

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

V. P. Kanawade et al.

vkanawad@kent.edu

Received and published: 8 June 2011

Response to Anonymous Referee #2

General Comments

New particle formation in forests is an important atmospheric process and likely linked to biosphere - atmosphere - climate feedbacks. Despite intensive research on the physical and chemical processes involved in atmospheric new particle formation many aspects such as the identity of nucleating vapours, exact nucleation process, and conditions favouring new particle formation are still under debate. This paper adds valuable information for the so far less characterized deciduous forests. The authors present field observations of particle number concentration and size distributions measured at the University of Michigan Biological Station in summer 2009. From observed parti-

C4574

cle number concentrations and measurements of H_2SO_4 , NH_3 , SO_2 , NO_x , OH and various VOCs the conclusion is drawn, that the prevailing high isoprene concentration in the mixed deciduous forest suppresses new particle formation as previously found in a plant chamber. Only two nucleation events were observed in early evening episodes characterized by high SO_2 and NO_x concentrations, indicative of an anthropogenic plume. The nucleation events are simulated with a box model incorporated with ion-induced nucleation to investigate the nucleation mechanism. The paper is well written, within the scope of ACP, and recommended for publication after the following comments have been considered.

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

Specific Comments

1. While a mechanistic explanation of why isoprene suppresses the formation of new particles is beyond the scope of this paper and possibly even unachievable from field observations alone, it is interesting to see that the OH concentrations found here are comparable to OH concentrations in the boreal forest, where nucleation events are frequently observed. For a full picture of trace gas concentrations it would be desirable that the authors add NH_3 , NO and NO_2 time series to figure 2 together with temperature and RH information. This information might be valuable for future comparisons and according to the list of measured parameters is available.

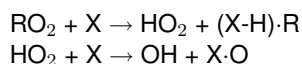
Reply: We thank the referee for making this important point. We have included NH_3 , NO, NO_2 (Fig. 2c), and temperature and RH (Fig. 2d) time series plots in the revised manuscript.

2. In view of recent observations of an OH recycling mechanism effective in the presence of low NO_x and isoprene (Lelieveld et al., 2008, Hofzumahaus et al., 2009) it

would be interesting to consider whether the same species X that converts HO₂ into OH could probably interfere with the proposed RO₂ that would form new particle in absence of isoprene?

Reply: Lelieveld et al. (2008) have proposed that isoprene can recycle OH in low-NO_x conditions. Other observations have also proposed OH formation from alkenes (such as olefin) reaction with ozone (Donahue et al., 1998, Paulson et al., 1997, 1999, Sadanaga et al., 2005). With regard to isoprene recycle of OH, Paulot et al. (2009) also proposed that OH can be regenerated via formation of dihydroxyepoxides (IEPOX = β-IEPOX + δ-IEPOX), under low NO_x conditions. It is possible that these IEPOX can interact with acidic, newly formed sulfuric acid particles and make them grow larger and faster. As we have examined in the manuscript (Page 11050 lines 25-30), it seems in the Michigan forest environment, isoprene was not oxidized further to make IEPOX and therefore, we excluded the possible role of IEPOX in aerosol nucleation.

Also, Hofzumahaus et al. (2009) suggested two possible reactions involving unknown X compound to convert HO₂/RO₂ into OH under low NO_x conditions;



However, the actual chemical identification of X is not known (Hofzumahaus et al. 2009). Although it is very hypothetical, it is possible that these X compounds and their reaction products with RO₂ and HO₂ can participate in biogenic nucleation. Nevertheless, it would require more field and laboratory experiments to determine the identity of the chemical species X involved in these reactions.

Additionally, Di Carlo et al. (2004) have also proposed that the missing OH reactivity may be due to some terpene-like temperature dependent unknown BVOCs species. It is also possible that these terpene-like compounds and their oxidation products (such organic acids and peroxides) could form new particles, in the absence of isoprene.

C4576

We included the following discussion in the revised manuscript (Page 13, L286-295):
"Recent observations have shown that OH recycling mechanisms are effective in the presence of low NO_x and isoprene (Lelieveld et al., 2008, Paulot et al., 2009). Hofzumahaus et al. (2009) suggested two hypothetical reactions involving unknown compound X (RO₂+X → HO₂ and HO₂+X → OH, both of the same rate as for the corresponding NO reactions) for reformation of OH. However, the actual chemical identification of X is not known. Additionally, Di Carlo et al. (2004) have also proposed that the missing OH reactivity may be due to some terpene-like temperature dependent unknown BVOCs species. It is also possible that these terpene-like compounds and their oxidation products (such organic acids and peroxides) could form new particles, in the absence of isoprene."

3. The use of ion induced nucleation mechanism in explaining the observed evening nucleation events is not well motivated. It should be discussed more clearly that/which other nucleation mechanisms could be responsible for the observed evening NPF events.

Reply: As we stated clearly in the discussion manuscript "At present, we cannot address if other nucleation processes such binary or ternary homogeneous nucleation (BHN or TNH) besides IIN also played a role in sulfur plumes, since the current BHN (Vehkamaki et al., 2002) and THN (Merikanto et al., 2007) theories are highly uncertain to make high fidelity simulations."

The reason is that the predictions of classical homogeneous nucleation theories contain large uncertainties in the range of a few orders of magnitude or more, due to lack of relevant thermodynamic data for small molecular clusters (Seinfeld and Pandis, 2006; Merikanto et al., 2007) and thus least constrained by observations. On the other hand, the IIN parameterization based on the laboratory measured thermodynamic data for the growth and evaporation of small cluster ions containing H₂SO₄ and H₂O (Lovejoy et al., 2004) and has been constrained by in-situ measurements of aerosol sizes and

C4577

precursors at a wide range of atmospheric conditions (Lee et al., 2003).

For your information, we have also tested current BHN (Vehkamaki et al., 2002), THN (Merikanto et al., 2007) and IIN (Modgil et al. 2005) parameterizations for a range of observed environmental conditions (temperature and RH) during two evening NPF events (refer to Fig. 1 below), assuming relatively higher concentrations of H₂SO₄ and NH₃. It is clear that BHN and THN are very unlikely to produce particles (nucleation rates of about $1 \times 10^{-6} \text{ cm}^{-3} \text{ s}^{-1}$), while IIN (nucleation rate of about $0.23 \text{ cm}^{-3} \text{ s}^{-1}$) is likely the mechanism in sulfur plumes.

Technical Comments:

1. Page 11050 line 22: Wrong reaction

Reply: corrected as $\text{RO}_2 + \text{HO}_2 \rightarrow \text{ROOH} + \text{O}_2$.

2. Page 1155 line 12: Why do the authors not use IUPAC recommended values for rate constants?

Reply: We have cited IUPAC (Atkinson et al., 2006) in the revised manuscript as the rate constants used (Finlayson-Pitts and Pitts, 2000) are in fact extremely similar to IUPAC preferred one (at 298 K).

Table 1. Reaction rate constants

Rate constants	Values used (Finlayson-Pitts and Pitts, 2000) ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	IUPAC preferred values ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)
$k_{\text{isoprene-OH}}$	101×10^{-12}	100×10^{-12}
$k_{\alpha\text{-pinene-OH}}$	53.7×10^{-12}	53.0×10^{-12}
$k_{\text{isoprene-O}_3}$	12.8×10^{-18}	12.7×10^{-18}
$k_{\alpha\text{-pinene-O}_3}$	86.6×10^{-18}	90.0×10^{-18}

3. At a couple of places in the manuscript, the authors should recheck the grammar.

C4578

Reply: We have corrected grammatical mistakes and re-constructed sentences where necessary in the revised manuscript.

Figure captions:

Fig.1 Sensitivity test for BHN (top panel), THN (middle panel) and IIN (bottom panel) parameterizations for a range of observed environmental conditions during two evening nucleation events.

References:

Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., Troe, J., Evaluated kinetic and photochemical data for atmospheric chemistry: Volume II - gas phase reactions of organic species, Atmos. Chem. Phys., 6, 3625-4055, 2006

Di Carlo, P., Brune, W. H., Martinez, M., Harder, H., Leshner, R., Ren, X., Trobberly, T., Carroll, M. A., Young, V., Shepson, P. B., Riemer, D., Apel, E., and Cambell, C.: Missing OH reactivity in a forest: Evidence for unknown reactive biogenic VOCs, Science, 304, 722-725, 2004.

Donahue, N. M., Kroll, J. H., Anderson, J. G., Demerjian, K., Direct observation of OH production from the ozonolysis of olefins, Geophys. Res. Lett., 25, 59-62, 1998.

Finlayson-Pitts, B. J., and Pitts, J. N.: Chemistry of the upper and lower atmosphere: Theory, experiments, and applications, Academic Press, San Diego, CA, 2000.

Hofzumahaus, A., Rohrer, F., Lu, K. D., Bohn, B., Brauers, T., Chang, C. C., Fuchs, H., Holland, F., Kita, K., Kondo, Y., Li, X., Lou, S. R., Shao, M., Zeng, L. M., Wahner, A., Zhang, Y. H.: Amplified Trace Gas Removal in the Troposphere, Science 324, 1702-1704, 2009

Lee, S.-H., Reeves, J. M., Wilson, J. C., Hunton, D. E., Viggiano, A. A., Miller, T. M.,

C4579

Ballenthin, J. O., and Lait, L. R.: Particle formation by ion nucleation in the upper troposphere and lower stratosphere, *Science*, 301, 1886-1889, 2003.

Lelieveld, J., Butler, T. M., Crowley, J. N., Dillon, T. J., Fischer, H., Ganzeveld, L., Harder, H., Lawrence, M. G., Martinez, M., Taraborrelli, D., Williams, J.: Atmospheric oxidation capacity sustained by a tropical forest, *Nature*, 452, 737-740, 2008

Lovejoy, E. R., Curtius, J., and Froyd, K. D.: Atmospheric ion-induced nucleation of sulfuric acid and water, *J. Geophys. Res.*, 109, D08204, 10.1029/2003JD004460, 2004.

Merikanto, J., Napari, I., Vehkamäki, H., Anttila, T., and Kulmala, M.: New parameterization of sulfuric acid-ammonia-water ternary nucleation rates at tropospheric conditions: *J. Geophys. Res.*, 112, D15207, doi:10.1029/2006JD007977, 2007.

Modgil, M. S., Kumar, S., Tripathi, S. N., and Lovejoy, E. R.: A parameterization of ion-induced nucleation of sulfuric acid and water for atmospheric conditions, *J. Geophys. Res.*, 110, doi:10.1029/2004JD005475, 2005

Paulot, F., Crounse, J. D., Kiaergaard, J. G., Kurten, A., Clair, J. M. S., Seinfeld, J. H., and Wennberg, P. O.: Unexpected epoxide formation in the gas-phase photooxidation of isoprene, *Science*, 325, 730-733, 2009.

Paulson, S. E., Sen, A. D., Liu, P., Fenske, J. D., Fox, M. J., Evidence for the formation of OH radicals from the reaction of O₃ with alkenes in the gas phase, *Geophys. Res. Lett.*, 24, 3193-3196, 1997.

Paulson, S. E., Chung, M. Y., Hasson, A. S., OH radical formation from the gas-phase reaction of ozone with terminal alkenes and the relationship between structure and mechanism, *J. Phys. Chem. A*, 103, 8125-8138, 1999.

Sadanaga, Y., Yoshino, A., Kato, S., Kajii, Y., Measurements of OH reactivity and photochemical ozone production in the urban atmosphere, *Environ. Sci. Technol.* 39, 8847-8852, 2005.

C4580

Seinfeld, J. H., and S. N. Pandis (2006), *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*, 2nd ed., 1232 pp., John Wiley, Hoboken, N. J.

Vehkamäki, H., Kulmala, M., Napari, I., Lehtinen, E. J., Timmreck, C., Noppel, M., and Laaksonen, A.: An improved parameterization for sulfuric acid-water nucleation rates for tropospheric and stratospheric conditions, *J. Geophys. Res.*, 107, doi:10.1029/2002JD002184, 2002.

Interactive comment on *Atmos. Chem. Phys. Discuss.*, 11, 11039, 2011.

C4581

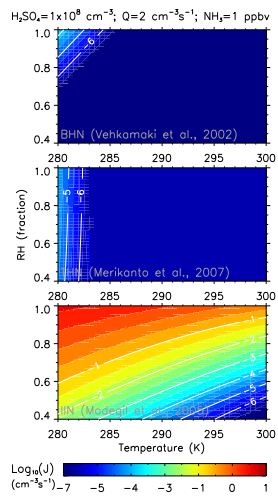


Fig. 1.

C4582