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Atmospheric Measurement Techniques Discussions

Interactive comment on "An instrument for the rapid quantification of PM oxidative potential: the Particle Into Nitroxide Quencher (PINQ)" *by* R. A. Brown et al.

R. A. Brown et al.

svetlana.stevanovic@deakin.edu.au

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Reviewer Opening Statement

This paper reports on the development of a steam-particle-growth system coupled to a cyclone for droplet collection followed by analysis of the liquid for particle bound ROS with a fluorescence probe. Recently, a number of papers have been published describing various designs aimed at measuring particle-bound ROS. This paper adds an additional method to this group. The authors have done a series of careful experiments testing the performance of the instrument, however there are a number of major issues to address. 1) The particle collection system of the instrument is nearly identical to

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other instruments already reported in the literature, with the exception that the cyclone design differs; exactly how it differs is not totally clear since exact details are not provided. 2) The instrument described measures only ROS associated with particles, yet it equates measurements of particle bound ROS with other assays that measure completely different particle species associated with the aerosols ability to induce oxidative stress. This conflation adds to the confusion that seems to exist in the new field of aerosol research. Prior to publication, these two major issues should be addressed.

Author Response Statement

The lines listed by the reviewer in their comments corresponds to the original submitted manuscript and not the one published for online discussion. As such the lines and pages listed by the reviewer or not relevant to the comments.

Comment 1

A major issue is that the instrument described in this paper is essentially identical to a PILS with a cyclone droplet collector instead of impactor. Orsini et al (2008) describes an instrument with PILS coupled to a cyclone (which the authors cite), and Peltier et al (2007) specifically describes and tests a PILS-mini cyclone system (not cited in this work). Since the proposed instrument is so similar to these existing instruments, details of how the new instrument differs, such as what are the technical advances in this new instrument over existing technology. For example, why not just utilize the existing methods? It appears that the authors are implying that the cyclone design is novel, ie, that it produces what they call a standing vortex. If this is indeed the main novel feature, the exact details of how the cyclone was designed and constructed to achieve this should be discussed in more detail. As it stands it is doubtful a reader could reproduce the results of this paper due to insufficient detail.

Answer 1

The authors disagree with this statement strongly. This paper is titled “An instrument for

the rapid quantification of PM oxidative potential: the Particle Into Nitroxide Quencher (PINQ)" and as such is a paper regarding an instrument (the PINQ) which measures the oxidative potential of PM. The PILS is a particle collector, which is an entirely different category of instrument altogether. The PINQ uses a combination of chemistry and purpose built collection and measurement stages which is clearly different than any other instrument published or commercially available for this purpose. This has been done in order to create an OP measurement instrument with as high time resolution and sensitivity as possible (< 1 minute). The authors believe the reviewer has mistaken the purpose of this paper as a discussion of the IAC, the particle collection stage of the PINQ. A large portion of the paper is dedicated to the design and collection efficiency of the IAC, which is entirely necessary given that the PINQs performance is predicated on this and it has not been described in a publication previously. However, the IAC is a single, if important piece in the larger PINQ. It is predominantly named separately in order for readers to easily distinguish between discussion regarding the particle collection stage and those regarding the PINQ instrument as a whole. Despite this important note, the IAC itself is distinct from the PILS and other commercially available and published steam collection devices. The initial inspiration for the IAC does indeed come from the modified PILS with a "wetted-wall cyclone" described in Orsini et al (2008). However, the variations from this system are substantial and include (but are not limited to): A liquid cooling system on the growth chamber to improve heat removal efficiency for elevated temperature applications; a completely new steam generator design to improve system stability and flowrate changes; and the development of a solvent resistant version of the wetted-wall cyclone compatible with DMSO which was termed a vortex collector. The decision to introduce this new term is not due to a change in mechanism from the one described by Orsini (2008), in this papers abstract it also describes "a standing liquid vortex which coats the inside deposition surface". Instead this was intended to separate the design clearly from that of a traditional PM cyclone as their purposes and design focus are different as discussed in Sect. 2.2. Some modifications have been made to the manuscript in Sect. 2.2 to emphasize these differences and

their purpose in the development of an oxidative potential monitor. The authors were not aware of Peltier et al (2007). It is relevant to this study and has been integrated into the manuscript. As to the comment regarding the reproducibility of this study, all key conceptual information and design considerations, as well as published resources used in the development, construction and testing of this system are provided. As requested by Referee #1, more detail has been added on internal dimensions of the system. Further information regarding detailed construction information, schematics, etc would require a manuscript several times the length of the current one and would provide little utility. Instead, the following statement has been added to the data availability: For a more detailed description on the design and construction of the instrument or interest in instrument evaluation, please contact the corresponding author.

Comment 2

A second major issue with this paper is the conflation of particle bound ROS and aerosol species that produce ROS in vivo, which is now often referred to as oxidative potential (OP). The title states that this is a method to measure PM OP, but it is more precisely a measure of ROS associated with particles. The title should be more specific, eg, possibly changed to something like . . . rapid quantification of ROS associated with particles ... Also, in the abstract it should be clearly stated that particle bound ROS is being measured. Throughout the paper care should be taken to delineate the two. Thus, it would be best not to equate what is being measured in this work with OP, eg, Pg 2 line 17 states: In order to achieve ROS quantification, termed herein oxidative potential, ... The two, particle ROS and OP should be delineated as they are associated with different aerosol chemical species and have potentially different health effects. Particle ROS, what the authors call exogenous ROS is what this paper is measuring and which has not been associated with any adverse health effects in population studies; at least this reviewer does not know of any. Maybe the authors can add citations supporting why particle-bound ROS is an important thing to measure. An example may be direct inhalation of combustion products, like cigarette

smoke? In contrast to particle-bound ROS, endogenous ROS, which is often referred to as OP and typically measured with the DTT or GSH assay, has been associated with adverse cardiorespiratory adverse health effects in some studies (Abrams et al 2018; Bates et al., 2015; Weichenthal et al., 2016; Yang et al., 2016). Thus, it is strongly suggested that the term oxidative potential be removed throughout the paper and replaced with particle-bound ROS, or similar notation, except in the cases where DTT assay is specifically referenced, eg, Table 1. Overall, the point is that this research area lacks an agreed upon terminology, but no matter what the authors decide to call what they measure, it is very important that it be made clear that it is fundamentally different than certain other assays that measure aerosol chemical species that generate ROS in vivo (eg, DTT or GSH, etc). Related to this, if particle-bound ROS is so reactive and has a short life-time, the justification for this instrument, why would one expect it to be a significant health hazard to a large segment of the population? It seems the instrument is most useful for measuring particle-bound ROS associated with very fresh combustion emissions. Where specifically would one then expect to deploy this instrument. A discussion along these lines should be added. This would further help clarify the difference between what this instrument is measuring vs methods using the DTT or GSH assays (ie, methods measuring aerosol oxidative potential not particle bound ROS).

Answer 2

The research supporting the association between the OP and health has been limited (to very few studies, mainly from 1 research group) and it is still in its pioneer stage. Insufficient evidence in this regard cannot be used to predict and suggest an explanation for observed health effects upon exposure to particulate matter. Oxidative potential that depicts the presence and concentration of in-vivo present (or generated) redox species, measurable by the DTT, AA or GSH, is not a widely accepted terminology to the best of our knowledge. There is no means to detect the total oxidative potential using any cell-free assay and thus it would not be accurate and representative to use the term oxidative potential for any of these techniques, including the DTT.

In addition, ROS present on particles will also contribute to the OP. It has not been established what is the contribution of exogeneous ROS to the total OP, but excluding it will be inaccurate. It is also unclear what is the detection capacity of DTT for different particle types. So, saying that DTT is measuring the OP is also a bold statement as this approach is limited to certain solvents and reactive species. We agree that in the lack of data supporting the link between the ROS and OP, we should use more precise terminology. To this end, a short note on the inability of current probes to described as a measure of oxidative capacity has been added in Sect. 1.2. Furthermore, the BPEAnit measurements performed with the PINQ are now referred to as measurements of PM-bound ROS. Authors cannot agree with few comments highlighted by the Reviewer. “The two, particle ROS and OP should be delineated as they are associated with different aerosol chemical species and have potentially different health effects.” This statement is not supported by any piece of literature data and thus we could not consider modifying the discussion in the manuscript. “Maybe the authors can add citations supporting why particle-bound ROS is an important thing to measure”. Authors strongly believe that this is more than obvious and that the research in the area in the last 10 years demonstrates this. Importance of particle-bound ROS is beyond cardio-respiratory health effects. We believe that any atmospheric scientist is aware of the importance of particle-bound ROS. Once in the atmosphere, they will be oxidised easier, creating potentially more toxic form of pollutants, secondary pollutants. ROS on particles will change organic composition, that is found to be responsible for the OP, regardless of the approach used to measure it. In regards to the last question: “Related to this, if particle-bound ROS is so reactive and has a short life-time, the justification for this instrument, why would one expect it to be a significant health hazard to a large segment of the population? It seems the instrument is most useful for measuring particle-bound ROS associated with very fresh combustion emissions. Where specifically would one then expect to deploy this instrument.” It is well known that the ROS on particles can be short-living and long-living. Persistent free radicals are also very important for the measurement of the oxidative reactivity of particles. This instru-

ment is designed to measure the reactivity of particles in real-time and is not limited to the fresh combustion emissions. It can be deployed for atmospheric measurements, chamber studies, mechanistic studies, just to name a few. It can be also utilised to detect the change in oxidative reactivity over long periods of time. As indicated before, there is no doubt that the particle-bound ROS is very important for observed health effects, but only a very well designed, large cohort study (or a few of them) can shed more light into what is posing a health hazard to the large population.

Comment 3

Pg 2 last line is not correct as two online DTT systems have been developed, see Puthussery et al. (2018), and Eiguren-Fernandez, et al, (o-MOCA), which is cited.

Answer 3

Page 3, Line 3 has been clarified to indicate that the limiting factor is in reference to time resolution of the instruments possible rather than the inability to create a real time system. For the referees interest there is also a third DTT system (Sameenoi et al., 2012). Puthussery et al. (2018) is not included as it was published after the submission of this manuscript.

Comment 4

Last paragraph of section 1.3.4: There is a difference between a solid insoluble particle and a hydrophobic particle. Can the authors give an example of an insoluble particle bound ROS species? For oxidative potential, this is extensively discussed in Fang et al, (2017). This is an important question since the authors are using this as design criteria. (More on this below).

Answer 4

The terms hydrophobic and insoluble were incorrectly used interchangeably as, in the case of the DCFH and DTT assays, the chemistry is performed in an aqueous solution and hence hydrophobic particles tend to be insoluble in that context. This has

been corrected in the updated manuscript in several places including Sect 1.3.4. The emphasis here is not on insoluble ROS, but on insoluble particles. The PINQ system collects these particles directly into the BPEAnit in DMSO solution, removing the requirement for particle solubility in the collection liquid used in several of the systems discussed in Sect 1.3.

Comment 5

Section 2.2.4, What specific system used a copper steam generation system the authors refer to? This is not common practice in most steam systems, including the commercially available PILS. References to the copper system should be removed unless specific instruments using it can be identified.

Answer 5 The authors agree that the use of copper is not common in these applications and have removed reference to it from the manuscript in Sect 2.2.4.

Comment 6

In the particle mass collection efficiency method was the aerosol neutralized after nebulization for the IAC leg, as done for the SMPS leg? If not the reason for not doing this and implications should be discussed since one may expect highly charged particles. Also, how is the impactor affected by these highly charged particles (if there was no neutralization)?

Answer 6

Neutralization in an SMPS is widely accepted standard practice to ensure correct sizing. The entire flow path was conductive to minimize electrostatic losses. Beyond this the authors do not believe that aerosol charge has any influence on the setup and the results presented. Charge plays no role in IAC collection and would not influence the impactor performance.

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Why is the impactor installed before the particles are dried? Was the cut size of the impactor actually 0.1 μm or did it remove larger droplets, but ended up effectively removing dried particles with diameters less than 0.1 μm?

Answer 7

The purpose of the impactor was not to generate a sharp cut-off at 100nm, but to make the resultant size distribution as small as possible so that the mass distributions were predominantly in the ultrafine range. Placing the impactor first lowered the effective cut-off size once the particles are dried, enhancing this effect. The cut-off size can be estimated as $\sim$74 nm based on the logistic function portion of the fitted curve for the particle size distribution with the impactor present (See Figure S4). This has been corrected and expanded in the updated supplementary material in Page S3, Lines 9-15.

Comment 8

Pg 16, line 8, if the particles are dried, depending on the RH achieved, the ammonium sulfate may not be spherical. Why not do a sensitivity test to see how the findings change if say the DMA sizing is corrected assuming non-spherical particles.

Answer 8

Ammonium sulphate particles are not perfectly spherical, however smaller particles tend towards sphericality (Zelenyuk et al., 2006). The particles in question here have a mean diameter between 30 - 40 nm which were dried to $\sim$20 % RH. Whilst inevitably they will be slightly aspherical, they will only be marginally so. The most suitable dynamic shape factor found would be 1.02 (Biskos et al., 2006), which results in no significant change to the mass percentage present in the ultrafine range due to the significantly higher contribution of uncertainty from the function fitting (80 $\pm$ 10). Hence it represents a needless complication of the analysis. The supplementary material has been edited to add this justification of the sphericality assumption in Page S4, Lines

1-5.

Comment 9

Pg 16, line 10, why does the the Dp log scale make the area under the curve not proportional to fraction of overall mass when the size distribution is plotted as dN/dlogDp? That is precisely the point of the size distribution function.

Answer 9

dN/dlogDp normalizes each bin concentration by its size width in order to allow comparison between instruments with different bin resolutions. It is still a measure of particle size, not mass. Particle mass of a chemically homogenous particle is equal to particle volume multiplied by density, and hence is not directly proportional to particle size. As stated in the manuscript the assumption is that the ammonium sulphate particles are approximately spherical, and therefore the volume of a particle can be estimated using the equation for volume of a sphere. Therefore, the particle mass distribution can be estimated by multiplying the particle number distribution by the volume of a sphere and the density of ammonium sulphate. As can be seen in Figure S3 this cubic relationship between particle size and particle mass results in the ultrafine particles accounting for a large portion of the number concentration, whilst at the same time accounting for only a small percentage of the mass concentration. Therefore, in order to investigate ultrafine collection using a mass based method it was necessary to further reduce the mean size of the distribution, as was shown in Figure S3 using an impactor. The supplementary material Sect. S2.3 has been edited to better explain this.

Comment 10

Pg 17 line 4, typo, 0?

Answer 10

The authors cannot find the typo listed in the online discussion paper.

Comment 11

Section 4.1.3. What is the difference between a hydrophobic particle and an insoluble particle? Is DEHS insoluble in very dilute systems? Does DEHS remain as the original sizes generated in the droplet collection system (ie, cyclone}? The point is the one thing that is unique about this instrument is the claim that it can measure at near 100 % efficiency insoluble particles, but only one form is tested. What about collection efficiency of solid particles? Will the instrument actually collect solid particles and thus have the ability to measure ROS associated with solid particle surfaces, say for example, fresh soot particles. Are comparisons of this vortex cyclone to the Orsini et al or Peltier et al mini-cyclone valid since their test were done with truly solid particles (PSL or soot}?

Response 11

The confusion between hydrophobic and insoluble particles has been responded to in Answer 4. The authors have responded to the “uniqueness” of this system in Answer 1. The IACs purpose is to entrain particles into a solution of DMSO and the BPEAnit probe in order for reaction between the probe and sample to occur. As a steam collection device, the collection efficiency is determined by: whether or sample particles form liquid droplets inside the growth chamber; and what the collection efficiency of grown droplets is. The ammonium sulphate mass collection experiments addressed the question of the collection efficiency of grown particles. The results presented in the manuscript show that the mass of ammonium sulphate collected into the sample liquid was within error of unity with the sample aerosol mass for both fine and ultrafine mass concentration. The DEHS experiments address the question of droplet formation. DEHS was selected not because it is insoluble in the DMSO collection liquid, but because hydrophobic DEHS particles are difficult to grow into water droplets. By showing that the collection efficiency for DEHS has a cut off size of < 20 nm, it is evident that the supersaturation achieved inside the chamber is sufficiently high to grow even very small hydrophobic particles. Whether the particles are solid or liquid phase does not

influence this result. The combination of these two experimental results shows that PM is collected into the capture solution regardless of size or chemical composition. While no direct measurements of solid insoluble particles collected into the liquid stream were performed, there is no mechanism that would somehow prevent these particles from being collected in the same manner as those tested. If the purpose of the IAC were to perform direct measurements on solid particles collected into the liquid, deposition of solid particles in the liquid flow path would be the only necessary effect not considered in this characterization. However, the IAC system was developed specifically for use with the BPEAnit probe in the PINQ system. The vortex collector ensures that the particles are collected directly into the liquid rather than impaction onto a plate where they could potentially adhere and not fully react with the probe. Once collected into the liquid the reaction between the probe and sample particles is diffusion limited. This means that any potential deposition of solid particles in the liquid line will not influence the final ROS measurement as reaction with the probe has already taken place. Comparability between the IAC and the Orsini et al (2008) and Peltier et al (2007) systems would only be limited through differences in line losses in the instruments and the sensitivity of the detection methods. The efforts made to limit liquid residence time and volume would minimize this impact in the PINQ system. The updated manuscript highlights this consideration in the comparison between the different collectors.

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Please also note the supplement to this comment:
https://www.atmos-meas-tech-discuss.net/amt-2018-333/amt-2018-333-AC2-supplement.pdf

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