Review of acp-2018-1256

Reviewer 3

February 4, 2019

1 General Comments

This paper examines the formation of nitro-aromatic compounds (NACs) in the Beijing summer under high NOx and high anthropogenic VOC conditions. NAC formation is of interest owing to their light- absorbing and toxicological properties. Formation properties of both the nitro-phenols (NPs) and the nitro-catechols (NC) are diurnal with the latter forming at night and the former forming predominantly during the day time. Excess NOx and VOC concentration thresholds were reported. Higher NOx generally favored formation of the NCs. Generally, VOC concentration thresholds of < 1 ppb were observed. It was concluded that aqueous phase oxidation was more important at night than daytime.

The study's subject matter is of interest to the ACP audience, and the paper is well written. NACs in biomass burning and in the atmosphere are becoming well investigated, and while fewer studies may examine NACs in the urban environment, a clearer statement about the novelty of the current research is due. For example, Figure 1 shows that NACs have been measured throughout the world, including at several urban sites in China. So, this paper should explicitly state why another study is needed on this topic now. Additionally, the study would benefit from showing the NC and NP compound peaks and their resolution in the LC-MS chromatograms. Next, the pollution events and K^+ need to clearly connect to the main story of the paper (e.g. Figure 3). The discussion suggests that biomass burning is mainly a non-factor despite the K^+ possibly showing otherwise, and the diurnal profile seems much more robust than any of the four so-called 'pollution events'. In other words, the importance of the individual pollution events and the source of the events is just isn't clear enough. These points should be better addressed during revision. Finally, the paper would also benefit from further analysis of the potential gas-phase concentrations of some of these compounds and quantification of the likelihood of volatilization losses. Use of vapor pressures or partitioning coefficients should help with this issue. Once addressing these concerns and the additional comments below, the paper should be publishable.

2 Specific comments

- 1. lines 19-21: This sentence should be revised for clarity. 'high NOx anthropogenic VOCs' is this one or two concepts? Also, not certain what 'influence factors' are. Please fix.
- 2. line 21: Is this total concentration an average? Or the top end of the range? Be specific.
- 3. line 29: just state that there was excess NOx for VOC oxidation. As written the sentence is awkward.
- 4. line 38: Where are the aerosol surface area data?
- 5. lines 112-117: Please provide a chromatogram that shows the separation. Many of these compounds are isomers, and it is important to see evidence of sound chromatographic resolution. Evidence of peak quality for this study is warranted.
- 6. Figure 1: these reaction schematics are not chemically balanced. If -H₂O is removed than it should be indicated in the reaction scheme. What happens to the NO₃? This reaction scheme should show the reader exactly what happens chemically. Are these compounds also present in the gas-phase?
- 7. line 162-165: This last sentence should be revised for clarity. Can't tell which conditions go with which season.
- 8. lines 173-174: So, it's a high NOx and a high anthropogenic VOC environment?
- 9. lines 179-181: Please clarify the sentence about 'Different NAC compositions'. How much higher is the RH in Hong Kong compared with Beijing in summer?
- 10. lines 205-209: It is unclear what is being discussed here with regard to the pathway, loss mechanisms, and groups. Please be specific and quantitative if possible.

- 11. lines 209-210: Why was the gas-phase not sampled for this study? It would have brought more clarity and we could have learned if the mass was simply distributed in the gas-phase as opposed to being 'lost'. It may be a good idea to use individual NAC concentrations, vapor pressures and day and night time temperature to estimate the total mass in both the gas- and particle-phase.
- 12. line 271: please clarify 'interacted conditions'
- 13. lines 275-277: Please rewrite this sentence for clarity.
- 14. Figure 6: While this figure is meant to indicate a general trend, it is unclear where the values in this figure came from. Are these averages? How much error are in these values? Please be specific.
- 15. lines 289-291: Again, a table containing the vapor pressures for these NAC compounds may help explain some of these observations. Try the CHEMSPIDER web site.
- 16. line 301: is this statistically 'significant'?
- 17. 347-348: The last sentence in this paragraph is unclear.