as defined in equation 1, is $1-R$. The references for the Rayleigh scattering cross-sections have been included in the revised paper.

C25) “Figure 3 – caption is missing on the bottom axis”

R25) This correction had already been included for AMTD.

C26) Figure 4 – As this Figure has been published elsewhere, I recommend simply citing the earlier work rather than republishing the same information. Also, I am not sure why the dashed line for the Acton/Pixis would fall so far below the experimental points?

R26) Figure 4: This figure has only previously been published as part of a conference proceedings; it provides useful context (received praise from reviewer #2) and is still appropriate to publish as part of this manuscript. We liked to keep it, as it illustrates a key advantage of CE-DOAS over IBBCEAS retrievals. With CE-DOAS retrievals fluctuations in the light intensity do not affect the retrievals, and integrations over hours are possible, without any major deviation from theoretical RMS. This is not discussed in the proceedings paper, and a key advantage over other CEAS methods employed thus far.

C27) “Figure 5 – caption is missing on the x-axes. What are the uncertainties in the mixing ratios? It is stated that the cross-section is “scaled” by $F(\lambda)$. By how much? Since the scaling was wave length dependent, please add a panel showing the scaling factor as a function of wave length. Could the scaling factor be expressed as a function of the mirror reflectivity?”

R27) Figure 5: The axis labels had already been added in AMTD. As noted by reviewer#2, the scaling is really not specific to CE-DOAS, and transparent from the equations given in the paper.

C28) “Figure 6 – Panel A. Consider changing the word “average” to “effective” as “average” implies an arithmetic mean (which I am not sure is correct here).”

R28) This change has been included in the revised version of the paper.

C29) “Figure 7 – Panel A, vertical axes are missing titles and units. SCD is missing units. Panel B – I am not sure what the authors are trying to show in this Figure. Is it connected in any way to Panel A? How was the O4 path length varied? Also, I am not sure of the detection limits for IO: At 12:25 pm, it is somewhere between 1 and 2 ppb, but -5 ppb are measured. Shouldn't the detection limit be at least as high as the offset uncertainty?”

R29) Figure 7: The labels had already been corrected for AMTD; other corrections have been updated in the revised manuscript.

C30) “Figure 8 – Panels B and C. Please label the extinction values with a subscript of their wavelength. Panel D. I assume that the main point of this Figure is in the fact that at 12:20 pm, when the aerosol is removed, the NO₂ number density deduced remained constant, whereas the Slant column density changed. Please also add a panel showing the changes in [O₄].”

R30) Figure 8: We have added O₄ and H₂O SCDs to this Figure.