

Interactive comment on “Suppression of new particle formation from monoterpene oxidation by NO_x” by J. Wildt et al.

Anonymous Referee #2

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Overall

The mechanisms of new particle formation (NPF) are not well understood despite substantial laboratory and field measurements during the past decades. This work addresses this important issue by studying biogenic VOCs emitted from real plants in reaction chambers. By keeping original VOC mixing ratio relatively constant and varying the mixing ratio of NO, the authors found that NPF is significantly suppressed under high NO_x conditions. Further, the NO_x effect is quantitatively explained based on basic photochemical reaction theory and appropriate assumptions, which is novel. In addition, the NO_x effect on the yield of secondary organic aerosols (SOA), which is also controversy, is addressed. The main conclusion is that NPF and photochemical ozone formation switch based on NO mixing ratios, and higher generation intermedi-

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ates from permutation reactions are limiting NPF. The content is suitable for ACP, and the measurements and data analysis are sound. Therefore, I recommend publication after addressing the following issues.

Specific comments

1. The measured particles are down to 7 nm, which is well above the size of newly nucleated particles. So it is not clear that the permutation reactions are responsible for particle formation or growth or both. This needs to be stressed and perhaps reflected in the paper title as well.
2. The major equation, Eq.(1) on Page 25838, is derived by assuming $Y(\text{RONO}_2)/Y(\text{O}_3)$ is constant, but $Y(\text{RONO}_2)/Y(\text{O}_3)$ is affected by NO level that changes from 0.3 to 103.5 ppb during the experiments, so the basis for this assumption needs to be clarified.
3. P25829, “In clean background air, where only small amounts of particulate matter exist, new particle formation (NPF) has been observed.” NPF has been frequently observed all over the world, even in polluted regions such as Beijing in China.
4. P25834, what is the size range of UCPC measurement? There are some overlaps in the size ranges of the UCPC measurements and SMPS measurements, do they compare well and which instrument was used for the overlapped size region? Also, is the UCPC measured number concentration corrected for size-dependent particle loss?
5. The treatment of isoprene: on P25838 it says “Although contributions of isoprene were always less than 10% they were always considered in summing up BVOC concentrations”; on P25839 it says “Because the isoprene contribution was less than 10% and fairly constant from experiment to experiment. . . the impact of isoprene was neglected. . .” There are clear inconsistencies here. If the effect of isoprene is neglected, isoprene should not be included in the total BVOC.
6. P25839: “The first was a decrease of J7 with increasing NO_x.” J7 is not shown in

the figure.

7. P25840, what is “incremental mass yield”? Is it different from the conventional “mass yield”? Please define.

8. P25841, from “To analyze SOA mass formation” to the end of this section, I am not following this section. What is $P_{MAX,meas}$? How does the equation derived, e.g., where is the parameter 0.117 from? And “as long as $BNR > 10$, $P_{MAX,norm}$ was independent of NO_x within the error margins of the data.” Do you mean “independent of BNR ”? Also it is obvious that there are data points outside the error margins rather than “within error margins”.

9. P25841, please specify “diffusion source”

10. P25843, “Mechanisms of SOA formation from molecules much larger than monoterpenes may favor a $RONO_2$ route and may differ from those discussed here for monoterpenes.” Lim and Ziemann studied C8-C15 alkanes, whose MW are not much higher than monoterpenes (e.g., α -pinene). Therefore, perhaps anthropogenic vs biogenic VOC is a better hypothesis for the difference.

11. P25846, “ $P(O_3)$ is thus a linear measure of Reaction (R_2) and therefore also a measure of the $[RO_2]$ which is withdrawn from the PRP channels.”, should it be “Reaction R_{2a} ”?

12. Table 1, it will be better to include $[NO]_0$ in the table, so readers do not have to calculate $[NO]_0$.

13. In Figure 3, there is sharp decrease of the number concentration for all three curves for $6 < x < 8$, what is the cause for that?

14. Figure 3, it would be good to include time trace of OH in this plot for comparison, since OH affects NPF, and $[OH]$ varies by a factor of 2 even for $[NO]_0 < 30$ as shown in Fig. 6. This is specifically related to Section 5.1.2.

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15. In Fig. 6, coloring the points by $[BVOC]_0$ would support the argument that “the scatter of OH is due to $[BVOC]_0$ ”

Technical corrections

1. P25828, Line 26, add “,” after “compounds”

2. P25829, Line 3, add “,” after “matter”

3. P25829, Line 7, change “play a key role for” to “play a key role in”

4. P25838, Line 22, change “%” to “percent”

5. P25841, Line 7, change “as function” to “as a function”

6. P25842, Line 7, remove “already”

7. In References, the reference of Seinfeld and Pandis, note pages.

8. SI information, P5, Line 13, change “in” to “is”

9. SI information, P8, Line 8, change “linear” to “linearly”

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