

**Review comments for “Qualification of an online device for the measurement of the oxidative potential of atmospheric particulate matter” (<https://doi.org/10.5194/egusphere-2025-2021>)**

This manuscript describes a novel instrument to measure aerosol OP online with two chemical reaction systems, AA and DTT and illustrates its performance with a wide range of characterisation experiments as well as a proof-of-principle field deployment.

This is a highly topical and relevant manuscript and I suggest publication of this manuscript after minor revisions as detailed below.

Line 62/62: It is mentioned in the manuscript that “*First, these methods **probably** underestimate PM redox activity due to the very short lifetime of some ROS...*”: In a recent paper by Campbell et al., 2025 (DOI: 10.1126/sciadv.adp8100) it is clearly shown that ROS and OP in a wide range of particle sources decay with half-lives of minutes to hours and that offline methods severely underestimate ROS and OP. Please add this reference.

Line 70: The instruments described in Fuller et al. 2014 and Wragg et al., 2016 are fully automated instruments, please indicate this more clearly. The current text suggests these instruments are “semi-automated”.

Line 76: In a recent paper by Campbell et al. 2024 (<https://doi.org/10.1016/j.envint.2024.109102>) a more or less continuous OP(AA) data set over three months is shown. Please correct the statement that there are no published continuous OP measurements.

Fig. 1: Upstream of the BioSampler, a “Filter holder with 20 $\mu$ M filter” is indicated. The function of this filter and the unit  $\mu$ M is not clear to me. Which particle sizes are removed here? Please describe in more detail.

Fig. 1: Why was the milliQ water reservoir on a magnetic stirrer? Please explain shortly.

Fig. 1: A reservoir containing DTT+DTNB+PM is shown. For the AA analysis, where are the AA and Biosampler flows mixed? Is there another reservoir bottle, that is not shown in Fig. 1? Or is the sample/AA solution kept in the detector for 30min? The AA analysis section should be explained in more detail.

Eq. 3: I assume V(BS) is variable over time, depending on humidity, temperature etc. How was V(BS) determined? Was the dilution by the addition of AA considered for V(FC)?

Line 104ff: This paragraph discusses the offline and online method together, which is a bit confusing. Please separate the description of online and offline more clearly.

Line 111/112: A 3-point measurement protocol was used to determine the consumption rates. How good is the linearity? Are any statistical analyses used to assess uncertainties of the kinetics determined?

Line 133: Measurements are repeated every 60 min. I assume this is the sum of 20min sampling and 30min analysis which leaves 10min. Please briefly mention what the 10min are used for.

Line 162/3: Same as above: the instruments described in Campbell 2019 and Wragg 2016 are fully automated. Please correct the respective wording.

Line 163: Eiguren-Fernandez et al. was published in 2017 instead of 2008.

Fig. 3: Maybe this is a misunderstanding. I think the particle collection efficiency of the BioSampler was characterized with KCl particles. The respective size distribution is shown in Figure S1. It seems that there are no particles above ca. 200nm.

How was the particle collection efficiency determined up to 5 micrometers? If this was all done with KCl particles, is the presumably very low number concentrations at large sizes (i.e., micron-size) not too low to determine a reliable collection efficiency?

Could you show a size distribution up to 5 micrometer of the particles used to calculate the collection efficiency as SI figure?

In figure 3 11.5l/min are shown. Later in the text it is mentioned that 10.5l/min are used. Please comment on this difference.

Line 244/5: When the particle collection efficiency decreases over time with the filling height of the BioSampler, how often does the BioSampler liquid has to be topped up? It is mentioned elsewhere in the manuscript, that the instrument presented here can run unattended for 2 weeks. Does the liquid content in the BioSampler stay constant over such a long time?

Line 249: Probably a typo: “summarized”, not “resumed”?

Line 299: It is mentioned that O<sub>3</sub> does not affect AA depletion. However, looking at figure S2, it seems that 50ppb O<sub>3</sub> increases AA depletion by about 1.5 to 2pmol/min. How does that relate to AA depletion rates at ambient concentrations (in units of pmol/min/m<sup>3</sup>)?

To interpret for example ambient data in figure 9a, where OP(AA) follows closely the diurnal ozone time trend such an assessment would be important, i.e., it would be interesting to know how much of the AA diurnal cycle can be attributed to direct oxidation of AA by ozone?

Other gaseous compounds (organic and inorganic) could also react with AA. If this was not investigated, please add a respective sentence that other gaseous components could potentially affect the measured AA depletion rates.

Line 307: Please indicate what the Cu and PQN concentrations in nM in the calibration solutions correspond to in µg/m<sup>3</sup> in air, taking into account the air sampling flow rates, the 20ml in the BioSampler etc?

Fig. 5: Calibration curves with PM are shown down to 5µg/m<sup>3</sup>. In the abstract it is mentioned that the LOD is about 20µg/m<sup>3</sup>. Please comment on this apparent discrepancy. How was the LOD in units of µg/m<sup>3</sup> derived?

Line 344/346: It is mentioned that the solutions are illuminated continuously, if I understand correctly, in the flow cells for detection for 10min (for AA) or for 15min (for DTT).

Was the degradation of AA not measured for 30min?

Was the DTT solution not pumped from the reservoir (labelled “DDT+H<sub>2</sub>O+PM” in Fig. 1) into the flow cell after being reacted in the dark for 15 or 30 min? Or did the reaction of DTT+PM happen inside the illuminated flow cell?

Fig. 7a: Are the relatively large error bars for the offline data and AA expected and typical for this offline method? If yes, you could emphasise more the much better repeatability of your online instrument compared to the offline method, which would be a big advantage of your instrument.

Line 401: It is mentioned that a “20µm filter” was placed in-line. Is this an impactor with a cut-off of 20µm or an actual filter? Please describe this device and its characteristics in more detail, especially its behavior with respect of retaining particles below 20µm.

Line 405: Please comment why the time resolution of the instrument increases when the DTT analysis is not done. I was under the impression that the two analyses (AA and DTT) are running in parallel.

Line 408: It is mentioned that 1.3ml of the BioSampler solution evaporate. Please indicate over what time span this evaporation was observed. Does that limit the time the instrument can be operated autonomously? Is the BioSampler liquid refilled automatically?

Fig. 9/S8: It seems that the diurnal DTT data is noisier than the AA data. Please add confidence intervals to the average diurnal cycles shown in figure 9. This would allow to estimate how much of the detailed DTT structure is due to day-to-day variability.

Line 448-452: The description that this instrument measures particle and gaseous OP at the same time is not consistent with the rest of the manuscript. As far as I could see Fig. S2 is the only place where gaseous responses of the instrument are characterised and I think the conclusion of this section is that gaseous components such as O<sub>3</sub> are not resulting in a strong instrument response (which I think needs more discussion, see comment above). If the conclusion section emphasises that gaseous OP is a main feature of the new instrument, then more data should be presented and discussed.