Comment on acp-2021-376
Anonymous Referee #1

In this work, the authors measured oxidative potential (OP) of particulate matter in five urban areas in midwestern US. Particulate matter (PM) is a significant health hazard, and its oxidative potential is thought to be representative of its toxicity. The authors assessed oxidative potential in 5 different endpoints on a weekly basis. These OP measurements are often difficult to make, but the authors had developed a system to automate the measurements of PM on filters. The results from the study showed large variabilities across sites and endpoints, and these variabilities, along with poor correlation with PM mass, suggest that PM2.5 mass alone is a poor indicator of potential health impacts. The discussion of the results was not very deep, and, in many cases, more detailed exploration is encouraged to better understand these results. In general, the manuscript is well written, but some of the main messages can be more clearly communicated, rather than buried in a lot of numbers and text. I believe that this manuscript should be published in ACP after some major revisions.

Major comments:

In general, this work reads like a measurement report. I was very impressed by the ability to make all these measurements, but somewhat disappointed with the lack of insights from the measurements. More specifically:

- A lot of information about each site was given in Section 2.1, but when discussing the spatiotemporal variability, there is virtually no discussion in these contexts in Section 3.3. Why does CMP behave so differently? What are the spikes? The same goes for Section 3.5, where the site-to-site comparison is discussed in the context of some statistical measures (correlation coefficient, COD). Again, what are the physical insights?

- Lines 257 to 280 were very hard to follow. The discussion jumped around from OP measure to another (sometimes mass-normalized, other times volume-normalized). The OP endpoints from this particular study were compared to those reported in the literature, but the discussion focuses on very shallow comparisons (e.g. higher, lower, different, the same). I am very confused about the purpose of this discussion: are these comparisons meant to validate the measurements? Are they meant to highlight the differences to illustrate differences between sources, or site characteristics? Are we expecting the OPs to
be the same, or different from previous studies? My suggestion is to focus on some main message, and then show the comparisons that illustrate the point.

- How are we supposed to make sense of the large differences between the various endpoints? They are different measures and operate differently, so they are expected to be different. So, if they are significantly different, then what? The suggestion from the authors is to measure all of them, but then how do we make sense of the different numbers, or trends? A closer examination of what each OP is measuring (and what chemical components are most linked with each measure) would be useful.

- Given that ACP is an chemistry-focused journal, I believe that discussion of chemical composition is well within the scope of this manuscript, and should not be separated for a later publication. Chemical composition is central to many of the questions I posed, and including some information of composition is necessary to make sense of these measurements.

Minor comments:

- Line 18 and elsewhere: it might useful to define what volume means. Presumably this is air volume, not particle volume

- The introduction is very well-written and reflects the current state of knowledge.

- Lines 85-93: this might be a good place to define some research questions and hypotheses, and address them accordingly at the end. It will help with adding some depth to the discussion and going beyond just reporting measurements.

- Line 100: “Chicago, Indianapolis and St. Louis” seem redundant.

- Section 2.2: are the methanol extracts also kept the same PM mass for OP measurement? In the water soluble extract, the volume of water was adjusted to achieve the same mass; how was this done for the methanol soluble extract?

- Line 160: when the dried methanol extract was reconstituted in water (DI water), are there insoluble components? For example, I can imagine some organic compounds are extracted by methanol and stick to the walls of the vial when dried, but does not dissolve in water during reconstitution.

- Lines 235-236: 5.7-21.7 does not seem to be significantly higher than 2.0-20.2. Perhaps show the median?

- Lines 240 and 281: how is the “time series” different from the temporal variation in “spatiotemporal variation”? There are a lot of overlapping points between Sections 3.2 and 3.3, and these sections are be significantly combined and condensed for easier reading. Or perhaps the author intended the discussions to be separate, and if so, it would be good to convey the differences in the section titles.

- Line 248-249: Just want to confirm: In line 217, the July 4th data were excluded from the regression analysis, but are included here in the discussion. It is a little confusing; perhaps some slight clarification would be useful.

- Line 294: why is different from SE US? The seasonal trend seems to be related to photochemical activity (higher in the summer). In general, the midwestern US provides an interesting contrast to previous studies because it has larger temperature differences between summer and winter.
- Line 350-355: this seems like a somewhat handwavy explanation for an anomaly, not really supported by evidence. What is the evidence for significant alkaloid compounds at this one particular site? Are there other studies that show Cu can complex with organic compounds and reduce OP?

- Lines 356-368: why focus on Fe-organic complex? The simpler explanation would be organic compounds that contribute to OP that extracted in methanol but not in water.

- Section 3.6: My suggestion is to point out that current regulations focus on PM mass only, and these results show how inadequate this approach may be. (The reason I suggest this is, at first, I felt it was obvious that OPm would not correlate with PM mass and was somewhat puzzled by the need to do this analysis. But upon second thought, this analysis is useful in a regulatory context.)

- Line 474: “the results ... provide”, not “provides”

- Figures and tables are generally too complex