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Interactive comment

Interactive comment on "Effects of NO_x and SO_2 on the Secondary Organic Aerosol Formation from Photooxidation of α-pinene and Limonene" *by* Defeng Zhao et al.

Anonymous Referee #1

Received and published: 26 April 2017

This manuscript describes the competing roles of NOx and SO2 on SOA formation of a-pinene and limonene. The ability of SO2 to enhance seed aerosol surface area appears to be a dominant factor, and that enhancing seed aerosol reduces the NOx suppression of SOA yields, at least in some monoterpenes. The authors use their AMS data to determine the role of organic nitrates in SOA, and find that organic nitrates account for a substantial fraction of the SOA mass. Overall, this is an interesting piece of work, and warrants publication in the ACP following some revision.

Major Comments

The nature of the experimental design was not so much to look at the impact of SO2 – but to look at the role of a sulfate seed aerosol. From the manuscript, my interpretation

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Discussion paper

is that the SO2 additions were used to nucleate (inorganic) seed aerosol. Was there any SO2 left over to impact VOC oxidation? It is not clear to me if the SO2 additions really paralleled the NOx additions, because the experimental design was different. That's not to say that these aren't valuable experiments that add to the literature! I merely question whether this was truly an 'SO2 addition' rather than a 'sulfate aerosol addition' to VOC oxidation experiments.

SOA yield is influenced strongly by OA mass. The authors plot SOA yield versus OH dose, which is certainly a useful figure to see – but it is hard to compare the SOA yields if the SOA mass has not bee accounted for. The authors need to also show SOA yield versus OA mass so that the readers can contrast the relationships to other studies. It would be useful to compare the SOA yields to other studies: how do the yield values compare to other measurements of OH oxidation of a-pinene? This will allow readers to place the studies in context.

The results of SO2 and NOx effects on SOA yield are consistent with the Sarrafzadeh and Eddingsaas studies, which found that the presence of seed aerosol suppresses the 'NOx effect' on SOA yield. However, they contradict previous studies (e.g. Ng et al. 2007, Presto et al. 2005). The authors need to do a better job of contrasting their studies – they attribute the difference to a vague collection of parameters (e.g. NO:NO2 ratio, OH concentrations, etc.). It would be extremely helpful if the authors could synthesize the information (i.e. put numbers on those parameters) to help readers understand the differences in experimental conditions across the studies. A table would be particularly helpful.

Lines 118: the use of the HR-ToF-AMS to derive elemental ratios uses the older Aiken method. However, as the authors note, the newer 2015 approach corrects some underestimation. Because readers may wish to compare results across studies in the future, it is appropriate and prudent to update the results to the newer calculations.

Line 128: the authors note that they account for particle wall loss and dilution loss, but not for vapor wall loss. Recent papers have shown this to be a chemically-dependent and substantial effect on SOA yields, and most rigorous SOA yield work now accounts for these effects. How will ignoring vapor wall loss influence the results – and the interpretation thereof?

In the Introduction, the authors do a good job of summarizing the reasons why such a study would be interesting. Much of the discussion focuses on the role of NOx on SOA yields – this is reasonable as most of the literature has focused on that problem! However, there is some relatively recent literature regarding the role of SO2 in affecting SOA chemistry and monoterpene OH oxidation that the authors should consider. In particular:

Photooxidation of cyclohexene in the presence of SO2: SOA yield and chemical composition. Shijie Liu, Long Jia, Yongfu Xu, Narcisse T. Tsona, Shuangshuang Ge, and Lin Du. Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-30, 2017

Synergetic formation of secondary inorganic and organic aerosol: effect of SO2 and NH3 on particle formation and growth. Biwu Chu, Xiao Zhang, Yongchun Liu, Hong He, Yele Sun, Jingkun Jiang, Junhua Li, and Jiming Hao. Atmos. Chem. Phys., 16, 14219-14230, doi:10.5194/acp-16-14219-2016, 2016

Formation of secondary aerosols from gasoline vehicle exhaust when mixing with SO2. T. Liu, X. Wang, Q. Hu, W. Deng, Y. Zhang, X. Ding, X. Fu, F. Bernard, Z. Zhang, S. Lü, Q. He, X. Bi, J. Chen, Y. Sun, J. Yu, P. Peng, G. Sheng, and J. Fu. Atmos. Chem. Phys., 16, 675-689, doi:10.5194/acp-16-675-2016, 2016

Anthropogenic Sulfur Perturbations on Biogenic Oxidation: SO2 Additions Impact Gas-Phase OH Oxidation Products of α- and β-Pinene. Beth Friedman, Patrick Brophy, William H. Brune, and Delphine K. Farmer. Environmental Science & Technology 2016 50 (3), 1269-1279. DOI: 10.1021/acs.est.5b05010

Is there any evidence for organic sulfates in the SOA from the AMS data? This has been a subject of some debate in the literature, and an additional datapoint would be useful. This may also clarify the role of acid catalysis, as I believe that has been linked to the formation of organic sulfates.

Minor Comments

Line 136. The authors note an average RH of 28-42% for the experiments. This seems like a relatively large range: will this affect the SOA yields, or interpretation of the data?

Re: Discussion of SO2 effects. The authors dominantly attribute the enhancement of SOA by SO2 to increased particle surface area, or perhaps to acid catalysis. These seem like extremely likely reasons; however, there is one study that suggests that SO2 will influence gas-phase oxidation products (Friedman et al.), which could also be a confounding factor unless all of the SO2 is in the particle phase before VOC oxidation commences. . . This would be a useful clarification.

Technical comments.

Line 26: should read “compared to low NOx”

Line 29: should read “SO2 can compensate for such effects”

Introduction: line 34: sentence has repetitive ‘importants’: consider removing at least one (e.g. “SOA is an important class of atmospheric aerosol” seems like an unnecessary statement for the journal’s audience). This adjective is used heavily throughout the introduction (lines 45, 49), and I recommend removing or replacing the adjective to improve readability

Line 56: hydroperoxides should be plural

Line 57: need comma between ‘NO’ and ‘forming’

Line 87: should read “might have either counteracting or synergistic effects on SOA. . .”

Line 126: remove the with following ‘multiplied by’

Line 135: should read ‘there was no aqueous..’

Line 221, remove comma between ‘that’ and ‘high’

Line 360: should read ‘in the ambient atmosphere’

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