Review of “Development and field-testing of an online instrument for measuring the real-time oxidative potential of ambient particulate matter based on dithiothreitol assay” by J. V. Puthussery et al.

This study describes the development of an automated, on-line system to measure the oxidative potential (OP) of particulate matter using the DTT assay. Measurements of OP and DDT activity have been increasing substantially in recent years with the acknowledgement that this may represent an indicator of the toxicity of PM. The system described in this manuscript represents the first automated measurement of DTT activity, and is therefore an important contribution to the atmospheric measurement community. Overall, the authors present a detailed, careful, and deliberate characterization of the system performance. The extensive ambient deployment of the system goes beyond most method papers. The writing is clear, the paper is well organized, and the figures are of high quality. I have several issues with the manuscript: I see some problems with the authors’ attribution of the DTT activity to specific sources – it seems they are trying to explain their results based on what they expect, which does not necessarily agree with their actual observations. I also think that the different contributions of insoluble particles to the mist chamber samples is a bigger deal than the authors describe, and certainly contributes to the differences in OP between the offline and online measurements, but also to their troubles attributing the DTT activity to specific sources. I recommend the manuscript for publication after my comments have been addressed.

Specific Comments:

I assume that this has been addressed in the references cited, but some discussion of the particle collection efficiency by the mist chamber is needed.

The difference between the MC ROS and filter ROS is quite surprising (50% higher in the on-line system), and definitely indicates the contribution of insoluble components. Some discussion of Phillips and Smith (2017) should be included here. I think the major implication of this is that a direct comparison of the MC and filter samples is not so straightforward. The MC samples include a lot of insoluble particles which clearly contribute to the DTT activity (similar to the MeOH extracted samples), which is not the case for the water soluble extracts. This muddles the comparison of the DTT activity to the other chemical components.

Pg. 9, line 18 – 20: I disagree with this statement. The collection of insoluble particles does not indicate that the MC performs better than conventional filter collection and extraction, but rather that the MC is subject to an artifact that may need to be accounted for.

Discussion on Pg. 2, lines 25 – 27: I agree there is great utility in an on-line measurement of oxidative potential, but this argument is rather weak. If Cu is really the most important species driving DTT activity, is there any evidence that Cu undergoes chemical changes during filter sampling?

Pg. 3, line 5: I do not understand this sentence?

Pg. 3, lines 17 – 20: this is somewhat misleading, since the ancillary components (syringe pumps, distribution valves, LWCC, spectrometer) will in total cost many thousands of dollars. My guess at the total system cost is $12k - $16k, and while this represents a lower cost than a method using the PILS or LSS, I don't think this qualifies as "low-cost".

Section 2.2: give the manufacturer and purity of all chemicals and reagents.

Section 3.2: the strong RH-dependence on the remaining water volume is not consistent with other M.C. studies (e.g., Hennigan et al., 2018) – this may be due to inconsistencies between different mist chambers, but this difference is worth mentioning.

I really do not understand the results in Fig. S3 (and associated discussion in Pg. 8 lines 10 – 25). Why does a 50% change in the sample volume (either + or -) not result in a 50% change in the DTT activity measurement?

Pg. 12, line 10 – 11: I don't agree with this logic – the authors state that traffic at their site after 10pm is almost nonexistent, which would suggest some of the EC is aged.

Pg. 12, line 23 – 24: this does not seem consistent with the data in Figure 5. The WSOC diurnal profile is flat throughout the day. Most (if not all) of the WSOC during summer at this location should be secondary – how then do the authors attribute the afternoon increase in DTT to SOA?

Pg. 13, lines 4 – 11: I disagree with this interpretation of the data. I do not think that Figures 4 and 6 show a strong contribution of Cu to the measured OP. See prior comments, but it's important to acknowledge that Figures 4 and 6 cannot be directly compared due to the contribution of insoluble particles to the Fig. 4 measurements.

Technical Corrections:

Pg. 1, line 9: "using the dithiothreitol…"

Pg. 1, line 17: date format should be 4 July

Pg. 2, line 17: delete comma before 'PM'

Pg. 4, line 28: try to avoid beginning a sentence with a number

Figure 3: I believe the incorrect dates are given in the caption for the time the instrument was not operated.

References:

Hennigan, et al. Technical note: Detailed characterization of a mist chamber for the collection of water-soluble organic gases, Atmospheric Environment, 188, 12 – 17 (2018).

Phillips, S. M., Smith, G. D., Spectroscopic comparison of water- and methanol-soluble brown carbon particulate matter, Aerosol Science & Technology, 51, 1113 – 1121 (2017).