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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Atmospheric conditions and composition that influence $PM_{2.5}$ oxidative potential in Beijing, China" *by* Steven J. Campbell et al.

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Reviewer 2

Based on the following four acellular assays: ascorbic acid (AA), dithiothreitol (DTT), 2-7- dichlorofluoroscin/hydrogen peroxidase (DCFH) and electron paramagnetic resonance spectroscopy (EPR), the authors of this study compared the oxidative potential (OP) and reactive oxygen species (ROS) production of PM2.5 in Beijing summer and winter. Furthermore, the authors also analysed the correlation of PM2.5 OP or ROS formation with different composition of PM2.5 and concentrations of some trace gases. Overall the topic of this study is interesting. Whereas the written of the

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Discussion paper

manuscript needs revision. If the authors fully address the following concerns in a revised manuscript, this work may be publishable in Atmos. Chem. Phys.

1. The manuscript title highlights the research focus of this study to be the influence of atmospheric conditions and particle composition on OP of PM2.5. The beginning of the abstract also indicates that there exists uncertainty of the atmospheric conditions and specific chemical components of PM2.5 driving the OP. However, the abstract did not show any new results from this study that decrease this uncertainty. A specific, quantitative, or conclusive information on the influence of which atmospheric condition and different particle components on the OP of investigated Beijing PM2.5 is lack. Therefore, a more informative abstract is needed.

The main aspect here is to identify how the response of four of the most widely-used OP and ROS assays are linked to other atmospheric components and processes using one of the most comprehensive atmospheric datasets acquired in recent years, during the APHH-Beijing campaign. Such comprehensive comparisons are sparse in the literature, and this campaign provided a particularly unique opportunity to correlate aerosol OP and particle-bound ROS with a uniquely comprehensive dataset. This novelty has now been highlighted further in both the abstract and conclusion in the main manuscript. Such studies constitute an essential step in terms of understanding assay response, as a well-constrained understanding of aerosol chemical influences on these assays allow better understanding of their response and thus a firm foundation to determine the health-relevance of such measurements.

We have now added more information regarding the links between aerosol OP and toxicity in air pollution epidemiology; please see Section S2 of the Electronic Supplementary Information.

2. The motivation for using the selected four assay methods rather than other assays in this study is not well depicted. For instance, whether the AA, DTT, DCFH, and EPR assay results have closer association with adverse health effects of PM2.5? This

context should be introduced.

These four acellular methods are amongst the most commonly applied in previous studies, and provide information on particle-bound ROS (DCFH), superoxide production upon aqueous particle suspension (EPR) and catalytic redox chemistry (AA/DTT), thus provide a broad assessment of the oxidising properties of particles. Discussion added to the revised manuscript (see lines 101-105, Section S2 of the ESI).

3. As the authors indicated in line 80-81, different acellular assays all have differing sensitivities to specific particle components that may contribute to aerosol OP. Therefore, it is not surprising to see the various performance of different assays in testing Beijing PM2.5 (e.g., results in Figure 2). Moreover, it is reasonable to see the various correlations among different assays. The unclear thing is that why the combined application of the selected four assays has advantageous in providing new information than using individual assays?

Although previous studies have demonstrated that different assays have differing sensitivities, the role of aerosol composition in promoting these assay responses is unclear. The APHH campaign provides a unique opportunity to compare these commonly applied assay responses to a comprehensive dataset. Using all four assays provides a broad assessment of the oxidising properties of PM2.5, and correlating them to an extensive composition dataset provides a unique opportunity to explore which chemical components in PM2.5 drive the assay responses. We have added additional discussion in the abstract (lines 34-37) and introduction (lines 101-105) to clarify the novelty of simultaneous application of multiple assays in the revised manuscript.

4. Line 309-310: why the mass fraction of organic peroxides in PM2.5 increase in winter? How can you justify?

We have now amended this statement, to clarify that that the concentration of particle-bound ROS as measured by the DCFH assay is more abundant in PM2.5 in winter compared to summer, as we cannot definitively say the sole cause of the observation

is due to organic peroxides.

5. The authors referred elemental carbon (EC) to be non-redox-active. However, many studies found that EC or black carbon can produce âĂćOH in water. Thus, it is necessary to double check this interpretation.

We agree with the reviewer and this statement has now been deleted from the revised manuscript.

6. For the EPR analysis, the authors used Tempone-H as spin trap to measure the production of O2 - . Whereas, this probe can also react with âĂćOH and other radicals. Moreover, TemponeH is sensitive to the pH of solution samples. Have the authors measured the pH of PM2.5 extracts? What is the relative fraction of O2 - among all the detectable radicals?

We agree with the reviewer that Tempone-H can react with peroxynitrite, peroxyl radicals and other radicals, although this occurs at more than an order of magnitude lower rate than that for superoxide (Dikalov et al. 1997). In relation to hydroxyl radicals, in the past we have performed experiments with Tempone-H using the Fe-H2O2 Fenton reaction and .OH generators such as menadione, where we find that high concentrations of these agents are required to induce notable EPR signals. When working with ambient aerosol samples, we find that the EPR-Tempone-H signal can be attenuated by use of superoxide dismutase (SOD), but whereas .OH scavengers such as mannitol have only a marginal effect. Assessing the relative fraction of O2-. in the sample is complicated by the slow reaction kinetics of the radical scavengers that have high specificity for superoxide. However, we have shown that SOD attenuates the Tempone-H-EPR signal of diesel exhaust particulates (an archetypal urban air particulate standard reference material) to the same extent as it does the signal from the superoxide generating agent pyrogallol, suggesting the majority of the signal from this particle is due to superoxide (Miller et al. 2009). We have added text to the EPR methods section in the revised supplementary material manuscript to highlight these limitations.

We thank the reviewer for their suggestion to test the pH of our particulate suspensions. Due to restrictions on our lab access and ability to receive particulate samples from other institutions, this is not something we are able to check at the current time, but we will do so in future experiments.

7. Carefully check the type setting of the whole manuscript. For examples, proper use superscript or subscript for PM2.5 and NH4 + etc.

We have amended any errors in the revised manuscript.

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