Comment on acp-2022-113
Anonymous Referee #1

Referee comment on "Radical chemistry in the Pearl River Delta: observations and modeling of OH and HO2 radicals in Shenzhen 2018" by Xinping Yang et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2022-113-RC1, 2022

Radical chemistry in the Pearl River Delta: observations and modeling of OH and HO\textsubscript{2} radicals in Shenzhen 2018

The paper by Yang et al. presents results from a measurement campaign in September / October 2018 at Shenzhen in the Pearl River Delta. Unfortunately, the collected data-set is not state-of-the art and the subsequent interpretation suffers from this lack of data and thus the manuscript does not bring any useful new insight into atmospheric chemistry. The shortcomings in the data-set compared with what is current state-of-the art are:

- OH reactivity has not been measured: the analysis of the radicals budget is based on calculated OH reactivity, which is unsatisfactorily, especially given that \(k_{\text{OH}}\) measurements are now widely available and add much confidence to the data set. Missing OH reactivity is widely observed under various conditions, and field campaigns quantifying OH and HO2 should also measure OH reactivity to unravel possible missing OH reactivity, rather than using the calculated OH reactivity as a lower limit to evaluate the experimental OH and HO2 data.
- The reference cell for stabilizing the laser wavelength did not work during the campaign: rather high NO concentrations have therefore been used in the FAGE for HO2 conversion, and it can be doubted that no interference from RO2 measurements occurred under these conditions. This is even more strange, as the authors indicate line 99, that there is no obvious difference in HO2 signal, when changing from 10 to 20 ppm. Does this mean the instrument works already under 100% HO2 conversion? Then, an RO2 interference seems very likely. However, 100% conversion efficiency is unlikely, as in a recent paper of the same group, describing a campaign carried out just a few months before in May / June 2018 (Ma et al., OH and HO2 radicals chemistry at a suburban site during the EXPLORE-YRD campaign in 2018, ACPD, doi.org/10.5194/acp-2021-1021), a conversion efficiency of 20% was obtained using 5 ppm. Or maybe the authors wanted to say that no obvious difference in HO2 concentration was observed. Then, the HO2 conversion rates under different NO
concentrations need to be specified.

- Your model underestimates OH concentration under low NO conditions. I am very surprised that you claim that this is due to an unknown chemical X species, without even loosing a word about possible interferences in the OH measurements. Such increasing OH interferences with decreasing NO concentrations have been identified unequivocally with different FAGE instruments, and an experimental technique has been developed to quantify such possible interferences, this needs to be discussed. And even though some FAGE systems might be more prone to this interference than others, the FAGE community seems to agree on, that occasional measurements with such a pre-injector system are indispensable during field campaigns, especially when low NO concentrations are expected during the campaign. Looking at your above-mentioned paper describing a field campaign a few months before this one, it seems that you had already developed such a pre-injector system at the time of the campaign, because you had already used it. So why did you not use it in this campaign? In my opinion it is idle to discuss OH measurements that are underestimated by the model at low NO conditions, as long as OH-interference to an unknown species has been excluded by experiments using a pre-injector.

I understand that a field campaign is a lot of effort, and the authors want to publish the data, but I feel that the present data set is too uncomplete to justify a stand-alone paper in ACP. Maybe the data can be published as a complementary data-set together with another field campaign?

Besides these fundamental shortcomings I have no other comments.