

We respond to the comments made by the referee below with our responses highlighted in red.

### Referee 3

High accuracy/precision measurements of aerosol light absorption continues to be a need as this measurement remains the controlling factor as realizing further reduction in the uncertainty in the aerosol direct radiative forcing contribution to global climate change. To this end, in situ techniques have been developed to address measurement bias in filter-based measurements that are reaching their utility limits. Chief among these in situ techniques is the photo-acoustic spectrometer. By directly measuring light absorption through the photo thermal effect, the PAS can provide a high accuracy measurement of aerosol light absorption. The “rub” is having a high accuracy calibration. To this end, PAS calibrations have utilized diluted NO<sub>2</sub> in air (or N<sub>2</sub>) and ozone in the RGB spectral range. However, with improvement in PAS measurement precision and because of growing need to better quantify the contribution of brown carbon (BrC) to aerosol absorption, new demands on improved measurement accuracy has arisen. But to address this need, improvement of the measurement accuracy of the calibration standard is needed. For example, while NO<sub>2</sub> works quite well at the green wavelengths, a photodissociation pathway limits the utility of this cal gas at 405 nm (a popular emission wavelength). The present study aims at tackling this gap by furthering the work of Fischer and Smith (2018) using ozone at the RGB wavelengths by carefully defining the PAS calibration conditions on bath gas. As one trained in chemical physics I particularly enjoyed the favor of this paper. As a matter of fact, this manuscript would easily fit in a journal of chemical physics. But, as the purpose of this work is to alert our aerosol community to the subtle but important consequences that bath gases have on energy transfer efficiency, and, in turn, on the overall accuracy of the PAS measurement, this manuscript is perfectly appropriate for AMT. This manuscript is very well written and thorough in its analysis, and thus deserves to be published. My comments are of a minor variety which can be readily corrected.

#### Response:

We are glad that the reviewer enjoyed reading our manuscript and we thank the reviewer for their very supportive comments. We address the reviewer’s minor comments below.

Page 2. Line 19: While discussing the measurement bias associated with the PSAP, the authors cite the Lack et al., study which reported a bias that ranges from ~50 - 80%. The authors could go a bit further and state that this bias exhibits an OA/BC dependence. While certainly not the focus of this paper, from a completeness point-of-view, citing this helps point to where some of the filter-based measurement bias likely originates from.

#### Response:

We agree with the reviewer on this point. We have modified page 2 line 19 onwards to read:

*Lack et al. (2008) report biases in the range 50 – 80% with larger biases associated with aerosol samples containing a large organic fraction relative to black carbon, although we have demonstrated recently that advanced correction schemes can remove the bias dependence on organic mass fraction with modest biases in derived absorption coefficients of up to 17% (Davies et al. (2019)). Biases are also attributed to processes...*

Page 3; Line 15: The authors write “. . .large NO<sub>2</sub> absorption cross section range causes saturation in the 405-nm spectrometers for concentrations. . .” This is a bit misleading. The primary issue for the use of NO<sub>2</sub> at 405 nm is that a photodissociation pathway opens up at wavelengths < ~ 420 nm. (See for example, Gardner et al., JGR 92 1987.) Please reword this to better reflect that photodissociation is what limits the use of NO<sub>2</sub> as a cal standard at 405 nm. Besides, the reason put forth by the authors that one must use the same concentration to calibrate both the red and blue channels sounds more like a strawman argument.

#### Response:

We agree with the reviewer. In our initial manuscript, we decided to avoid discussing the NO<sub>2</sub> photolysis pathway to avoid giving the impression that photolysis of a gas strongly degrades its utility as a calibrant; indeed, O<sub>3</sub> photodissociates at the wavelengths used in our work. The key point is that NO<sub>2</sub> is lost irreversibly through photolysis (forming stable NO and O<sub>2</sub> products)

and the nascent NO products are not efficiently quenched by air. On reflection, we have sided with the reviewer that we should state that the NO<sub>2</sub> photolysis pathway limits the use of NO<sub>2</sub> as a calibration gas and we have added the following statement after ‘preventing the fast (~1 hour) and simultaneous calibration of all our photoacoustic spectrometers from a single source of calibration gas’:

*Importantly, NO<sub>2</sub> photodissociates at optical wavelengths <430 nm, with NO<sub>2</sub> lost irreversibly from the sample to form stable nascent NO and O<sub>2</sub> products (Tian et al. 2013). This photodissociation pathway limits NO<sub>2</sub> as a calibration standard for photoacoustic spectrometers at short visible wavelengths.*

Page 9, line 7: What is the nominal signal level of the background contribution (S<sub>bgcorr</sub>) to the overall PAS signal. I’d like to have a sense of how great this background correction is. Presumably, since this contribution is constant irrespective of the aerosol loading, depending upon the background signal amplitude, this contribution could be more important at lower signal levels. Are we talking about S<sub>bgcorr</sub> = 0.1 Mm<sup>-1</sup> or 1 Mm<sup>-1</sup> or 10s Mm<sup>-1</sup>. I would like to have my fears allayed that in the limit of weak aerosol absorption signal (the atmospherically relevant situation) that the reported PAS signal for the aerosol is not the result of subtracting two big numbers to get a small number.

Response:

The reviewer raises a very important point. The background correction is indeed constant and is invariant with aerosol/ozone concentration.  $S_{corr}^{bg}$  is a corrected raw microphone response and has arbitrary values (not units of Mm<sup>-1</sup>). In atmospheric measurements (from an aircraft) of aerosol, the sensitivity of absorption measurements depends on absorption strength and this background response introduces uncertainties in the measured aerosol absorption of 0.2, 2.0 and 20.5% at 100, 10 and 1 Mm<sup>-1</sup> absorption strengths, respectively (see Davies *et al.*, Atmos. Meas. Tech. Discuss., 2019). Importantly for this work,  $S_{corr}^{bg}$  is typically <10% of the raw photoacoustic signal during ozone calibrations. We have added a statements on line 9 of page 9 to state:

*$S_{corr}^{bg}$  is constant over a calibration and typically represents <10% of the photoacoustic signal during calibrations with ozone.*

At the risk of being a bit pedantic, could you please reorder the legend on Figure 3b. As currently displayed, the traces are solid, dotted, and dashed, while the legend is solid, dashed, and dotted. This is certainly a cosmetic request, but makes it easily for the reader. Also, are error bars present on the PAS signal (and are just too small to be observed on the plot scale) or are they not present. If the latter, please add.

Response:

We thank the review for suggesting reordering the legend, which we have now done. With regards to vertical error bars, these error bars are already present on the PAS sensitivity plots (Figure 3). However, we had overlooked a statement to describe the error bars included in the figure legend. Therefore, in the figure legend for Figure 3, we have included the following statement:

*The measured data include vertical error bars that represent one standard deviation in the measured sensitivity, although these error bars are not visible on the vertical scale shown. Horizontal error bars represent the uncertainty in O<sub>2</sub> mass fraction arising from the standard errors in the mass flow controller flow rates that control concentrations of O<sub>2</sub> and N<sub>2</sub> in the bath gas.*

This reviewer is most intrigued by the potential consequences of reduced pressure at aircraft sampling altitudes on quenching rates. The authors kick this can down the road but this could be quite interesting from both a fundamental energy transfer perspective as well as a practical aspect. Staying with this theme, I cannot help but wonder if NO<sub>2</sub> as a calibration gas - available with either N<sub>2</sub> or air as the bath

gas - might also exhibit a similar quenching sensitivities to differing bath gas mixtures as displayed by ozone. As highlighted above, one would expect that bath gas quenching could shift the quantum yield for NO<sub>2</sub> photodissociation at 405 nm.

Response:

We agree with the reviewer that the pressure dependence in ozone quenching rates is of great interest. Indeed, we state on page 19 line 19 that studying the pressure dependence in this quenching is the subject of ongoing work. With regards to NO<sub>2</sub>, we refer the reviewer to work by Kalkman and Kesteren (DOI: 10.1007/s00340-007-2895-0) who show that the quenching is maximised for a bath gas in the limit of pure O<sub>2</sub>, although it is difficult to ascertain whether this maximum corresponds to complete quenching of energy into translational degrees of freedom for generation of a photoacoustic signal.

The last request, which the authors are encouraged to do, but certainly not required given the target audience. It would be nice to add a figure displaying the potential energy surfaces (even as a simple 2-D plot) for the various O<sub>3</sub> dissociation pathways. This is certainly the chemical physicist in me requesting this as that is how I can readily see what is going on. For those researchers not accustomed to chemical physics, such a figure would help clarify the subtle pathways present in ozone.

Response:

This was certainly tempting when we were writing the manuscript; indeed, three of the co-authors have chemical physics backgrounds. Instead, we refer the reader (Page 11, lines 23 – 27) to the work of Grebenshikov *et al.* (2007) to inspect the potential energy surfaces along the O<sub>2</sub>-O dissociation coordinate. We prefer to point the reader to the relevant literature and not repeat these readily-available figures in this contribution, particularly given the target audience.