

Interactive comment on “Oxidation photochemistry in the Southern Atlantic boundary layer: unexpected deviations of photochemical steady state” by Z. Hosaynali Beygi et al.

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We would like to take this opportunity to thank the referee for the comments and helpful suggestions. Your input was greatly appreciated and we hope you find the replies by the coauthors satisfactory.

Referee #2:

1. For me there are some unclearities about the calibration of the CLD instrument. Was it a one point calibration? I have some doubts whether it is applicable to calibrate the instrument with a standard of 2ppbv for measurements in the pptv range. Answer: During the campaign it was only possible to do calibrations in the mentioned range

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(given our limited resources on a month long ship cruise); this is because low pptv level calibrations (e.g. 50pptv) requires the use of large volumes of air in order to dilute the gas. However the linearity of the instrument was tested over a large range of levels prior to the campaign. These tests demonstrated that changing the concentration of the calibration gas only affected the linearity at very high concentrations (several hundred ppbs), which were beyond the concentration range observed during this campaign. Information derived from the infield calibrations were used in order to correct for sensitivity changes (cts/ppbv) of the instrument on a daily basis. It was observed during the campaign that the sensitivity was relatively stable with average values of 18121 (± 49.8) cts/ppb for NO and 10945 (± 129.5) cts/ppb for NO₂.

2. The authors describe that they determined the LOD "based on the reproducibility of the SA measurements carried out on a daily basis ...". Is this a common procedure? (One could determine the LOD as zero gas + 3sigma.) n sigma is not the confidence level, but the confidence level depends on n. IUPAC recommends 3 sigma for a confidence level of 0.99 in case the measured values are normally distributed. Why do the authors use 2? Answer: As the referee has pointed out, there are different defined methods for calculating the DL of an instrument. Our calculations are based on the following definition of the detection limit: "The concentration of an element that gives a signal equal to two times the peak-to-peak noise level of the baseline." (source: Daniel C. Harris, Quantitative Chemical Analysis, 6th Edition). For determining the DL in this case not only did we have data from Synthetic gas measurements (which is common practice for determining DL) but we were extremely lucky to also have night time values measured in the pristine conditions of the marine environment far away from any anthropogenic influence. A comparison of the STDEV of the synthetic gas measurements and the STDEV of the night time values showed good agreement between the two methods (table 1 and 2). Therefore our DL could be determined with better certainty than usually possible. About why we used 2sigma; since it is common practice as seen in other papers, not only for the CLD instrument but also for the other atmospheric instruments (from several different groups) that were used for this study

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as listed in table 4 (in the paper).

3. As the authors are interested in concentrations (and not only whether the chemicals can be detected or not) it might be reasonable to determine the limit of quantification (LOQ). Answer: The LOD was used as this value is normally calculated for the CLD instrument. Since this study included data from several different instruments and groups, the use of the LOD facilitates the comparison of the detection limits of the different instruments is given in table 4.

4. p 7052 line 8: It is not possible to compare measured values to a standard deviation. To decide whether two expected values are equal one can use e.g. the F-test. Answer: We agree with the referee. This mistake is due to the missing section in the sentence, we have changed it to: "The standard deviation of the measured night time values was compared to the standard deviation of the SA measurements."

5. In table 2 values are listed that are below of the indicated LOD. This does not make sense. Answer: We agree with the referee with regard to this point, however we would like to point out that we are not looking at an absolute number here, but rather at an average value over the course of one night. These values are only shown in the table for comparison sake and have not been used in any calculations in this study.

Technical notes:

6. p 7050 line 11: I suggest to leave away the hint to chlorophyll plots (unless they are important for the here presented study). Answer: We agree with the referee. We will remove the part of the sentence on page 7050, "including regional chlorophyll plots", as it does not have any significant relevance to the study.

7. p 7052 line 27: "relatively highest": erase "relatively" because highest can only be relative to something else. Answer: We agree.

8. p 7054 line 19: x in Ex and Ex should be subscripts. Answer: We agree.

9. p 7063 line 9 and p 7065 line 3: the singular of species is also specie Answer: We

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agree.

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