

We thank the referees for their insightful questions and comments, which helped improving the quality of the paper. Our answers are listed in the following in red, after the reviewer's comments, which are in black. The modifications in the text are marked in yellow.

Anonymous Referee #1

General comments:

The paper from Zhou et al., describes the development of a new online system for measuring the ROS concentration of PM. The paper makes a comparison between the newly developed online system and conventional offline system for ROS measurement. It also highlights the advantages of using an online system for measuring ROS concentration and the negative effects of long filter storage time on the offline ROS measurements. The authors then put the instrument in the field and used it many campaigns, which demonstrate the workability of the instrument. From reading the paper, it seems to me that the authors are confused with their terminology. They have been using the term oxidative potential and ROS interchangeably, which are actually different. Oxidative potential is the capability of the PM to generate the reactive oxygen species. What the authors are measuring is the ROS, which is already in the particulate phase. The species like quinones, metals can generate the ROS in a suitable reductive environment so they could be considered as the precursors of ROS, but the author's instrument specifically measures the particulate ROS and not the potential of such species to generate ROS. In that sense, I think the experiments conducted using Fe are meaningless.

In the literature, the oxidative potential (OP) is considered as a measure of the capacity of PM to oxidize target molecules (Janssen et al., 2014). This can happen by the capability of (a) particle borne components to act as reactive oxygen species (ROS) or (b) of particle borne components to mediate ROS formation in the target environment. Acellular chemical assays try to quantify either one or both of these effects. However, all assays have their limitations and do not provide a full answer to either of the two oxidation processes. We agree with the reviewer that the DCFH assay targets mostly point (a), by measuring the capacity of the PM components to oxidize 2',7'-dichlorofluorescein (DCFH) to the fluorescent compound dichlorofluorescein (DCF) in the presence of horseradish peroxidase (HRP). We do show that the efficiency of the reaction of DCFH to oxidants/peroxides varies substantially and that components known to induce redox cycling (e.g. metals and quinones) do not seem to react with DCFH. In the corrected version of the manuscript we highlighted the point raised by the reviewer that DCFH measures the capability of particle borne components to act as reactive oxygen species, rather than the potential of the components to mediate ROS formation. The related modifications in the new manuscript are as follows:

Page 8: 2) Response of the DCFH assay to selected components with expected capability to act as reactive oxygen species (Sect. 3.1.2 and 3.3.2).

Page 10: We also tested the response of the instrument to compounds expected to exhibit the capability to act as reactive oxygen species,

Page 10: Response curves of the selected compounds with an expected capability to act as reactive oxygen species compared to H₂O₂ are shown in Fig. 3.

Page 11: Also components known to induce redox cycling (e.g. metal ions and anthraquinone) do not seem to react with DCFH. Thus we conclude that DCFH measures the capability of particle borne components to act as reactive oxygen species, rather than potential of species to mediate ROS formation.

Our main goal of conducting the experiments with Fe and anthraquinone was to clarify potential matrix effects of these components to the ROS signal. Iron exists widely in different emission sources as well as in ambient particles (Dall'Osto et al., 2016; Valko et al., 2005). Water soluble Fe (II) exists in genuine atmospheric particulate matter (Oakes et al., 2012), which might react with the pre-existing ROS on particles thus influencing the ROS signal. We further evaluated the matrix effects of the genuine atmospheric particulate matter (as it is supposed to contain Fe (II)) to the H₂O₂ signals in the same Section (Sect. 3.3.2). We think these tests are indeed required.

Another concern is that the authors have not talked anywhere about the collection efficiency of their PILS. If they have done these tests in previous papers then they should report those figures again in this paper.

Our particle collector was constructed according to Takeuchi et al. (2005). These authors did an extensive characterization of the collection efficiency. For the combination of a hydrophilic cellulose filter, supported by a 5.0 µm pore size hydrophobic membrane filter they determined a collection efficiency for water-soluble particles of 80 % for 100 nm particles and higher than 97.7% for particles > 280 nm. This information was now added in the revised manuscript on Page 4.

Added text: The collection efficiency for water-soluble particles was determined by Takeuchi et al. (2005) to be 80 % for 100 nm particles and higher than 97.7 % for particles > 280 nm.

The reviewer feels that more details regarding the online instrument operation procedure and field set up needs to be added.

Based on the specific comments below and by the second reviewer, more specific information has been added in Sect. 2.2:

2.2 Instrument maintenance and portability

The instrument can be easily disassembled and rebuilt to be used in both laboratory and field campaigns. The instrument is not yet fully automatized. The following manual operations are required: 1) calibration; 2) replacing the hydrophilic and hydrophobic filters in the aerosol collector and the denuder every 2-3 days during ambient measurements; while in laboratory experiments, we exchanged the denuder for each laboratory experiment (~ 5 h) to be on the safe side; 3) regularly switching the air inlet channel to the particle-free mode (ROS blank) and checking the air flow during the measurement (before the experiment, during the experiment and after the experiment) to insure that the air sample flow was constant at 1.7 L min⁻¹; 4) cleaning of the ROS analyzer with 1 M H₂SO₄ for ~ 12 hours every two weeks to remove contaminations in the system; 5) replacing all the tubes used in the system every half year.

Specific comments:

Page 3, lines 10-15: It was mentioned that PILS is also called mist chamber. PILS is generally used to refer to a very specific aerosol collection device (Orsini et al., 2003). Whereas, mist chamber aerosol collector is usually used when referring to Cofer Scrubber (or mist chamber) (King et al., 2013). The device mentioned in this study is also an aerosol particle collector (Takeuchi et al., 2005), however the nomenclature used in this paper could cause some confusion for the readers. Hence, instead of referring as PILS it would be better to refer to it as aerosol/particle collector.

Indeed, the main part of our aerosol collector is a “mist chamber”. We use now the term “aerosol collector” throughout the manuscript (as the design is based on Takeuchi et al., 2005).

Page 10: Lines 5-10: The air stream 1.7 LPM was mixed with OF-UPW and sprayed into the mist chamber with 0.3 ml/min. Was there any loss in volume of OF-UPW which was filtered from the hydrophilic filter?

We think here you are referring to Page 4, Lines 5-10: Yes, there is a potential loss in the volume of the OF-UPW. The air leaving the mist chamber will be saturated by water by taking up some water depending on the humidity of the sample air. If we assume a dry sample air the uptake of water would be 10 %. Since we do our calibrations with filtered ambient air, we do not introduce a large error by not considering RH of the sample air in our calculations.

What was the volume of extract used for ROS concentration analysis?

The OF-UPW is continuously injected at 0.3 mL min^{-1} together with an aerosol sample flow of 1.7 L min^{-1} . The full aerosol extract (minus a small fraction lost due to saturation of the air as mentioned above) is pumped out of the aerosol collector and mixed with 0.4 mL min^{-1} of working solution. This resulted in a total flow rate of 0.7 mL min^{-1} .

We modified the description to (page 4): The 1.7 L min^{-1} air stream was mixed with the OF-UPW, which was continuously sprayed into the mist chamber with a flow rate of 0.3 mL min^{-1} , where the aerosol particles were incorporated into the water droplets. The liquid containing the water soluble fraction of the aerosol was collected at the bottom of the aerosol collector at a flow rate of 0.3 mL min^{-1} and then mixed with the working solution at a flow rate of 0.4 mL min^{-1} for analysis. This resulted in a total flow rate of 0.7 mL min^{-1} . Therefore, the measurement of ROS is continuous, which provides real time measurement of ROS.

Was the same volume used for both online and offline analysis?

In general, we extracted a filter punch of 14 mm Ø in 10 mL of OF-UPW. However, the filter area and/or the volume of the OF-UPW was sometimes adjusted to keep the extracted ROS concentration in the measurement range of the instrument. The extract was then injected into the ROS analyzer in the same way as the online method with a rate of 0.3 mL min^{-1} and mixed with the working solution at a rate of 0.4 mL min^{-1} for analysis. Thus the mixture of the flows was the same for online and offline analysis.

The text was added for clarification to the manuscript (page 5): In general, we extracted a filter punch of 14 mm Ø of the filter area in 10 mL of OF-UPW for 15 min at 30 °C. However, the filter area and/or the volume of the OF-UPW was sometimes adjusted to keep the extracted ROS concentration in the measurement range of the instrument. The vial was then vortexed (Vortex Genie 2, Bender& Holbein AG, Switzerland) for 1 min to ensure homogeneity and filtered through a $0.45 \mu\text{m}$ nylon membrane syringe filter

(Infochroma, Switzerland). The extract was then injected into the ROS analyzer in the same way as the online method with a flow rate of 0.3 mL min^{-1} and mixed with the working solution at a rate of 0.4 mL min^{-1} for analysis. Thus the mixture of the flows was the same for online and offline analysis.

The ambient air sampling duration adopted for the online system and the minimum sampling time required to get a ROS concentration which is above the detection level of the online system, should also be mentioned.

The instrument is measuring continuously. This is different from the method described in King and Weber (2013). We do not collect a certain amount of sample before the analysis is taking place. Basically our instrument collects 1.7 Liter air into a total solution of 0.7 ml for the analysis. We have a ROS detection limit of 2 nmol m^{-3} of sampled air as described in the manuscript.

Regarding the hydrophilic and hydrophobic used in this study, how frequently was it required to replace them? Was there clogging of filter pores (i.e. pressure drop) which could affect the air flow. More details about the daily maintenances (frequency of filter replacements, frequency of replacing the solvents etc.) and discussion about the portability of the system can be included. Some more discussion about the extent of automation of the system (was all the online system experiments described in this paper performed without any manual assistance?) would be beneficial.

We checked the air flow during the measurement regularly (before, during and after the experiment) to insure that the air sample flow was constant at 1.7 L min^{-1} . In case of the laboratory experiments we changed the hydrophilic and hydrophobic filters before each experiment to avoid pollutant interferences from the previous experiments as well as clogging of the filter pores. During ambient measurements we changed the hydrophilic and hydrophobic filters every 2-3 days. This does not mean that it was necessary to change it that frequently. It was more done so as a precaution. We did not systematically investigate this issue.

Usually we prepared the OF-UPW, which lasted for several days of continuous measurements. We did not observe an increase of background signal during this time. The instrument is not yet fully automatized. We needed to manually switch the aerosol inlet to the particle free inlet when performing the ROS blank measurements.

We added the description of the particle free inlet on page 14: Further, we regularly checked the ROS blank by measuring particle-free air by switching a 3-port valve and sampling through a particle filter (disposable filter units, Balston, UK) installed in another line.

Some other parts like the denuder, the hydrophilic and hydrophobic filters used in the aerosol collector need to be manually changed accordingly. We added the details of instrument maintenance and portability on page 7, Sect. 2.2, which we have mentioned in the previous general comments.

References:

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