

Review of “Impact of anthropogenic emissions on biogenic secondary organic aerosol: Observation in the Pearl River Delta, South China” by Zhang et al.

This manuscript presents the annual variations of SOA tracers from biogenic VOCs at nine sites in PRD region. The measured biogenic SOA tracers are found to be correlated with Ox and anthropogenic sulfate, indicating the impacts of anthropogenic emissions on biogenic SOA formation. This is an extensive study by analyzing 170 filters. Overall, the data analysis is solid and the manuscript is well-written. I recommend publication after major revisions.

Major Comments

1. Recent studies¹⁻² demonstrated that C5-alkene triols and 3-methyltetrahydrofuran-3,4-diols are largely GC/EI-MS artifacts from the degradation of methyltetrol sulfates and dimers. The authors used figure 7 (ternary plots) to argue that these tracers are indeed formed from different pathways rather than thermal decomposition. However, I beg to differ. The lack of correlation between IEPOX-derived SOA tracers and be explained by that the three tracers in figure 7 arise from the thermal decomposition of different dimers/OS and the parent dimers/OS concentration varies with sites and season. To fully prove that the three tracers are not decomposition products, the authors need to sample authentic methyltetrol sulfate standard with GC-MS.
2. The authors use the BSOA vs sulfate slope to infer the magnitude of sulfate control on BSOA. As the authors have performed the same measurements in the same region for a long time, I encourage the authors to look at their historic measurements, based on which to estimate the sulfate-control magnitude. As shown in figure 1, the O₃ concentration has been relatively flat in the past 13 years, but SO₂ concentration has largely declined. This provides a nice opportunity to deconvolve the effect of sulfate vs O₃ on BSOA formation.

Minor Comments

1. Line 34. Replace “high-generation” with “later-generation” throughout the manuscript including acronyms.

2. Line 231-232. The correlation between SOA_{M_H} and sulfate is intriguing. The formation of SOA_{M_H} tracers, like MBTCA, does not involve sulfate. Thus, how to explain the correlation?
3. Please show the correlation of isoprene SOA tracers with sulfate and Ox, like figure 5.
4. Figure 5. With so many data on the plots, it is difficult to examine the correlation at each site. I suggest to make a scatter plot for each site and then synthesize a figure like figure 4.
5. The correlation between β -caryophyllenic acid (CA) and levoglucosan is interesting. Does biomass burning emit CA?
6. Line 331. The authors need to be careful about the salting-in effect, because it is highly compound-specific. Xu et al. 2015 proposed that sulfate introduces salting-in effect on IEPOX, but this is just a hypothesis. It would be overreaching to argue that sulfate has salting-in effect on β -caryophyllene SOA.

Reference

1. Cui, T.; Zeng, Z.; dos Santos, E. O.; Zhang, Z.; Chen, Y.; Zhang, Y.; Rose, C. A.; Budisulistiorini, S. H.; Collins, L. B.; Bodnar, W. M., et al. Development of a Hydrophilic Interaction Liquid Chromatography (Hilic) Method for the Chemical Characterization of Water-Soluble Isoprene Epoxydiol (Iepox)-Derived Secondary Organic Aerosol. *Environmental Science: Processes & Impacts* **2018**.
2. Watanabe, A. C.; Stropoli, S. J.; Elrod, M. J. Assessing the Potential Mechanisms of Isomerization Reactions of Isoprene Epoxydiols on Secondary Organic Aerosol. *Environ Sci Technol* **2018**, 52, 8346-8354.