

Atmos. Chem. Phys. Discuss., referee comment RC1
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Comment on acp-2021-979

Anonymous Referee #1

Referee comment on "Linking Switzerland's PM₁₀ and PM_{2.5} oxidative potential (OP) with emission sources" by Stuart K. Grange et al., Atmos. Chem. Phys. Discuss.,
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This paper uses filter samples collected at a number of sites in Switzerland over a period of roughly a year to determine particle oxidative potential by three methods for PM_{2.5} and PM₁₀. The paper adds to a growing list of research that assumes OP is a relevant metric to relate aerosol chemical properties to adverse effects on human health, although they present no data on this in this paper. The paper investigates what sources contribute most to the measured OP and claim to investigate what the chemical components are that drive it (objective (ii) line 90). They also assess the performance of the assays, concluding that one of them is a more specific metric, which is interpreted, I guess, to mean a better connection to human health (more on this below)? The paper essentially reinforces the view that with declining vehicle tail pipe emissions, the two main emission sources of concern are particles emitted from vehicle brakes and abrasion of tires and roadways and wood burning (residential). The paper, however, does not really address what specific compounds drive the OP since they do not sufficiently chemically speciate the OA (they only find traces of wood burning linked to OP (i.e., sugars), which are likely only markers, and they do not actually measure metal ions which are the species that would be driving the OP assays. (For example, the lines 370-374 really apply to all the specific PM components measured, including the metals). The paper is well written and the data is interesting. However, there are areas where the authors could provide more clarity, but overall, it is an important contribution.

Detailed Comments:

Simple linear models involving various species are used to reconstruct the observed OP levels, and they seem to do a reasonable job given the high r^2 . However, other research has shown that OP measured in a filter extract is not likely simply due to the sum of individual species, there can be interaction between species. Why does this appear not to be an issue in this data set?

Few details are given on the assays. I think it would be useful at a minimum to note what the filter extraction liquid was for each assay (it was not water, simulated lung fluid for DTT and AA, but not DCFH?) and why was this done, e.g., Calas et al. 2017 does not appear to show a difference in ambient samples for the OP_DTT assay in pure water vs. SLF, so what is the justification? It would be useful to explain and support why this is claimed to be important given that the authors make the point many times that lack of standard methods impedes this area of research. Also, how is the DCFH assay used so that the results are reported in units similar to the other two assays (ie, doe DCFH assay really have units of nmol/min/m³, last line of section 2.3.1.)– this does not seem possible? And finally, the authors state that a liquid concentration of roughly 25 ug/L was used for the OP tests, but in their methods cited (Calas et al., 20218), a concentration of 10 ug/mL was used instead, a huge difference (ug/L vs ug/mL)?

Relating to the above, what does “All extracts were conducted at iso- and low-mass PM concentration...” mean. (What is the meaning of iso-...?)

Line 375 to 380 relating to the inclusion of ammonium nitrate in the models. The reason could be more complex than what is stated, e.g., ammonium nitrate could largely control particle water, which in turn controls aqueous reactions that affect OP, or ammonium nitrate could just be a tracer for secondary processes in general or more photochemically aged aerosol, which has been shown to affect metals solubility and OP (eg, Wong et al, *Environ. Sci. Technol.* 2020, 54, 7088–7096; Antinolo, et al., 2015, *Nature Comm*, 6(6812), 1-7; Li et al, 2013 *Atmos. Env.*, 81, 68-75; Zhu et al, 2020, *Envir. Sci Technol.*, 54, 8558-8567, and others on formation of secondary OP species) The point is, atmospheric aging alters aerosol particle chemical properties. When interpreting their data, the view by the authors seems to be that almost everything as primary.

Finally, in the Abstract and at the end of the paper it is stated that AA may be a more specific metric for OP than the other assays. This is apparently based on the idea discussed starting on line 362; that the linear models for predicting OP_AA at the various measurements sites have a wider range of tracers in them, but they still all point to the same source, brakes/road dust and wood burning. What does that mean; that AA really is only influenced by species from these two sources, whereas the other assays are also sensitive to other species that may not be from these sources? One could interpret this as; the AA assay is sensitive to fewer sources for OP (not a good thing), or that it does not include influences from species that have no effect on OP (that would be a good thing)? How do the authors even know how to decide this so as to determine what is the better assay, there is no evidence shown that these are the only main sources that produce adverse health effects under the oxidative stress paradigm (there is no health data presented in this paper)? One may argue the opposite, that actually an OP assay that is more comprehensive, that includes more sources that can contribute to oxidative stress, is ideal. Note, DTT included NH₄HO₃, but AA did not, and see comments above on this. The discussion (or argument) on the relative merits of these three assays based on the findings of this study should be discussed more thoroughly. The current logic for the assessment of these assays is not clear to me.