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Interactive comment on "Suppression of new particle formation from monoterpene oxidation by NO$_x$" *by* J. Wildt et al.

Anonymous Referee #1

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The paper studies the influence of NOx on aerosol particle formation from the oxidation of monoterpene emissions from plants. Addition of NOx strongly suppresses the new particle formation (NPF) but enhances ozone formation. It is shown that peroxy radicals are involved in the NPF. From the measurements it is concluded that first generation peroxy radicals are not rate limiting for the particle formation but that permutation reactions of higher generation peroxy radical like molecules limit the rate of new particle formation.

Overall, the paper describes an interesting and timely study on the influence of BVOC emissions on new particle formation. The qualitative result of the influence of NOx on NPF are convincing. The paper is well structured, concise and well written. Numerous assumptions and simplifications have to be made to be able to handle the complex

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chemical mechanisms without precise knowledge of the concentration and temporal evolution of the various involved species. These assumptions are clearly stated and the underlying derivations are explained in detail in the supplementary material.

In general, the paper is suitable for publication in ACP after taking into account the major comments below which may lead to some re-interpretation of the main results.

Major comments:

1.) CPC cut-off diameter of 7 nm: The particle formation rate is always given as J_7 and it is stated that the CPC (TSI 3025A) starts detecting particles at a diameter of 7 nm (p.25834 l.15-17). TSI gives the lower detection diameter for the 3025A UCPC as 2.5 nm or 3.0 nm and in Mentel et al., 2009, a lower size of 3.0 nm is stated. Why do you assume 7 nm?

2.) Wall losses influence nucleation rate, growth rate, SOA yield, PM_MAX: This comment is especially important in case the 7 nm cut-off diameter is correct, but needs to be considered also if the cut-off diameter is 2.5 or 3.0 nm. In all situations where the growth rates for the particles are low, the first detection of particles is decoupled from the original nucleation and there are many minutes or even hours between the nucleation and the detection. This time lag varies strongly with the particle growth rate and it influences the observed particle concentration, the derived nucleation rate, the SOA yield and PM_MAX because the wall losses of the condensing vapours as well as the size-dependent wall losses of the particles in the range between molecular size and 7 nm (as well as removal of particles by flow out of the chamber) depend on this time lag (see Kerminen and Kulmala, J Aerosol Sci., 2002; Ehrhart and Curtius, ACP, 2013). For long lag times J_7, SOA yield and PM_MAX are underestimated compared to a situation without wall losses and quantitative statements such as the slope of -2 in Fig. 10 as well as the exponent of 2.3 (p25839, l.27) become dependent on the size of the reactor chamber and other factors like the rotation speed of the mixing fan. In a stirred reactor of $\sim$1.5 cubic meter the wall loss life time of condensable gases will be on the

order of one minute and therefore the nucleation and growth of the particles is in strong competition especially for those cases where the NPF is observed 2-5 hours after the start of the OH formation. Have these loss rates been determined? How are they included in the determination of J, etc.? If the derived slope in Fig 10 is not -2, then also the statements about the mechanism and the role of first generation peroxy radicals as well as higher generation peroxy radical like molecules have to be reconsidered (e.g. Sect. 5.1.4).

3.) Which are the smallest NPF rates that can be reliably measured? Formation rates J_7 of 0.02 cmˆ-3 sˆ-1 are listed in Table 1. How high are background particle concentrations before start of an experiment? How large are NPF rates (e.g. from contaminant $H2SO4$, as stated on p. 25853) when all lights are switched on and only ozone and water vapour are added but no BVOCs? How reproducible are measurements of background NPF?

4.) Please add error estimates and error bars for all data of Figures 4-10.

Minor comments:

p.25836 l.5: What is the detection limit of the NOx monitor?

Technical corrections:

Supplement:

p.5, l.13: change to "...is an increasing..."

p.12, l.26: change to "...had no substantial impact on results..."

p.13, l.5 "range"

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 25827, 2013.