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Interactive comment

Interactive comment on "Development of an instrument for direct ozone production rate measurements: Measurement reliability and current limitations" *by* Sofia Sklaveniti et al.

Anonymous Referee #2

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This is a review of the scientific article "Development of an instrument for direct ozone production rate measurements: Measurement reliability and current limitations" by Sofia Sklaveniti et al. The paper describes in detail the design of an instrument to detect ozone production as P(Ox). The proposed technique is based on the principle of operation of the MOPS instrument (Cazorla and Brune 2010). The new instrument includes improvements related to sampling and sensitive detection methods. The authors include substantial technical information in regard to the design as well as simulations to assess its performance. They also discuss its advantages as well as caveats and limitations. The paper is well written. However, there are some significant aspects inherent to the development of this research that need to be addressed prior to potential publication. Below specific comments.

1. Sadanaga et. al. (2017) published an article in which they present an instrument to measure ozone production rates that share very similar strategies as the ones presented by Sklaveniti. The instrument proposed by Sadanaga et. at. is based on the MOPS differential measurement, but uses ozone-to-NO2 conversion followed by NO2 detection with a very sensitive technique. The conversion step consists of adding a large excess of NO to titrate ozone exiting the clear and shaded tubes. This work was published early in 2017. This conversion strategy is the same as the one proposed in the article by Sklaveniti et. al. Another similarity is the material used for the sampling tubes, which in both cases is quartz. However, Sklaveniti et. al. did not cite or discuss the article by Sadanaga. I can speculate that the authors were unaware of the paper by Sadanaga et. al. The ozone conversion strategy is one of the major aspects that would grant novelty to the article by Sklaveniti provided they had published it first. Therefore, academic rigour makes mandatory that Sklaveniti et. al. include a complete section to refer to the work by Sadanaga and discuss similarities and differences with their own instrument. The reference is: Sadanaga et. al., New System for Measuring the Photochemical Ozone Production Rate in the Atmosphere Environ. Sci. Technol., 2017, 51 (5), pp 2871–2878. DOI: 10.1021/acs.est.6b04639

2. I am concerned about the use of quartz for the ambient and reference tubes. Quartz is a material whose surface has chemically active sites prone to adsorption processes. Quartz was not used for the MOPS because significant ozone losses were observed under ambient conditions. The authors do recognize the limitation of using quartz and even acknowledge being unable to zero the instrument when both tubes are exposed to the sun. Nevertheless, it seems to me that the magnitude of the effect of quartz on ozone loss was not thoroughly assessed. The authors present only one test for ozone loss performed under sunny conditions. In addition, Figure 3 shows experimental data with a scale between 0-300 ppbv. I am concerned that the size of the scale is not revealing the true effect of ozone losses. More importantly, the difference in ozone

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Discussion paper

losses between both tubes could have a significant impact. Additionally, the way the experiment was performed possibly affected the results. For example, if a high concentration of 300 ppbv of ozone was first administered and then concentrations were lowered, this possibly yielded lower losses in magnitude than what potentially could be observed under real conditions. Authors should clarify details about the experimental procedure because high ozone concentrations would have a chemical treatment effect on quartz that ambient concentrations would not cause. From my perspective, the article would benefit if the authors included an evaluation of the effect of ozone losses under real conditions of ozone concentrations and sunlight. As a separate note, the article by Sadanaga also emphasizes in ozone loss tests in dark conditions. This is an additional similarity that needs to be explained.

3. In regard to residence time and flow pattern, the authors discuss their pulse experiment in terms of plug flow and compare their results with the ones for the MOPS. The second version of the MOPS includes substantial improvements to aim for laminar plug flow, so that air molecules reside approximately the same time inside the chambers. However, in the technique proposed by Sklaveniti, a 10% dilution with zero air is applied at the inlet. It seems that at doing so, the authors possibly induced a flow pattern that aims for complete mix as opposed to plug flow. Nevertheless, the discussion is done in terms of plug flow or laminar flow. This apparent contradiction needs to be clarified. Finally, did the authors evaluate a potential flushing effect cause by the zero air on the gases in the central jet? Are measured P(Ox) values similar with and without dilution? It would be appropriate to include some data to demonstrate the benefit of adding dilution to the main flow.

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