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Atmospheric Chemistry and Physics Discussions

Interactive comment on “Isoprene suppression of new particle formation in mixed deciduous forest” *by* V. P. Kanawade et al.

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Response to Anonymous Referee #1

General Comments In this study the authors describe the results of a field study of new particle formation (NPF) carried out in a Michigan forest. Measurements were made of key species including OH, H_2SO_4, NH_3, NO_x, SO_2, particle size distributions, and VOCs, especially isoprene, monoterpenes, and sesquiterpenes. The data were used with modeled VOC emissions to attempt to explain the relative absence of NPF in this forest compared to boreal forests in Finland. A few NPF events were consistent with events of high anthropogenic H_2SO_4 pollution leading to ion-induced nucleation, but it was proposed that high isoprene/monoterpenes ratios suppressed NPF in most circumstances. This explanation is consistent with results of recent plant chamber

experiments, but this is the first time it has been demonstrated in a forest. No clear mechanism for suppression was proposed, although it did not appear to involve a reduction in OH concentrations by isoprene as had been proposed in the plant chamber studies. The results have important implications for understanding the effects of future changes in forest species composition, which will be influenced by changes in global temperature, on atmospheric aerosols and cloud formation. The manuscript is well written and is worthy of publication in ACP.

Reply: We thank the referee for his/her helpful comments. Below we provide the point to point response to the comments.

Specific Comments 1. Pages 11049-11051: I suggest that in addition to comparing the relative rates of reactions of OH radicals with isoprene and monoterpenes (as was done here) that you perform the same calculations for the relative rates of reactions of monoterpenes with O_3 and OH radicals. I suspect that from the information given that monoterpenes react to a much larger extent with O_3 than with OH radicals in Finland than in Michigan and the Amazon. Monoterpene reactions with O_3 tend to form more SOA than those with OH radicals, and so these less volatile products could be a reason for the effect of R on NPF events.

Reply: We agree with the referee that monoterpenes react to a much large extent with O_3 than with OH radicals in the Finland than in the Michigan and the Amazon. To test this (as suggested by referee), we have calculated the ratio of relative rates of reaction of monoterpenes with O_3 and OH radicals, ($k_{MT-O3}[O_3]/k_{MT-OH}[OH]$), where k_{MT-O3} (86.6×10^{-18} cm^3 molecule^{-1} s^{-1}) and k_{MT-OH} (53.7×10^{-12} cm^3 molecule^{-1} s^{-1}) are the rate constants of monoterpenes with O_3 and OH radicals (Finlayson-Pitts and Pitts, 2000), respectively. Based on the averaged diurnal variation of monoterpenes, O_3, and OH concentrations observed in the Michigan forest (Fig. 3 in the discussion manuscript), the averaged noontime peak ($k_{MT-O3}[O_3]/k_{MT-OH}[OH]$) ratio was 0.76±0.08, lower by a factor of 2.38 compared to found in the Finland (1.81±0.32). This ratio was even much lower (0.14±0.07) in the Amazon, due to considerably low ozone concentrations [<20 ppbv (Kesselmeier et al., 2002)] during the wet season. This suggests that relative rates of reaction of monoterpenes with O_3 were dominant in the Finland than in the Michigan and the Amazon. We also agree with the referee that monoterpenes reactions with O_3 tend to yield more SOA than those with OH radicals, as previously shown in smog chamber experiments (Larsen et al., 2001;Yu et al., 1999). However, the measured monoterpenes and O_3 concentrations in the Michigan forest were comparable to those in the Finland forest. Even though, we still did not see conventional NPF, and we believe that it has something to do with R than monoterpene-O_3 products alone.

We included the following discussion in the revised manuscript (Page 14, L321-332): "Smog chamber experiments also have shown that MT reactions with O_3 tend to yield more secondary organic aerosols than those with OH radicals (Larsen et al., 2001;Yu et al., 1999). We have calculated the ratio of relative rates of reaction of MT with O_3 and OH radicals, ($k_{MT-O3}[O_3]/k_{MT-OH}[OH]$), where k_{MT-O3} (86.6×10^{-18} cm^3 $molecule^{-1}$ s^{-1}) is the rate constant of MT with O_3 (Finlayson-Pitts and Pitts, 2000). The averaged noontime peak ($k_{MT-O3}[O_3]/k_{MT-OH}[OH]$) ratio in the Michigan was 0.76±0.08, lower by a factor of 2.38 compared to found in the Finland (1.81±0.32). This ratio was even much lower (0.14±0.07) in the Amazon; this is likely due to considerably low O_3 concentrations [<20 ppbv (Kesselmeier et al., 2002)] during the wet season. These results suggest that the relative rates of reaction of MT with O_3 are dominant in the Finland than in the Michigan and the Amazon."

2. It seems that one possible explanation for the effects of R on NPF events is that organic acids play an important role in nucleation by clustering with sulfuric acid, as was suggested by Zhang et al., Science, (2004). Organic acids formed from isoprene oxidation will be more volatile than those formed from monoterpenes, and if they compete with and prevent larger organic acids from clustering with sulfuric acid, NPF could be suppressed.

Reply: We agree.

We included the following discussion in the revised manuscript (Page 15, L347-353): "Another possible explanation for the effects of *R* on NPF events is that organic acids play an important role in nucleation by clustering with H_2SO_4, as was suggested by Zhang et al., (2004, 2009). Bonn et al., (2003) also have shown that large organic acids can be formed from α-pinene ozonolysis and it is possible that these large organic acids can participate in biogenic nucleation. However, organic acids formed from isoprene oxidation can be more volatile than those formed from MT, and if they compete with and prevent larger organic acids from clustering with sulfuric acid, NPF could be suppressed."

Technical Comments:
There are a few grammatical errors that can be fixed with another careful reading by the authors.
Reply: We have corrected grammatical mistakes in the revised manuscript.

References:

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