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Oxidant production from source-oriented particulate matter – Part 1: Oxidative potential using the dithiothreitol (DTT) assay

General comments

In this work, the authors took advantage of a source –oriented sampling technique that was based on single particle mass spectrometry data to separate ambient PM samples into different source categories in real time and then collect them into different Chem Vol samplers. The source-segregated particles in two size fractions, ultrafine (UF) and submicron fine fractions (SMF) were then quantified of their oxidative potential using the DTT assay. This is a novel and unique approach in identifying the important aerosol sources in terms of health effects endpoints (not necessarily in PM mass contributions). It appears that the single mass spectrometry data had limited success in separating sources as a large fraction of PM (43-60%) were in the "Nighttime inversion (CV10)" sampler, representing a mixture of sources or an unidentified source. Despite the weakness in sorting sources, some useful results were obtained, such as summer-winter difference by the same source category, and the difference between the different size fractions of the same source (i.e., results illustrated in Figure 2). The mechanistic approach taken by the authors also yields insights into whether there are significant missing redox-active components beyond metal species for a given source (Figure 3).

There are a few significant issues that need to be addressed before this work is accepted for publication. They are described below.

Specific comments

1. Iron is known to catalyze ROS formation through Fenton reaction; however, the DTT activity of Fe was measured to be very low (significantly lower than the DTT activity of Cu) (Lin and Yu, 2011; Charrier and Anastasio, 2012). As such, the DTT assay is not suitable to evaluate the redox activity of Fe and the oxidative potentials of PM sources that contain significant Fe content, such as vehicular emissions and unknown metals (seen from Figure 1) would be under-estimated. The bias caused by inability of DTT assay reflecting ROS production capability by Fe needs to be explained in text and briefly mentioned in the abstract.
2. It appears that the research group also measured the rate of production of OH radical and will report the results in the companion manuscript (page 24152, lines 21-24). Was there any correlation observed between Fe content and OH production rate? It will be good to include in this manuscript a brief description of the relevant OH radical production results.

3. The earlier work of the authors (Charrier and Anastaio, 2012) showed that the rate of DTT loss due to Cu and Mn is not linearly proportional to the metal concentration in the DTT assay. This concentration dependency is an artifact of the analytical procedure as the concentration of Cu or Mn in extracts could be arbitrarily varied by using different proportions of PM mass and the DTT solution volume in the DTT assay. This concentration dependency needs to be removed when calculating contributions of individual metal species to DTT activity for comparison with the measured overall DTT activities by the mixture. To remove this concentration dependency, the lower concentration range that generates linear response should be used. It is also perhaps more reasonable that the lower concentration levels (generating linear DTT response) simulate more closely the concentrations actually encountered in lung fluids inside humans.
4. The part on apportionment of volume-normalized oxidative potential using modeling results of emission inventory sources is highly speculative and uncertain. Identification and separation of sources using the single particle mass spectrometry data as illustrated in this work did not work out very well. The authors did not present evidence for evaluating how well the matching of the source categories as identified by single particle mass spectrometry and those listed in emission inventories. In addition, the source-based oxidative potential determination was based on a very limited set of data, i.e., one ChemVol source sample per season. The combined uncertainties could be huge. I suggest removing this part of the results from the paper.

Minor comments

Figure 3 shows two source categories with * identifying cases where the measured and calculated rates are statistically different. But visual inspection suggests the last two source categories in summer UF and winter UF plots (Figs. 3a and 3c) (which are not marked with *) are also cases where the measured and calculated rates are statistically different. At least the authors also indicate in the text (page 24162, lines 9-10) that winter UF “nighttime inversion (CV10)” (last source category in fig. 3c) is such a case. Please check and rectify the inconsistence

P24160, line 15: change “where j refers to season” to “where i refers to season”.
P24164, line 17: change “Fig. S4a-c” to “Fig. S5a-c”.