Supplemental materials to: Spatial and vertical extent of nucleation events in the Midwestern USA: Insights from the Nucleation In ForesTs (NIFTy) experiment

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1 Event classification

Data from all four aerosol particle sizing instruments operated during NIFTy were analyzed to determine event frequency and characteristics based on a subjective classification protocol (Dal Maso et al., 2005;Boy and Kulmala, 2002):

- Event class A: Formation of an aerosol particle mode (with a number geometric mean diameter (nGMD) below 25 nm) which subsequently exhibits clear and sustained growth.
- Event class B: Formation of a new aerosol particle mode but it was not visible at the lowest aerosol particle sizes considered. Some growth was observed, but was not continuous, thus determining a growth rate was difficult.
- Event class C: Increased ultra-fine aerosol particle concentrations were observed but the mode did not exhibit clear and sustained growth.

All days for which valid data were collected that did not meet these criteria were allocated to a non-event class.

2 Detailed chemical and physical time series at MMSF on two event days.

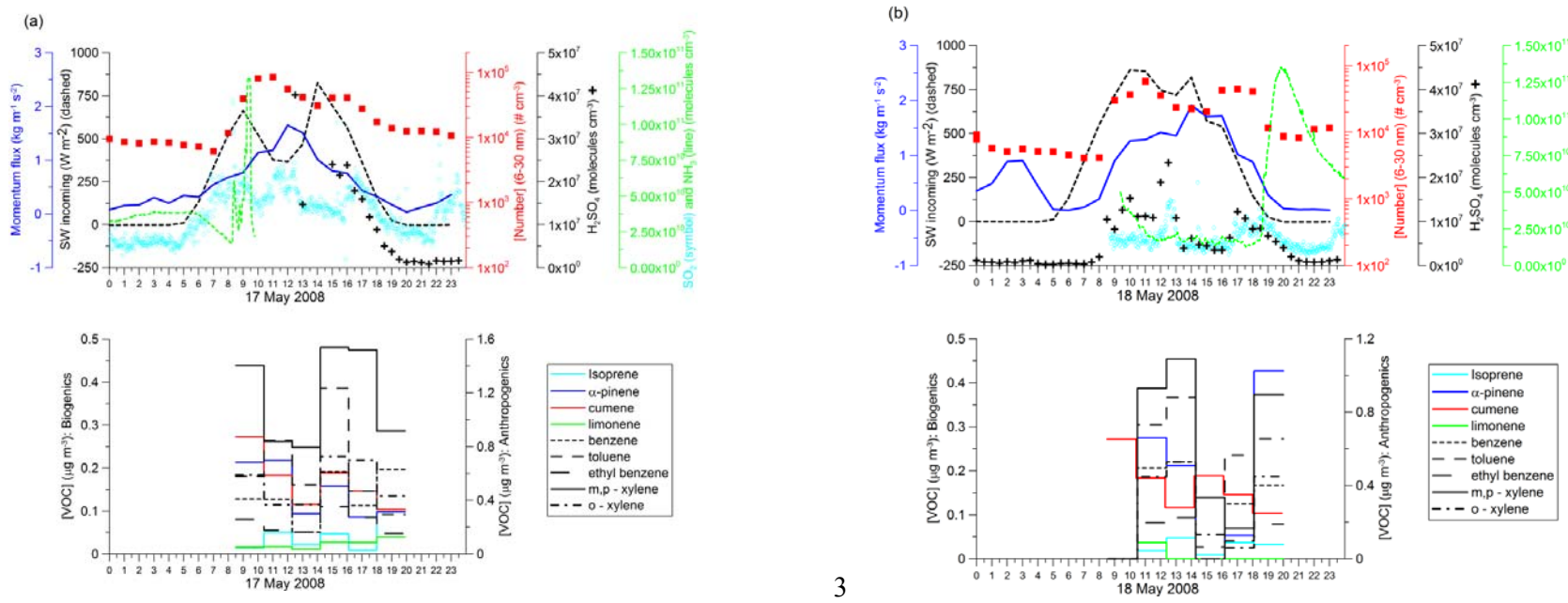

Figure S1. Upper frames: Time series of the momentum flux (used as a metric of turbulence intensity), incoming shortwave radiation, ultrafine aerosol particle number concentration (Dp = 6 to 30 nm), sulfuric acid (H_2SO_4), ammonia (NH_3), sulfur dioxide (SO_2) at MMSF during (a) 17 May, and (b) 18 May 2008. Both days were characterized by double-peak nucleation events (see main text Fig. 4 for the size distributions). The lower frames show the speciated 2-hour average VOC concentrations on those days. In the lower frames the concentration of VOCs that are principally of biogenic origin is shown on the left-hand axis while those of predominantly anthropogenic origin are shown on the right-hand axis.

3 Condensational sink and Nucleation parameter values and comparison with data from Hyytiälä

Average NP values at MMSF are higher on event than non-event days (Fig. S2), and are higher than NP values at Hyytiälä on event days. When NP is computed for Hyytiälä using a wavelength specific radiative flux (UV-A), new aerosol particle formation in April and May only initiated when NP > 2.7×10^{-25} W m molecules^{-1} K^{-1}. Scaling the threshold of NP > 2.7×10^{-25} W m molecules^{-1} K^{-1} for Hyytiälä (Boy and Kulmala, 2002) by a factor of 17 (to convert a radiative flux in the UV-A band to total down-welling shortwave radiation (Johnson et al., 1976)) gives 4.6×10^{-24} W m molecules^{-1} K^{-1} which is a factor of six lower than the threshold of 3.0×10^{-23} W m molecules^{-1} K^{-1} implied by data from MMSF. This discrepancy may be due to variations in the relationship between shortwave and UV-A that derive from factors such as cloud cover, aerosol optical depth and water vapor (Grant et al., 1996), but it may also reflect either the higher condensational sink at MMSF which means a higher NP is needed for larger production of H_2SO_4 (from SO_2), or that a larger radiative flux is required to destabilize the atmosphere at MMSF.

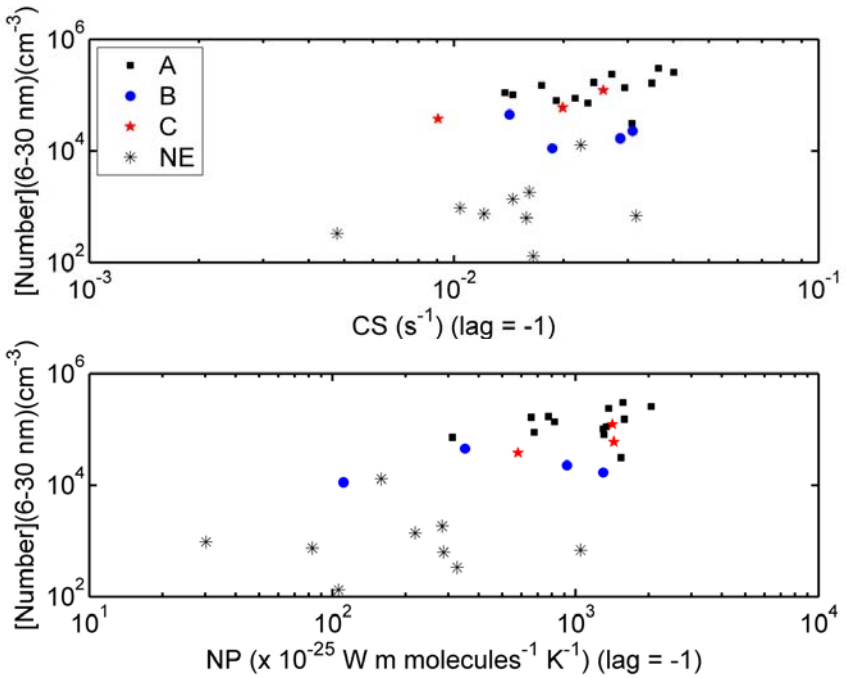

Figure S2. Scatterplots of the (a) condensational sink (CS) and (b) the nucleation parameter (NP) of Boy and Kulmala (2002) versus number concentration of aerosol particles with Dp = 6 - 30 nm at MMSF during 1-31 May 2008 conditionally sampled by event class. Note CS and NP were computed for one-hour prior to the aerosol particle number concentration maximum on event days and at 11:00-12:00 (LST) for non-event days. The aerosol particle number concentration (for Dp = 3 to 30 nm) is computed for the hour of highest total aerosol particle concentrations at 46 m on event days and for 12:00-13:00 LST on non-event days.

4 Assessing the role of VOCs

It has been proposed that oxidation products of monoterpenes and other VOCs may be directly involved in aerosol particle nucleation or stabilization of nuclei clusters (Bonn et al., 2009). Thus we examined the relationship between possible production of low-volatility condensable products from the measured VOCs and the concentration of ultrafine aerosol particle concentrations for all days when ultrafine aerosol particle concentrations and H_2SO_4 or the VOC concentrations are available. This analysis assumes the measured VOCs are adequate indicators of the gases that will be oxidized to generate potentially nucleating gases, and that Fractional Aerosol Coefficients (FAC) adequately represent production of low volatility vapors, and thus must be viewed with caution. Each of the measured VOC (isoprene, α-pinene, limonene, cumene (isopropylbenzene), benzene, toluene, ethyl benzene, o-, m-, and p-xylene) was ascribed both a FAC that described the fraction of the compound that has the potential to be oxidized to a condensable vapor and a reacted fraction that describes the fraction that can be oxidized based on its reaction rate with the hydroxyl radical (see Table S1 for the values used). It is acknowledged that this approach neglects the availability of oxidants and the relationship with condensed mass (Griffin et al., 2003), but is applied here to broadly represent the potential for the production of oxidation products with low volatility that might participate either in nucleation or condensation. Total condensable mass from FAC and the fractions from biogenic and anthropogenic gases as measured during the morning hours (09:00 to 13:00 LST) exhibit a weak negative correlation with ultrafine aerosol particle concentrations (Fig. S3), while mean morning H_2SO_4 (computed for the same time period as the VOCs) indicates a relatively strong positive relationship with the maximum aerosol particle number concentration (r^2 =0.5 for a power law fit). This implies nucleation occurrence and particle production rates are much more strongly related to H_2SO_4 than VOC concentrations or low volatility oxidation products there from.

Table S1. The FAC and reacted fraction values used in analysis of the VOCs. The values shown are taken from (Grosjean, 1992) except for isoprene for which the FAC is from (Lu et al., 2009) and the reacted fraction is assumed to be an average of the other biogenics.

	Fraction aerosol coefficient (%)	Reacted fraction
Isoprene	2	0.33
α-pinene	30	1
cumene (isopropyl benzene)	4	0.13
Limonene	3	0.12
Benzene	0	0
Toluene	5.4	0.12
Ethyl benzene	5.4	0.15
(m,p)-xylene (average)	3.5	0.34
o-xylene	5	0.26

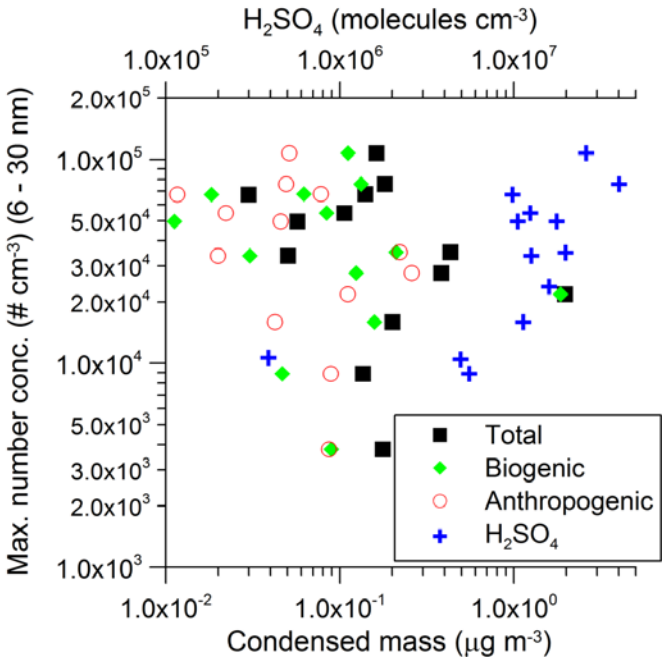

Figure S3. Daily maximum ultrafine aerosol particle number concentration plotted as a function of FAC derived condensed mass from the morning VOC concentrations (i.e. derived from the sum of the VOC concentrations in the 09:00-11:00 and 11:00-13:00 (LST) samples). Also shown is the relationship between the daily maximum aerosol particle number concentration and mean morning H_2SO_4 concentrations (computed as the average of the observations from 09:00-13:00 (LST)).

5 References

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