Interactive comment on "An On-line Monitor of the Oxidative Capacity of Aerosols (o-MOCA)" by Arantzazu Eiguren-Fernandez et al.

Anonymous Referee #2

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This paper presents an instrument for semi-continuous measurements of aerosol oxidative potential with the DTT assay. Generally, the paper is well written and the data (what there is of it) appears to be of good quality. The subject is of interest and this is an appropriate journal for publication. At times, however, the authors make rather broad (generally very positive), but unsupported statements regarding their method. They also fail to cite other work and seem to implicitly criticize other methods based on general statements. One gets the distinct impression of a highly biased view. This tends to diminish what could otherwise be a nice paper. I suggest the authors try to present a more balanced paper. I also suggest that the conflict of interest statement be seriously considered. The fact the authors are from a company that aims to sell and profit from this instrument is surely a potential conflict of interest to be identified. It also tends to account for the tone of this manuscript.

> The authors appreciate the reviewer's agreement that the presented material is both appropriate and worthy of publication.
>
> We have rewritten the introduction to more fully describe prior methods, and to highlight in what ways the method we present differs, without stating which approach is "better". We point out that the online DTT assay method present is neither proprietary not incompatible with other collection methods. We also add a Disclaimer stating that the company holds patents on the particle collection technology, and that these patents are licensed to another entity for commercialization. As a note to the reviewer, our firm is <u>not</u> selling these instruments. Indeed, our position is essentially the same as that of a University that patents, publishes and licenses.

Specific comments are below.

Line 14. It is rather odd in a paper that will ultimately be published to refer to it as a manuscript. Suggest minor edit.

> The authors have changed the word manuscript to "paper".

Line 20, explicitly define extreme temperatures? What is the point of this line? What is it referring to? Why not just come out and state it; it is being asserted that this technique is better than steam based condensations systems (curiously this is often stated by these researchers but no data has ever been shown to support this, this is acknowledged later in the paper, lines 84-85).

> The authors are raising the concern of equilibrium partitioning changes at elevated temperatures when volatile, water soluble compounds are in the presence of large wet surfaces (as present in all condensation based instruments). The temperatures to which the sample is subjected in the o-MOCA system during collection is below 30-35^{o}C (Hering et al., 2014) which is closer to ambient conditions than the temperatures reached during collection using steam injection. However, the authors have removed this paragraph being speculative in the context of OP in particulates where the effects of gas/particle partitioning have not been explored.

Line 61, the authors should cite papers on other methods for measuring DTT online and offline using a different approach [Sameenoi et al., 2013; Sameenoi et al., 2012]. Their method is not the first online DTT instrument; two others have come before. These other DTT analytical methods should also be discussed.

> Authors have modified this paragraph in the introduction to recognize previous methods and on-line instruments developed to measure the OP of ambient particles.
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> *Several on-line systems developed to monitor the oxidant capacity of airborne particles have been reported previously. King and Weber (2013) reported a method using a mist chamber to capture soluble gases and particles, coupled to automated analysis based on the DCFH assay. Venkatachari and Hopke (2008) and Wang et al (2011) report an automated DCFH assay method for measurement of ROS activity*

for water soluble component of ambient particles captured with a Particle in Liquid Sampler. Yet, as pointed out by these authors, the DCFH assay is not as specific as the DTT assay described above, reporting also activity related to reactive nitrogen compounds. In addition, a study conducted by Chen et al (Chen et al., 2010) , showed that photo-oxidation by the laser light utilized for fluorescence excitation in the DCFH assay can create false-positive results and background values increase with time.

An more recent on-line method using the DTT assay is reported by Sammeenoi et al., who coupled their analysis to a Particle in Liquid Sampler (Sameenoi et al., 2012). This sampler uses steam injection to condensationally enlarge the particles, and impacts the droplets onto a surfaced that is continually washed by the water condensate, thus capturing the water soluble components associated with the collected particles. As both water-soluble (Fang et al., 2016) and insoluble components (Shinyashiki et al., 2009;Verma et al., 2012;Wang et al., 2013;Li et al., 2015) of airborne particles have been associated with the OP, it is important to have the ability to measure the contribution of each fractions to the total OP. This is important as each fraction may have different physiological effects (Delfino et al., 2010).

Line 67-68. Please provide references showing how the DTT assay can distinguish between metals and organics to overall OP.

A brief explanation about the procedure and references (Eiguren-Fernandez et al., 2015;Eiguren-Fernandez et al., 2010) have been added to explain how to differentiate between metal and organic activity.

Additionally, this approach has the ability to distinguish between the contribution of metals and of organics to the overall oxidative capacity by the selective removal of metal associated activity before conducting the assay. With the addition of a metal chelator to the solution we eliminate the metal associated activity to obtain the oxidative activity due to organics alone. Thus, the contribution of metals to the overall oxidative potential of the sample is obtained from the difference in the DTT activities without and with the chelator (Eiguren-Fernandez et al., 2010;Eiguren-Fernandez et al., 2015).

Line 68. Very few references are provided for DTT-health associations; also noted by the 1st reviewer regarding inflammatory markers. DTT-measured OP has also been associated with various health endpoints in recent epi studies. See for example, [Bates et al., 2015; Fang et al., 2016; Weichenthal et al., 2016; Yang et al., 2016].

A sentence and references have been added to address the reviewers comment regarding other health endpoints associated with particle OP.

Recent epidemiological studies have also found an association between the DTT-measured OP with various health endpoints such as asthma and congestive heart failure (Bates et al., 2015;Fang et al., 2016;Yang et al., 2016).

Line 72 to 73: It states, that the DTT method is too time consuming to be widely applied. Exactly what does that mean? How do the authors know that and what is the proof to support this? Proof that seems to be counter to this statement is that sufficient DTT data has been generated for use in epidemiological studies, see above. This is a broad, imprecise and possibly largely incorrect statement.

Although the DTT assay has been used in epidemiological studies the standard DTT assay is very labor intensive. It requires several steps: start the reaction time by adding the DTT, followed by the extraction of an aliquot at specific reaction times (between 3 and 5 time points), and stopping the reaction by the addition of a quenching reagent prior to adding the DTNB for final absorbance measurement. All these steps are done manually and there is a certain number of samples that can be run by an individual in a single day. Although recently a semi-automated method has been developed (Fang et al), not many researchers have this capability in their laboratory.
The statement regarding the labor-intensive and time-consuming procedure for conducting the DTT assay has also been noted by other researchers (Fang et al., 2015;Venkatachari and Hopke, 2008) and thus simply represents a practical limitation for broader adoption.

Line 74, how does the filter extraction process alter the sample, whereas the method presented here does not? Be specific. For example, what specific components that contribute to DTT activity would be sensitive to differences between the two different methods. Specific transition metals (Cu and Fe) and quinones are mentioned in the Intro. Eg, do Cu and Fe suffer from positive or negative artifacts? Charrier et al postulates that transition metals comprise much of the DTT activity at sites in California [Charrier and Anastasio, 2012].

It is true that transition metals comprise most of the activity of samples in California (Charrier and Anastasio, 2012;Eiguren-Fernandez et al., 2015;Eiguren-Fernandez et al., 2010) and that filter extraction should not result in changes in their OP activity. However, not all PM samples present trace metals as major components of their chemical composition. Depending on sources, the contribution of the organic components is more important (Verma et al., 2012;Ntziachristos et al., 2007) and in this case the extraction may result in changes in the chemical composition. In addition, the particle extraction efficiency from the filters depends on the particle size, with lower extraction efficiencies for the smallest particles (UFPs). A different extraction efficiency, as well as component solubility, may result in a different physical and chemical composition of the suspension, and thus, the OP measurements may not be representative of the real ambient sample.

Line 77, does the DCFH assay measure the oxidative capacity of PM? Be more specific distinguishing between what DCFH and DTT measures.

Both methods have been used to measure the oxidative capacity of the PM. The DCFH assay provides a measure of several ROS and RNS species, and thus, its non-specificity towards only the oxidative compounds may lead to an over estimation of the OP and total ROS concentrations of the particles. The DCFH assay also suffers from several well-known problems: an unstable nature with slow oxidation in air, and photo-oxidation by the laser light utilized for fluorescence excitation (Chen et al., 2010). Thus, DCFH detection can generate false-positive results and background values increase with time.

A sentence and Chen et al. reference have been added to indicate the limitations of the DCFH assay.

Yet, as pointed out by these authors, the DCFH assay is not as specific as the DTT assay described above, reporting also activity related to reactive nitrogen compounds. In addition, a study conducted by Chen et al (Chen et al., 2010) , showed that photo-oxidation by the laser light utilized for fluorescence excitation in the DCFH assay can create false-positive results and background values increase with time.

Line 78, Sameenoi reference does not belong in this list; it measures DTT. In fact in this paragraph the authors are mixing up two completely different assays and making broad statements that may not apply to both assays. Eg, heating the sample in the PILS may alter the peroxides on the particle in the DCFH assay, how does heating affect the components in the DTT case? Is there evidence to support these claims in other PILS data/comparisons? What specific DTT active components are affected (see note above)?

This paragraph has been modified to better identify the different methods used to measure the OP of ambient particles.
See authors response above.

Line 84, a rather odd statement, mainly innuendo; i.e., line starting with While it is not known: : :

The sentence has been rephrased.

Lines 85 to 90 (or so), while total DTT is undoubtedly of value, being able to separately measure water-soluble vs insoluble components is also of value since they likely have differing physiological effects, see for example [Delfino et al., 2010].

The reviewer is correct. It is important to characterize all the components that can induce oxidative stress, and there are studies associating the OP of WSOC with different adverse outcomes. Authors have stated the importance of both fractions on the total OP activity of the particles and as noted by the reviewer, the likelihood of different physiological effects. The authors are confident that o-MOCA could be configured easily to measure either or both, total OP activity or WSOC activity, by placing of an inline filter before the assay module.

As both water-soluble (Fang et al., 2016) and insoluble components (Shinyashiki et al., 2009;Verma et al., 2012;Wang et al., 2013;Li et al., 2015) of airborne particles have been associated with the OP, it is important to have the ability to measure the contribution of each fractions to the total OP. This is important as each fraction may have different physiological effects (Delfino et al., 2010).

The last line of the introduction is mainly speculation.

This sentence has been removed.

Section 2.1: It is repeatedly asserted that that this system quantitatively measures in-soluble species, yet no proof for this is provided. Based on the design it does seem feasible, but to make this claim it should be shown that insoluble particles are quantitatively collected and transported through the particle collection and liquid handling system.

Collection efficiency of the liquid system has been tested in the laboratory for both hydrophilic and hydrophobic particles. Consistently good collection efficiencies have been obtained independent of particle composition or phase.

Since collection is directly into water via droplet encapsulation of particles and the resulting suspended particles are close to being neutrally buoyant, there is little opportunity for particles to encounter surfaces during transport. Neutrally buoyant particles are driven away from walls in laminar tube flow (Matas et al., 2004) and transport in microfluidic devices has been studied and losses in comparable peek tubing were found to be negligible (Jochem et al., 2016). Based on these studies we assume that losses during transport from the collection vial to the reaction vial are minimal.

Line 107, what exactly does very gentle water condensation process mean?

The sentence has been removed.

Line 117-118. Again, speculation without support.

It has been reported that particle growth using the three-stage, water condensation growth system, occurs at moderated temperatures (30-35oC) and that samples collected with this technique report similar results for inorganic compounds as PILS and URG-filter based sampler, and filter collection for organic compounds such as PAHs (Eiguren Fernandez et al., 2014;Hecobian et al., 2012).

It might be worth pointing out that this particle growth method greatly limits the max sample flow rate. This has implications.

The collection system used for the o-MOCA runs at 3 Lpm. However, other systems based on the same particle growth technology have been built and successfully grow particles at 7, 15 and 100 Lpm. A liquid collector running at 7 Lpm and based on this technology has been used for the efficient collection of airborne viruses (Lednicky et al., 2016;Pan et al., 2016). The limitation on the sampling flow rate is not on the particle growth method but in the liquid collection, as the deposition of the particles in the liquid needs to be gentle in order to eliminated loses when impacting in the surface.

The information regarding the possibility of using higher flow rate liquid collection systems, and references, have been added.

The sample flow rate of the o-MOCA configuration can vary from 1.5 to 4.0 L/min, although liquid collectors with higher flow rates could be used with slightly higher collection volumes (Lednicky et al., 2016;Pan et al., 2016).

Section 2.2: The chemical module in this work is somewhat similar to that described by Fang et al [Fang et al., 2015]. The authors know of this paper as it is cited in line 165. Since Fang published the first automated analytical system for DTT analysis, and this paper uses a similar approach (dual syringe pumps with reaction vial), that work should be cited and comparisons made. How are they similar, how do they differ? What are the advantages of this system?

The systems are very similar in their approach regarding hardware components (syringe pumps and custom-made reaction vial assembly). The improved DTT assay stems from the elimination of the second step for quenching the reaction and mixing of the DTNB with the DTT containing solution such that the second reaction vial used by Fang et al is not needed. The mixing of DTT and DTNB is done online using a “mixing Tee”. This simplification minimizes sample dilution and thus increases the LOD of the method. Our system has also added a loop prior to the syringe pump to eliminate cross contamination of the samples with the internal volume of the valve.

A sentence has been added to indicate similarities and differences with the Fang et al. semi-automated system.

Although our chemical module has similarities to the semi-automated system developed by Fang et al (Fang et al., 2015), the o-MOCA has been improved to couple with a liquid particle collector, eliminate unnecessary steps in the DTT assay and to reduce sample cross contamination during on-line analysis.

Line 273, this is a rather broad and largely incorrect statement. Cross contamination is not a significant issue for all online systems, instead being mainly an issue with only liquid based systems.

The reviewer is correct, the sentence has been corrected to indicate that this is more of a problem with liquid-based systems.

As in many liquid-based on-line systems, the potential for carry-over from injection to injection, and sample to sample is of concern.

Line 260, too broad a statement, the results of Fig 4 apply only to this system.

The statement has been corrected and now reads:

Based on these results, the addition of 100 nmol was selected for further studies.

Regarding the use of a filter (frit) to remove insoluble particles. In this approach all samples will then pass through the filter containing collected insoluble particles from all previous samples. It would seem that this arrangement could potentially lead to significant artifacts, depending on ambient conditions.

This is an important point raised by the reviewer. High particle concentrations in the suspension, or continuous running of the sampler for long periods of time, could lead to frit clogging. The main problem resulting from frit clogging would probably be changes in pressure in the system and in extreme cases, back flushing of the liquid in the lines. Chemical artifacts, like reaction of the DTT with the particles retained in the frit are not expected as the liquid passes through the filter rapidly and reaction time between the insoluble, particle-bound redox active compounds and the DTT in solution is minimal. Changes in liquid pressure due to frit clogging could be monitored for replacement scheduling. In addition, any considerable changes could be noted by running the PQ standard at predetermined times (i.e. at the end of every sampling day, or 10 samples) and the deviation from the mean values used to evaluate system performance. Changing the frit during maintenance could be another possibility

Line 339. Not sure what unattended means in light of the previous discussion on stability of the reagents? Were the reagents changed daily or were they sufficiently stable?

Running the system unattended means that the system ran without having a person changing sampling water, reaction solutions or cleaning lines. The optimized system started running and collecting samples on Friday and ran through the weekend without any personnel participation.

Field testing data to prove the performance of the instrument is very sparse consisting of only 3 days of operation and no comparison to other standard methods, such as filter collection and analysis. This is a major weakness of this paper. (As an aside, the time axis in Fig 6 is difficult to read). For example, in the field data analysis it is claimed that the measured DTT activity follows a similar trend as PM2.5 mass and BC concentrations. From Fig 6, this seems unlikely. Why not do a regression analysis and report the correlation to support this. Even better, run the instrument longer and provide a stronger data analysis section truly demonstrating the power of the instrument. Essentially, the very limited

field data provides little evidence that the instrument is accurately measuring DTT. That is, magnitudes seem reasonable compared to other studies, but really there is not evidence that the observed fluctuations in DTT are real. This is surprising given the emphasis afforded to this in the conclusions.

The validation of the system was based on a well characterized diesel exhaust particulate (DEP) sample. The DTT consumption rates obtained with the o-MOCA and the standard benchtop method were similar, so authors are not concerned about "the instrument measuring accurately the DTT activity". However, if the reviewer's intent is to say that we are not sure how well the measured DTT activity represents the "real" OP of the collected samples or the DTT activity measured by a more traditional filter extraction based approach, he is correct. Nevertheless, OP measurements using the DTT assay on filters have not been proven to be "accurate" either, as filter collections are known to have sampling artifacts, chemical changes may happen during the long sampling periods, and extraction processes may also change the properties of the samples.

Authors agree that further comparisons are needed between different methods; however, the results between OP measured from the suspension and filter collections may differ. Differences between collection and analysis methods may not prove that either the o-MOCA or the filter collections are reporting the real particle OP. In addition, it is difficult to collect enough PM2.5 mass in 3 hours on a filter for conducting the standard DTT assay, which would lead to incorrect measurements of the OP activity in the filter. A future field campaign, with longer sampling periods and parallel filter collections will help further validate the o-MOCA as a new system for measuring the OP of ambient PM.

As suggested by the reviewer, figure 6 has been modified to better show the different DTT activities measured and the PM2.5 mass and BC concentrations during the test period. Authors have also followed the reviewer recommendation and calculated the correlation between PM2.5 mass and DTT activity, and BC and DTT activity. Results have been added to the paper.

To better assess the validity of the results obtained with the o-MOCA, we determined the correlation between the DTT activity measured with the o-MOCA and PM2.5 mass and BC concentrations measured at the nearby AQMD station. PM2.5 and BC hourly data was averaged for the 3-hr period of collection of the o-MOCA. Good correlations with both, PM2.5 mass (r2= 0.60) and BC (r2=0.72) were obtained, Previous studies have also shown good correlation between DTT and mass and EC (Janssen et al., 2014;Hu et al., 2008).

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