

Interactive comment on “Formation of hydroxyl radical from San Joaquin Valley particles extracted in a cell-free solution” by H. Shen and C. Anastasio

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This study analyzes OH formation rates from PM collected at one urban and one rural location in California. It also compares OH formation rates from different size fractions (PM 2.5 vs. PM coarse fraction), and during different seasons (summer vs. winter). OH production is also evaluated in the presence and absence of ascorbic acid, and role of transition metals (Cu and Fe) is identified in that OH generation. The manuscript is well written; detail oriented, well organized, and is recommended for publication after consideration of possible issues raised below. The most important issues that need to be clarified and discussed in more detail are:

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1. What was the storage time before the samples were analyzed? We can see from the text that the samples were collected during the period between 2006 and 2009, but not when are those samples analyzed. In terms of similarity (comparison) between PM oxidative activity for samples collected from different locations, seasons, size fractions, this study provides probably reasonable reliable results, but in terms of absolute PM oxidative activity, samples should be analyzed immediately, or at least short after collection. If the samples were not analyzed immediately, then the authors should discuss how big influence will that storage time have on the measured oxidative potential? Did the authors checked and analyzed couple of samples immediately after collection? Answering these questions will help readers in defining how relevant are the results from this study to the oxidative potential of freshly generated ambient particles that will be inhaled by humans. In the other words, the implication of this study to the actual atmospheric aerosol is needed. For example, Chen and Hopke (2010) measured short-lived, highly reactive fraction of the reactive oxygen species (ROS) from the limonene/ozone reaction, as the fraction that was lost when samples were stored for 24 hours in a freezer. That fraction was found to account for up to 17% of the total ROS measured immediately after the collection. How much are the authors expect to lose after some longer storage time (years)?

Reply: We have added a table to the Supplemental Material (Table S1) that lists the dates of PM collection and the storage times for each of the samples (at -20 degree Celsius) prior to OH and HOOH measurement. The storage times for our OH measurements ranged from approximately 1 to 4 years. We did not measure ROS generation in samples immediately after collection, although we agree that this is a good idea for future work. Despite this, and despite our long storage times in the freezer, storage should not affect ROS generation for our samples in the presence of added ascorbate (which was the main condition of our work), as we describe in response to question #3 below. In addition, we have qualitative evidence that storage did not have a major effect on levels of ROS formation in solutions in the absence of ascorbate (Asc), although we did not specifically test this. However, even if storage did reduce ROS production in the

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absence of Asc, this pathway is minor compared to ROS generation in the presence of Asc, a pathway which will not be significantly affected by storage.

2. Type of filters used in this study should be clarified. If quartz fiber filters were used, then the authors should be aware that in general quartz material could generate OH radicals (believed by health community for why the quartz fiber can be harmful for the pulmonary system). That effect can be even higher when quartz is in contact with organic material than in simple blank samples that were used as a control in this study. Thus, a couple of parallel teflon filters should be collected and analyzed together with quartz in order to eliminate that possible positive artifact.

Reply: The two types of filters we used to collect PM_{2.5} samples in this study were described in our previous paper (Shen et al., 2011). We have added this information to Table S1: most of our PM_{2.5} samples were collected on pure Teflon filters, while two were collected on TX40 filters (Teflon-coated borosilicate glass microfibers) (Table S1). We see no evidence that either filter type affected OH formation. We measured OH formation from all our filter blanks and observed minimal OH generation from these blanks; the rates of OH formation from both types of filter blanks were similar to the rates in our solution blanks. On the other hand, there was a large difference in OH generation between the two Fresno and Westside PM_{2.5} samples that were collected on TX40 filters (Fig. 5; FRWI09 and WESU07), consistent with the results for samples collected on pure Teflon filters. Thus we have very good evidence that the filter materials had no impact on our results.

3. The authors did not mention anything about the possibility that the ROS (and it includes OH radicals as well) can be already present on the particles before inhalation or extraction, and not formed only endogenously or via reduction of oxygen species by the reduced forms of transition metals. Significant amounts of ROS were measured in respirable ambient particles prior to inhalation (Venkatachari et al. 2005; 2007), as well as in the secondary organic aerosol (SOA) formed under laboratory conditions. Is it possible that those species can be responsible (at least partially) for high OH

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production by the Fresno winter 2009 (PM 2.5 fraction, normalized to air volume) or Fresno winter 2007 (PM_{cf}, normalized by mass) samples in the absence of ascorbate?

Reply: There are at least three mechanisms by which particles can chemically generate ROS during aqueous extraction: (1) dissolution of particle-bound ROS such as peroxides (HOOH, ROOH, ROOR'), (2) reactions of particle-bound ROS precursors, e.g., reduced forms of redox-active species such as Fe(II), to make ROS in solution, and (3) redox-cycling reactions where particle components (e.g., Cu) interact with endogenous reductants (e.g., ascorbate) to form ROS. In methods such as ours, where ascorbate is added to the extraction fluid as a reductant, all three of these mechanisms contribute to ROS formation, although mechanism (3) appears to dominate (see below). In methods where a reductant is not added, mechanisms (1) and (2) are responsible for ROS formation; it would be very difficult to distinguish between these mechanisms. For example, in work such as Venkatachari et al. (2005 and 2007) the ROS measured by the technique are a combination of ROS that was initially present on the PM (mechanism (1)) and ROS formed in solution as a result of reactions involving reduced species from the PM (mechanism (2)). There are also "biological" mechanisms for ROS formation, such as the macrophage-mediated production of ROS in response to particle deposition, but we do not include these under the umbrella of "chemical" formation.

In this paper and in our previous work (Shen et al., 2011), we focus on the third mechanism above, examining ROS formation by particle components in the presence of a physiologically relevant concentration of ascorbate. But the reviewer brings up a good point that we have largely ignored mention of the other two mechanisms. For highly reactive ROS such as OH, whose lifetime in particles is on the order of microseconds or less (e.g., Anastasio and Newberg, 2007), the initial particle burden of OH upon PM inhalation will be negligible. However, both mechanisms (1) and (2) above might still be important "indirect" sources of in vivo OH, by providing precursors for OH such as peroxides or reduced forms of transition metals. The author correctly points out that our experiments in the absence of ascorbate give an estimate of the ROS contributions

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from these pathways. Comparing the amount of ROS formed in the absence of Asc to the amount formed in the presence of Asc gives information about the relative importance of these mechanisms. For our Fresno samples, the median ratio of the OH formation rate in the presence of Asc to the OH formation rate in the absence of Asc is 47. The same picture holds for HOOH, where the analogous median ratio is 42 (Shen et al., 2011). These ratios strongly suggest that *in vivo* redox reactions (mechanism (3)) are the dominant important chemical sources of ROS from inhaled particles.

However, it is possible that our ROS levels might be underestimated because of a loss of ROS or ROS precursors during our long storage times, as pointed out by the reviewer in question #1. There is strong evidence that we are not underestimating ROS formation in our extractions with ascorbate, since metals are the major redox-active species (e.g., Figure 9 in the current manuscript) and they are stable during storage. In our extractions without ascorbate, there might be some loss of ROS or ROS precursors during storage, but we did not measure ROS formation immediately after PM collection and so we do not have the experimental data to test this idea. We can qualitatively address this question by comparing our HOOH results in the absence of ascorbate to measurements of HOOH from particles by Paulson and co-workers, which were made within 24 hours after PM collection in a different extraction fluid (pH 3.5, 0.1 mM EDTA) that also contained no added reductant (Arellanes et al., 2006). As we showed in Shen et al. (2011), our average HOOH level from Fresno PM_{2.5} in the absence of ascorbate (0.44 ± 0.24 nmol m⁻³-air) was comparable to the average for PM_{2.5} collected near the 110 freeway in southern California (0.35 ± 0.26 nmol m⁻³-air) and higher than PM_{2.5} collected on the UCLA campus (0.16 ± 0.18 nmol m⁻³-air) (Arellanes et al., 2006). This suggests that there was not enormous loss of HOOH and HOOH precursors from our PM during storage at - 20 degree Celsius, although of course these particles are from different polluted locations within California. Venkatachari et al. (2005 and 2007), using a non-specific measurement of ROS, found peak particle "ROS" concentrations of 7.6 nmol m⁻³-air in summer in Rubidoux, CA (in the South Coast Air Basin east of Los Angeles) and 1.3 nmol m⁻³-air in winter in New York City,

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based on calibration with HOOH. It is difficult to compare these results meaningfully to ours because their technique is not specific to certain ROS and because their use of sonication during extraction will produce ROS levels in the samples that are likely higher than in the associated blanks.

Finally, it is possible that ROS initially present on the particles (i.e., mechanism (1) above) is responsible for the high OH production by the Fresno winter 2009 fine PM (air-volume normalized result) and/or the Fresno winter 2007 coarse PM (mass-normalized result) without added ascorbate. While particle-associated OH will be negligible (because of the short lifetime of OH), other ROS species such as peroxides can decompose to OH in solution. However, as we indicate above, this mechanism for ROS formation cannot be distinguished from solution reactions of particle-associated reductants such as Fe(II).

We've added part of this discussion to the manuscript, in Section 3.2.

4. Number of samples analyzed for each condition (with asc or without, etc) should be mentioned also in the main text of the manuscript and not only in the text describing Figures, since that is good indicator that more studies should be done in this field to support the presented results. Probably it will be the best to discuss that under "Implications and uncertainties".

Reply: Our results reveal a number of important characteristics of OH generation by ambient particles, but we agree that we had a small sample size and that more studies are needed to support the present results. Although the sample size is clear in the figures, we now explicitly state the number of samples in the Methods section and we have added a mention in the Conclusion section that our sample size is small.

References

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Please also note the supplement to this comment:

<http://www.atmos-chem-phys-discuss.net/11/C8623/2011/acpd-11-C8623-2011-supplement.pdf>

Interactive comment on *Atmos. Chem. Phys. Discuss.*, 11, 16861, 2011.