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Production of new particles over forests is an important source of cloud condensation nuclei that can affect climate. While such particle formation events have been widely observed, their formation mechanisms over forests are poorly understood. Our observations made in a mixed deciduous Michigan forest with large isoprene emissions during the summer show surprisingly rare occurrence of new particle formation (NPF). No NPF events were observed during the 5 weeks of measurements, except two evening ultrafine particle events as opposed to the typically observed noontime NPF elsewhere. Sulfuric acid concentrations were in the 10^6 cm^{-3} ranges with very low preexisting aerosol particles, a favorable condition for NPF to occur even during the summer. The ratio of emitted isoprene carbon to monoterpene carbon at this site was similar to that in Amazon rainforests (ratio >10), where NPF is also very rare, compared with a ratio <0.5 in Finland boreal forests, where NPF events are frequent. Our results showed that large isoprene emissions can suppress NPF formation in forests although the underlying mechanism for the suppression is unclear and future studies are needed to reveal the likely mechanism. The two evening ultrafine particle events were associated with the transported anthropogenic sulfur plumes and the ultrafine particles likely formed via ion induced nucleation. Changes in landcover and environmental conditions could modify the isoprene suppression of NPF in some forest regions resulting in a radiative forcing that could influence climate.

1 Introduction

While having a large impact on regional climate, aerosol particles also affect human health, air quality and visibility. Particle nucleation (formation of a liquid or solid particle from gas phase species) occurs nearly everywhere in the Earth's atmosphere (Kulmala et al., 2004) and these newly formed particles contribute 15–55% of the global cloud condensation nuclei (CCN) production (Spracklen et al., 2008). CCN production rates

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and the impact of anthropogenic and natural emissions on these rates are crucial for quantifying the aerosol indirect effects on the radiative forcing of climate. New particle formation (NPF) events also have a distinctive seasonal variation globally, with the higher frequency in spring and fall (~30–50%) and the lower frequency in summer and winter (~10–15%) (Kulmala et al., 2004). Observations show sulfuric acid (H_2SO_4) (Kuang et al., 2008; Sipila et al., 2010; Vehkamäki et al., 2002) is the main particle nucleation precursor, but ammonia (NH_3) (Ball et al., 1999; Merikanto et al., 2007), organic compounds including amines and organic acids (Hoffmann et al., 1998; Metzger et al., 2010; O'Dowd et al., 2002; Smith et al., 2009; Zhang et al., 2004) and charged ion clusters (Lee et al., 2003; Yu and Turco, 1997; Lovejoy et al., 2004) can be also involved in particle nucleation under different atmospheric conditions. At present, the processes leading to formation of new particles in various atmospheric environments, especially in the boundary layer, remain unclear.

Forests cover about a third of the earth land surface but contribute about two thirds of biogenic volatile organic compound (BVOC) emissions (Goldstein and Galbally, 2007; Guenther et al., 1995). The global emission of isoprene, which is the main BVOC, is estimated to be 440–600 teragrams of carbon (TgC yr^{-1}) (Guenther et al., 2006). The latest estimate of secondary organic aerosol formation by BVOCs ranges from 10–90 TgC yr^{-1} , a significantly large fraction of the total organic aerosol budget on a global scale (Hallquist et al., 2009; Heald et al., 2008). There are also large uncertainties in these estimates, depending on estimation method (e.g., top-down versus bottom-up) and the detailed chemistry of secondary organic aerosol formation (Hallquist et al., 2009).

Field observations and laboratory experiments show that low volatility oxidation products of biogenic monoterpenes (MT) and sesquiterpenes (SQT) (e.g., *cis*-pinonic or *cis*-pinic acids, organic peroxides, and criegee intermediate compounds) can contribute to aerosol nucleation (Bonn and Moortgat, 2003; O'Dowd et al., 2002; Hoffmann et al., 1998; Tunved et al., 2006; Burkholder et al., 2007). Isoprene oxidation products can also be important in aerosol growth as observed in laboratory studies (Claeys

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et al., 2004; Surratt et al., 2010) and field observation (Froyd et al., 2010; Zhang et al., 2009), under both low and high nitrogen oxides ($\text{NO}_x = \text{NO} + \text{NO}_2$) conditions. However, recent studies based on plant chamber experiments have suggested that in actual forests, isoprene emissions could suppress biogenic NPF (Kiendler-Scharr et al., 2009). This suppression would reduce the aerosol climate cooling effects over forests, because increasing temperatures in the northern latitudes would increase isoprene emissions and could lead to reduced NPF rates, while fewer aerosols would allow more solar radiation to warm the surface. But atmospheric observation evidence of isoprene suppression of NPF in actual forest environments is currently lacking.

NPF has been observed widely in various forest environments, such as Finland boreal forests (Sihto et al., 2006; Makela et al., 1997), European coniferous forests (Held et al., 2004) and African savanna forests (Laakso et al., 2008). In contrast to these forests, NPF has not been reported from Amazonian forests, even though this is one of the regions where intense atmospheric observations have been made for decades (Martin et al., 2010; Zhou et al., 2002; Pöschl et al., 2010). The exceptions are some unique cases, when ultrafine particles formed in the outflow of clouds were transported from the free troposphere down to the boundary layer (Rizzo et al., 2010). In Amazonian forests, the aerosol surface area was too large for active NPF and low volatility oxidation products of BVOCs were instead scavenged rapidly to the pre-existing aerosol particles.

The forests in the northern Michigan are largely composed of bigtooth aspen (*Populus grandidentata* Michx.), quaking aspen (*P. tremuloides* Michx.) (two predominant species), beech (*Fagus grandifolia* Ehrh.), paper birch (*Betula papyrifera* Marsh.), maple (*Acer rubrum* L., *A. saccharum* Marsh.), red oak (*Quercus rubra* L.), white pine (*Pinus strobus* L.) and bracken fern (*Pteridium aquilium*) (Pearsall, 1995) and therefore, are representative of a typical northern mid-western United States deciduous forests. Isoprene emissions are particularly large (>95% of the total terpenoid emissions) compared to MT and SQT emissions (Ortega et al., 2007). The mixed deciduous type Michigan forest thus provide an ideal environment to study NPF from BVOCs, as

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the BVOC emission fluxes, particularly for isoprene, have been systematically studied for more than ten years (Pressley et al., 2005; Apel et al., 2002; Westberg et al., 2001). However, despite intensive studies in the Michigan forest, ultrafine particle measurements have been limited, except one study which showed formation of Aitken mode particles in the size range from 15–40 nm from breaking waves on Lake Michigan (Slade et al., 2010) and another study showing Aitken mode particle formation associated with intense sulfur plumes (Delia, 2004). Studies from a similar deciduous forest site in the mid-western USA (Indiana) have observed frequent NPF events but the cause of these events was linked to the close proximity of large urban areas, with elevated concentrations of H_2SO_4 (in the 10^7 cm^{-3} range) and sulfur dioxide (SO_2) (Pryor et al., 2010).

Here, we present first comprehensive study of ultrafine particles in a relatively clean Michigan forest during the summer of 2009. Aerosol particles in the diameter range from 3–109 nm were measured at the University of Michigan Biological Station (UMBS) at ground level (5 m) from 1 July–3 August 2009. H_2SO_4 , NH_3 , SO_2 , NO_x , OH, and various VOCs (including isoprene and MT) were also measured at the same site. We further calculated isoprene, MT and SQT emission rates with the Model of Emissions of Gases and Aerosols from Nature (MEGAN) model (Guenther et al., 2006). Simulations with a microphysical box model incorporated with ion-induced nucleation (IIN) (Lovejoy et al., 2004) were also performed to investigate the nucleation mechanism responsible for the two early evening ultrafine particle events seen in the Michigan forest. A brief description of methods used is provided in the following section.

2 Methods

2.1 Observation site

The data presented in the present study were taken during the Program for Research on Oxidants PHotochemistry, Emissions, and Transport (PROPHET) Community

Atmosphere-Biosphere Interactions Experiments (CABINEX)-2009 campaign at the UMBS (45.56° N, 84.72° W) from 1 July–3 August 2009. The detailed campaign information, including the platform and measurements, is also available at <http://esse.engin.umich.edu/prophet/CABINEX.html>. Figure 1 shows the location of the UMBS measurement site on a regional map, along with point sources ($>10^3$ tons) of SO₂ and nitrogen oxides (NO_x = NO+NO₂) for 2009. The unique feature of this site is that isoprene, MT and SQT have been measured since 1998 (Westberg et al., 2001; Apel et al., 2002; Pressley et al., 2005; Pressley et al., 2006; Barket Jr. et al., 2001; Kim et al., 2009; Ortega et al., 2007). The specific ecosystem at this site is in the transition zone between mixed hardwood and boreal forest on a high-outwash plain deposited by glacial drift (Pearsall, 1995; Schmid et al., 2003). The measurement site is heavily forested with minimal interferences of local anthropogenic pollution sources. This site is ideal for studying atmospheric chemistry under a wide range of environmental conditions, including clean continental air from central Canada, mixed air masses of biogenic and anthropogenic influence, and urban plumes from Midwestern industrial centers (Cooper et al., 2001; Carroll et al., 2001).

2.2 Aerosol and trace gas measurements and trajectory calculations

Aerosol size distributions were measured with Kent State University's three sets of different scanning mobility particle spectrometers (SMPS). Particle sizes in the diameter range from 3–109 nm were measured with a nano-differential mobility analyzer (NDMA, TSI 3085) with a water condensation particle counter (CPC, TSI 3786) and aerosol sizes in the diameter range from 4–157 nm with a NDMA (TSI 3085) with a butanol CPC (TSI 3776) at the ground level (5 m) in the canopy and aerosol sizes in the diameter range from 20–800 nm with a Long-DMA (TSI 3081) with a butanol-CPC (TSI 3772) at above-canopy level (26.6 m). In this study, we used data measured with the NDMA (TSI 3085) in combination with a water-CPC (TSI 3786) at the ground level (5 m) in the canopy from 1 July–3 August 2009.

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H₂SO₄ and NH₃ were also measured with Kent State University two chemical ionization mass spectrometers (CIMSs) in the canopy during the same period (Benson et al., 2008; Benson et al., 2009; Benson et al., 2010; Erupe et al., 2010; Nowak et al., 2006; Tanner and Eisele, 1995; Young et al., 2008). H₂SO₄ was measured using NO₃⁻ ions as reagent. The detection limit of H₂SO₄-CIMS was $\sim 2 \times 10^5 \text{ cm}^{-3}$ and the uncertainty associated with the measurement was estimated to be $\sim 60\%$ at maximum (Erupe et al., 2010). Protonated ethanol ions were used for the NH₃ detection. The detection limit of NH₃-CIMS was ~ 0.06 ppbv and the overall uncertainty associated with the measurement was $0.03 \text{ ppbv} \pm 30\%$ (Benson et al., 2010).

A variety of volatile organic compounds (VOCs), including isoprene, MT, and isoprene oxidation products [e.g., methylvinylketone (MVK) and methacrolein (MACR)] were measured by the Washington State University proton transfer reaction mass spectrometer (PTR-MS) (Lindinger et al., 1998; de Gouw and Warneke, 2007). The PTR-MS instrument uses H₃O⁺ as an reagent ion; the detection limit ranged from 0.01–0.1 pptv (de Gouw and Warneke, 2007). Hydroxyl (OH) radicals were measured by the Indiana University laser induced fluorescence (LIF) instrument (Dusanter et al., 2009); the detection limit was $\sim 2 \times 10^5 \text{ cm}^{-3}$ with the estimated uncertainty of $\pm 18\%$ (1σ). Isoprene and speciated MT fluxes were measured by National Center for Atmospheric Research (NCAR) using a cartridge Relaxed Eddy Accumulation (REA) system. Samples were collected on Tenax GR and Carbograph 5TD adsorbent tubes and analyzed with an Agilent 7890A gas chromatograph with a flame ionization detector for quantification and a 5975C electron impact mass spectrometer for identification. SO₂ was measured by the University of Houston with a Thermo Environmental 43i-TLE pulsed UV-fluorescence analyzer; the detection limit was 0.058–0.095 ppbv with an uncertainty of $\pm 10\%$. NO and NO₂ were measured by the Washington State University with a chemiluminescence detector (the measurement accuracy was 7.5%). Meteorological parameters such as air temperature, relative humidity (RH), wind speed, and wind direction were also measured by the Washington State University with a Vaisala Weather Transmitter (WXT520) (Pressley et al., 2006).

Backward trajectories of air masses were calculated with the National Oceanic and Atmospheric Administration (NOAA) Air Resources Laboratory (ARL) Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPPLIT) PC version model (Draxler and Rolph, 2010) using gridded wind fields from the Eta Data Assimilation System (EDAS) (Kanamitsu, 1989).

2.3 SCIAMACHY NO₂ column retrievals

The SCanning Imaging Absorption spectroMeter for Atmospheric CartograpHY (SCIAMACHY) instrument was launched on the European ENVironmental SATellite (ENVISAT) spacecraft in March 2002 in a sun-synchronous orbit at an altitude of 800 km (Bovensmann et al., 1999). The instrument measures backscattered solar radiation in the ultraviolet, visible, and near-infrared regions of the spectrum, from 0.24–2.38 μm, in the nadir and limb modes. In the nadir mode the horizontal resolution is 30 km×60 km, and the instrument achieves global observational coverage within 6 days. In the present study, we have used retrievals of the tropospheric column abundance of NO₂ using the Differential Optical Absorption Spectroscopy (DOAS) algorithm (Richter et al., 2005) to locate large point sources of anthropogenic emissions in the regional vicinity of the UMBS measurement site.

2.4 Model of emissions of gases and aerosols from nature

Emissions rates of isoprene, MT and SQT were estimated using the MEGAN model, version 2.04 (Guenther et al., 2006; Sakulyanontvittaya et al., 2008). MEGAN model is a global model with a base resolution of ~1 km that is used for estimating the net emission rates of gases and aerosols from terrestrial ecosystems into the atmosphere. A site-specific version of MEGAN was used to simulated biogenic VOC emissions during CABINEX using site-specific emission factors, landcover and weather conditions. Isoprene and MT emission factors (mg compound m⁻² ground area h⁻¹) were based on the REA flux measurements conducted during CABINEX while SQT fluxes, which

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were not measured during CABINEX, were based on earlier observations at this site reported by Kim et al. (2009). Individual MT and SQT were classified as light dependent, light-independent, or fractions of both based on the observations of Ortega et al. (2007) at this site. Thirty minute average variations in emissions estimated with MEGAN were driven by changes in landcover data and environmental conditions. Landcover inputs consisted of monthly average Leaf Area Index (LAI) based on MODIS satellite observations. LAI variations were used to characterize changes in total foliage and leaf age according to procedures described by Guenther et al. (Guenther et al., 2006). Above canopy temperature, photosynthetically active radiation measured at the site were used as inputs to the MEGAN canopy environment model. Leaf temperature and incident solar radiation of sun and shade fractions were calculated at five canopy depths and used to drive the short-term and long-term components of the Guenther et al. (2006) algorithms for simulating the emission response to light and temperature.

2.5 Aerosol microphysical box model incorporated with IIN parameterization

The sulfuric acid-water aerosol microphysical ion nucleation (SAMIN) box model (Kanawade and Tripathi, 2006) was used in our nucleation simulations. SAMIN includes the IIN parameterization (Modgil et al., 2005) which was based on the IIN kinetic model (Lovejoy et al., 2004). The IIN model uses the laboratory measured thermodynamic data for the growth and evaporation of small cluster ions containing H_2SO_4 and H_2O (Lovejoy et al., 2004) and has been constrained by in-situ measurements of aerosol sizes and precursors at a wide range of atmospheric conditions (Lee et al., 2003). Positive ions are less likely to nucleate compared to negative ions (Froyd and Lovejoy, 2003), and the IIN kinetic model treats positive ions as a single species and treats the neutral and negative ions explicitly (Lovejoy et al., 2004). SAMIN simulates IIN parameterization, H_2SO_4 condensational growth and evaporation, water vapor equilibrium, particle-particle coagulation and sedimentation removal. These processes are achieved using a noniterative semi-implicit scheme with integration time step of 60 s. The model covers particle sizes from 0.3 nm to $\sim 1 \mu\text{m}$ diameter, which are

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geometrically divided into 40 bins.

3 Results and discussion

3.1 Non-NPF events

There were no typical NPF events at noontime during the summer of 2009 in the Michigan forest (Fig. 2a). Out of 5 weeks of continuous measurements, we observed only two abrupt ultrafine particle events (16 July and 2 August) during the early evening, as opposed to the noontime where well-characterized nucleation and persistent growth have been typically observed in locations worldwide (Kulmala et al., 2004). Ultrafine particle events were identified when there was clear evidence of particles in the diameter from 3–10 nm (N_{3-10}) and these small particles grew larger for at least 3 h continuously. In this section we examine non-NPF conditions and in the following section we discuss two early evening ultrafine particle events.

The mean particle concentration in the size range from 3–10 nm was 86 cm^{-3} at noontime. The noontime peak H_2SO_4 concentration was $2.6 \times 10^6 \text{ cm}^{-3}$, and under very low condensational sink (CS , which is proportional to the measured aerosol surface area density; $1.5 \times 10^{-3} \text{ s}^{-1}$) (Fig. 2b), this H_2SO_4 concentration should be sufficient to trigger NPF (McMurry et al., 2005), as observed elsewhere over the world, including in Finland boreal forests (Petaja et al., 2009). These results indicate that the relatively clean Michigan forest had favorable condition for NPF, in terms of H_2SO_4 and CS during the summer. Usually the global NPF frequency is lower in the summer ($\sim 10\text{--}20\%$) and higher in the spring and fall ($\sim 30\text{--}50\%$) (Kulmala et al., 2004). Therefore, when considering this generally low NPF frequency in summer, one would expect at least 4–5 days of NPF events during 5 weeks, but the Michigan forest did not show such conventional noontime NPF events at all with the reasonable H_2SO_4 and extremely low CS conditions (Fig. 2b). This result suggests that there may be a mechanism in which NPF was “blocked” or “suppressed” in this biogenic environment.

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The Kiendler-Scharr et al. (2009) plant chamber experiments have shown that isoprene suppresses biogenic NPF and such suppression effects are also dependent on the ratio (R) of emitted isoprene carbon to MT carbon. They showed a complete “shut-down” of NPF when R reached ~ 20 , by increasing isoprene concentrations but keeping other BVOCs constant in their chamber experiment. Our MEGAN model-calculated isoprene and MT emission rates in the Michigan forest were $1.32 \pm 0.7 \text{ mgC m}^{-2} \text{ h}^{-1}$ and $0.05 \pm 0.02 \text{ mgC m}^{-2} \text{ h}^{-1}$, respectively, and thus R was 26.4 ± 4.5 . We have also compared these results with two other forests with extreme cases of NPF frequencies. In Amazon forests where NPF was never seen (Martin et al., 2010; Zhou et al., 2002), isoprene and MT emission rates were $1.9\text{--}8.8 \text{ mgC m}^{-2} \text{ h}^{-1}$ and $0.22\text{--}0.76 \text{ mgC m}^{-2} \text{ h}^{-1}$, respectively, and thus R was 15.2 (Greenberg et al., 2004); the Michigan values were very close to this case. In contrast, in Finland boreal forests where frequent NPF was observed (Sihto et al., 2006; Makela et al., 1997), isoprene and MT emission rates were $0.03 \text{ mgC m}^{-2} \text{ h}^{-1}$ and $0.16 \text{ mgC m}^{-2} \text{ h}^{-1}$, respectively, and R was 0.18 (Spirig et al., 2004) (Table 1). These R values in these three forests showed the same trend with the ratios of isoprene and MT concentrations (Table S1). These results thus are consistent with the Kiendler-Scharr et al. plant chamber study (Kiendler-Scharr et al., 2009) which showed that NPF is inhibited by isoprene at high R values (>10).

To directly compare the relative oxidations rates of isoprene and MT by OH reaction, we also looked at the $(k_{\text{isoprene-OH}}[\text{isoprene}])/(k_{\text{MT-OH}}[\text{MT}])$ ratio, where $k_{\text{isoprene-OH}}$ and $k_{\text{MT-OH}}$ are the rate constants of isoprene and MT with OH, respectively; this ratio is also directly related to R . Based on the averaged diurnal variation of isoprene, MT, and OH concentrations observed in the Michigan forest for 8–16 July 2009 (Fig. 3a), the averaged noontime peak $(k_{\text{isoprene-OH}}[\text{isoprene}])/(k_{\text{MT-OH}}[\text{MT}])$ ratio was ~ 26 (Fig. 3b). This ratio was also similar to that observed in Amazon forests (~ 20) (Kesselmeier et al., 2002). In Finland boreal forests, this ratio was <1 (Sellegrri et al., 2005) (Fig. 3b). These results further confirm that oxidation of isoprene with OH dominates over oxidation of MT with OH in the Michigan and Amazon forests, where NPF was suppressed.

Kiendler-Scharr et al. (2009) also speculated that the isoprene suppression effects on NPF were due to the OH depletion by isoprene. Our OH measurements in the Michigan forest were of the order of $1.2\text{--}1.5 \times 10^6 \text{ cm}^{-3}$ (noontime peak), between those in Amazon forests ($5 \times 10^6 \text{ cm}^{-3}$) (Martinez et al., 2010) and Finland boreal forests ($7 \times 10^5 \text{ cm}^{-3}$) (Petaja et al., 2009). This was also close to that measured previously at the same site, which showed that OH was actually higher than model-predicted (Di Carlo et al., 2004), in line with a recent study showing that isoprene may regenerate OH radicals in biogenic environments (Paulot et al., 2009). Therefore, we believe that isoprene did not suppress OH in the Michigan forest, although the absence of NPF was due to the excessive isoprene concentrations compared to MT.

Recently, Surratt et al. (2010) showed that isoprene-OH oxidation products (e.g., isoprene epoxydiols (IEPOX) at low NO_x and methacryloylperoxynitrate (MPAN) at high NO_x conditions) can partition to atmospheric aerosols. Single particle measurements made in a wide range of the free troposphere even far away from the isoprene source regions also identified the presence of organosulfates, indicative of the IEPOX partitioning on acidic sulfate particles, at low NO_x conditions when total concentrations of MVK and MACR (both primary isoprene oxidation products) exceeded 1.2 ppbv (Froyd et al., 2010). The measured NO and NO_2 concentrations at this site were <0.25 ppbv and <2 ppbv, respectively, during the summer 2009. We have calculated the ratio of $(k_1[\text{RO}_2][\text{NO}])/(k_2[\text{RO}_2][\text{HO}_2])$, where the rate constant $k_1 = 7.5\text{--}9 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ (Finlayson-Pitts and Pitts, 2000) for $\text{RO}_2 + \text{NO} \rightarrow \text{RO} + \text{NO}_2$ and $k_2 = 0.5\text{--}1.5 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ (Finlayson-Pitts and Pitts, 2000) for $\text{RO}_2 + \text{HO}_2 \rightarrow \text{OH} + \text{NO}_2$. The calculated daytime ratio was <0.1 and suggest that the reaction of organic peroxy radicals with HO_2 is predominantly more active than with NO. Thus, the Michigan forest atmosphere during the summer can be considered as a low- NO_x environment. The (MVK+MACR)/isoprene ratio, which is indicative of the extent of isoprene oxidation, was very low (~ 0.2), consistent with a previous report at the same site (Apel et al., 2002) (Fig. 3c). These results indicate that the majority of isoprene molecules were not fully oxidized to produce low volatility species such as IEPOX. This trend is also consistent with Henze and Seinfeld

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(Henze and Seinfeld, 2006) study showing that isoprene oxidation is often incomplete near the source region due to its high emission rates. The (MVK+MACR)/isoprene ratio measured in the Michigan forest was also surprisingly similar to that in Amazon forests (Kesselmeier et al., 2002), whereas this ratio was much higher (>1) in Finland boreal forests (Rinne et al., 2002) (Fig. 3c).

It has been previously postulated that biogenic NPF can be attributed to MT- and SQT-ozone (O_3) reactions (Bonn and Moortgat, 2003; Hoffmann et al., 1998; O'Dowd et al., 2002; Burkholder et al., 2007). MT and SQT concentrations in the Michigan forest were 0.35 ± 0.24 ppbv (this study) and 0.02 ppbv (Kim et al., 2009), respectively. These values were in fact comparable to the conditions observed in Finland boreal forests (Table S1). The measured O_3 concentrations in the Michigan forest (e.g., noon-time peak ~ 32 ppbv) (Fig. 3c) were also comparable to those in Finland boreal forests (Suni et al., 2003). Regardless of these reasonable concentrations of MT, SQT and O_3 in the Michigan forest, biogenic NPF did not occur. These results again show that rather than the absolute concentrations of MT or SQT, actually the R values appear to be more important in regulating biogenic NPF processes. For the case that MT- and SQT- O_3 reaction products produce new particles (Bonn and Moortgat, 2003; Bonn et al., 2008; Burkholder et al., 2007; Hoffmann et al., 1998; O'Dowd et al., 2002), it may be possible that isoprene OH oxidation products (e.g., formaldehyde) can also react with MT and SQT ozonolysis products (e.g., Criegee intermediate compounds) and in turn suppress nucleation.

Comparing the Michigan (no NPF), Amazon (no NPF) and Finland boreal forests (frequent NPF), there are two distinctive factors regulating biogenic NPF: R and the ratio of (MVK+MACR)/isoprene. Both the Michigan and Amazon forests have much higher concentrations and emission rates of isoprene during the summer, than Finland forests. Given the relatively high concentrations of isoprene, high R values, and the results from the Kiendler-Scharr et al. (2009) plant chamber study, NPF would not occur in the Michigan and Amazon forests. In comparison, in Finland forests where the R values and isoprene emissions are substantially lower, NPF took place

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with a frequency of $\sim 10\%$ even during the summer (Kulmala et al., 2004). Also, the (MVK+MACR)/isoprene ratio was very low in the Michigan and Amazon forests compared to Finland, indicating the incomplete oxidation processes for isoprene, due to proximity of the isoprene source relative to the sampling location. Compared to the Michigan forest, additional reasons that Amazon forests did not have NPF events may be very low H_2SO_4 ($< 5 \times 10^5 \text{ cm}^{-3}$) due to low SO_2 [0.02–0.03 ppbv (Andreae and Andreae, 1988)], under pristine conditions and the extraordinarily high aerosol surface area (Table 1) due to high concentrations of primary biogenic aerosols.

Suni et al. (2008) have shown frequent nighttime events of charged ion cluster growth measured by an air ion spectrometer (AIS) in southern Australia under high isoprene emission conditions, and these results may appear to be inconsistent with isoprene suppression of NPF. But another study (Suni et al., 2009) also showed that this forest site was strongly influenced by air masses transported from marine air masses, so this may not be a pure biogenic environment. This site is also unique in terms of showing very frequent ion cluster growth events even in winter, so it was possible that the IIN process was important in this forest. As AIS only measures charged clusters, it is difficult to directly compare ion cluster growth events determined by AIS with NPF events reported by a regular differential mobility analyzer (DMA, TSI 3085), for example; in Finland boreal forests, when AIS showed nighttime ion cluster growth events, DMA-measured size distributions did not show NPF (Kulmala et al., 2004), because small clusters identified by AIS (2–4 nm) did not grow further to be measured by DMA (Junninen et al., 2008).

3.2 Two early evening ultrafine particle events

While there was no conventional noontime NPF event from the Michigan forest, there were two early evening ultrafine particle events (16 July and 2 August) both between 18:30–21:30 LT. These two evening events had strikingly similar features in trace gas and particle number concentrations, and they both were associated with high SO_2 . For example, during the 16 July event, N_{3-10} ($\sim 100\text{--}7000 \text{ cm}^{-3}$) were closely correlated

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with the simultaneous rise of SO_2 (maximum >3 ppbv, one order of magnitude higher than the background SO_2 , ~ 0.2 ppbv) and H_2SO_4 (in the range of $1\text{--}2 \times 10^6 \text{ cm}^{-3}$) (Fig. 4a). The in-situ measured NO and NO_2 were also well-correlated to abrupt rise of SO_2 (correlation coefficient of 0.89), suggesting an anthropogenic origin of the plume.

5 These results thus strongly suggest that the observed ultrafine particles were not produced locally, rather transported along with anthropogenic sulfur plumes. Around noon-time, there was a very small increase in N_{3-10} from $\sim 100\text{--}1000 \text{ cm}^{-3}$ (e.g., 16 July, Fig. 4a). However, these particles did not grow enough to show aerosol size distributions with a typical “banana shape” [found in conventional NPF events, for example, (Kulmala et al., 2004)]. During the 2 August event, NH_3 was also fairly correlated with N_{3-10} , with the highest mixing ratio of 2.7 ppbv; there were no NH_3 measurements on 16 July.

In order to localize the anthropogenic plume source, we have used a combination of satellite-based observations of tropospheric NO_2 column and back trajectory information (Fig. 5). Air masses over the Michigan forest site oscillated between those originating from relatively clean regions in the north ($\text{NO}_2 < 1 \times 10^{15} \text{ molecules cm}^{-2}$) and those originating from polluted regions to the southwest or south ($\text{NO}_2 > 5 \times 10^{15} \text{ molecules cm}^{-2}$). Remarkably, only on the two ultrafine particle event days, the air parcel back trajectories passed near Minneapolis, Minnesota where a large coal-fired power plant (Sherburne Power Plant, SPP) is located, about 35 h (16 July) and 30 h (2 August) prior to arriving at the measurement site. On 31 July, the air parcel back trajectories likely to curl Minneapolis but we did not observed ultrafine particles, due to persistent rain event along the back trajectory which scavenged ultrafine particles.

25 To investigate the nucleation mechanism that might be responsible for the observed ultrafine particles on these two events, we performed aerosol microphysical box model simulations, incorporated with an IIN parameterization (Lovejoy et al., 2004), using the measured key aerosol precursor concentrations such as SO_2 , OH , and H_2SO_4 . These two event days had very similar features in air mass history (Fig. 5), temperature,

relative humidity (RH), wind direction and wind speed (Fig. S1). The initial conditions for the box model simulations for two ultrafine particle events (16 July and 2 August) were chosen in the following manner. (i) Temperature and RH were taken from back trajectory calculations at each hour. (ii) The initial particle surface area density (SA) (2.25 $\mu\text{m}^2 \text{cm}^{-3}$) was taken from the average value of the measured particle size distributions on a clean day to represent the low SA, as air masses for both two event days experienced rain before passing the Sherburne power plant (SPP) in Minnesota, MN (where model simulations started; that is, the model running time $t = 0$). As the model simulations preceded, the total SA at each time step was also continuously updated based on the evolved aerosol size distributions;

$$SA_{i,t} = \sum_{i=1}^{i=n} \pi d_i^2 N_{i,t} \quad (1)$$

where n is the number of size bins ($i = 1, 2, 3, \dots, 40$), d_i the particle diameter in the i th size bin, and $N_{i,t}$, and $SA_{i,t}$ the particle number concentration and surface area density in the i th size bin at time t , respectively. (iii) The semi-sinusoidal shaped, diurnal variation of OH along the trajectories was taken from the average OH diurnal variation measured at the forest site during 8–16 July 2009. The sensitivity test for the prescribed OH diurnal cycle was also performed by decreasing and increasing averaged OH diurnal cycle by a factor of 2, to account for possible OH variations due to NO_x conditions in plumes. The sensitivity analysis showed that the mode diameter shifts to higher particle diameter (within the 1σ variation) with increasing OH and the number concentrations do not change significantly. (v) The contribution of the transported anthropogenic SO_2 downwind of the emission region was estimated by taking into account its atmospheric lifetime (Kunhikrishnan et al., 2004) using the following equation;

$$C = C_0 \times e^{\left(-\frac{t_{\text{trans}}}{\tau}\right)} \quad (2)$$

where C_0 is the initial SO_2 at the source region (which is the unknown value); C is

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the concentration after the time t_{trans} (3.5 ppbv measured at the forest site on the both the event days); τ is the atmospheric lifetime of SO_2 due to its chemical (via reaction with OH) and depositional losses [$\tau \approx 20$ h in summer, (Pham et al., 1995)]; t_{trans} is the transport time between SPP and forest measurement site (35 h taken from trajectory calculations). Based on this method, we have set the initial SO_2 of 15 ppbv at SPP, which is somewhat less than, but still within the order of, the SO_2 (maximum ~ 70 ppbv) measured in power plant plumes (Sorooshian et al., 2006). And SO_2 at each subsequent time step were further calculated from the Eq. (2). (iv) The initial H_2SO_4 was set as $5 \times 10^7 \text{ cm}^{-3}$ near SPP, consistent with a measurement made in power plant plumes (McMurry et al., 2005). H_2SO_4 in the air parcel during the transport were updated by taking into account the loss of H_2SO_4 by particle nucleation and growth and production from the reaction $\text{OH} + \text{SO}_2 \rightarrow \text{HSO}_3$ [$k_3 = 9.4 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ at 298 K (Finlayson-Pitts and Pitts, 2000)] and the prescribed SO_2 and OH at each time step described above. (v) Ion production rate (Q) of 2 ion pairs $\text{cm}^{-3} \text{ s}^{-1}$ was used to represent the typical lower troposphere conditions (Rosen et al., 1985). Fig. S2 shows these prescribed parameters in detail for the 16 July event; the prescribed parameters for the 2 August event were very similar.

With these prescribed and measured key atmospheric parameters (Fig. S2), IIN model simulations showed very similar features for both the ultrafine particle events. The IIN results showed that the nucleation burst occurred at the very first time step (time, $t = 1$ h) (Fig. S2) due to high H_2SO_4 in the plume. These freshly nucleated particles grew slowly over a day during the transport and reached sizes >4 nm at $t = 35$ h. The model predicted N_{3-10} and particle size distribution at the end of the model run (at the time when air masses arrived at the forest site) are in good agreement with the observed N_{3-10} and particle size distribution on both the event days (Fig. 4b for 16 July event). These results imply that IIN involving high SO_2 and H_2SO_4 can explain the observed ultrafine particles in the Michigan forest under the sulfur plume influence. In comparison, IIN simulations for non-event days (e.g., 20 July), where air masses originated from clean regions to the north of the forest site, showed no nucleation due

to low H_2SO_4 , even with sufficiently low CS .

Our IIN simulation results are different from Boy et al. (2008), which showed that IIN fails to reproduce the measured ultrafine particle concentrations in Finland boreal forests. Compared to Boy et al. (2008), our simulations indicate that nucleation occurred rapidly in sulfur plumes, because the conditions were more favorable for nucleation due to the higher SO_2 and H_2SO_4 . The air masses also experienced rain events before arriving at SPP (as seen from backward trajectory calculations) to allow very low surface areas. The high H_2SO_4 and low surface area thus provided an ideal condition for nucleation. Our results are, on the other hand, consistent with Brock et al. (2004), which showed that high SO_2 in power plant plumes can trigger IIN and these freshly nucleated particles are transported over long distances to less polluted regions. At present, we cannot address if other nucleation processes such binary or ternary homogeneous nucleation (BHN or TNH) besides IIN also play a role in sulfur plumes, since the current BHN (Vehkamäki et al., 2002) and TNH (Merikanto et al., 2007) theories are highly uncertain to make high fidelity simulations.

We have further calculated particle growth rates (GR) from the measured particle size distribution data. GR derived from the measured aerosol size distributions were $5.5 \pm 1.9 \text{ nm h}^{-1}$ and $6.6 \pm 0.7 \text{ nm h}^{-1}$ on 16 July (Fig. 3a) and 2 August, respectively. These growth rates are also within the same order as those measured in Finland boreal forests (Sihto et al., 2006; Makela et al., 1997), European coniferous forests (Held et al., 2004) and African savanna forests (Laakso et al., 2008); $2\text{--}10 \text{ nm h}^{-1}$. However, the calculated GR from condensation of H_2SO_4 alone were 0.14 and 0.11 nm h^{-1} on 16 July and 2 August, respectively, accounting for only $2\text{--}3\%$ of the measured GR . These results suggest that species other than H_2SO_4 , such as BVOC oxidation products may play a major role in the growth of nucleation-mode particles over the forest, consistent with field observations (Sellegri et al., 2005) and laboratory experiments (Zhang et al., 2009) showing that oxidation products of BVOCs can contribute to growth of newly formed nano-particles in biogenic environments.

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4 Conclusions and atmospheric implications

While many studies have been devoted to understanding how new particles form in the boundary layer, the conditions necessary for NPF event are not well understood despite the ubiquity and the global occurrence of NPF (Kulmala et al., 2004). We present a comprehensive observation of ultrafine particles in a Michigan forest which showed that conventional NPF does not occur in a mixed deciduous forest where biogenically emitted isoprene was abundant. This finding is in line with Kiendler-Scharr et al. (2009) plant chamber study showing that isoprene suppresses NPF. These results thus provide the first atmospheric evidence that the specific pattern of the emitted BVOCs can affect secondary aerosol formation in biogenic environments. While our atmospheric observations show that isoprene indeed suppresses NPF, our measurements also show that OH was not depleted in the Michigan forest, although such OH depletion may occur in well-controlled chamber experiments (Kiendler-Scharr et al., 2009). At present, the underlying mechanism how biogenic NPF is inhibited by isoprene is not clear and future studies are required to answer this important atmospheric science question. While there was a lack of NPF in this mixed forest, we also showed that ultrafine particles can be formed via IIN in a sulfur-rich plume. Once they were transported to the forest, these ultrafine particles grew rapidly by species other than H_2SO_4 , including oxidation products of BVOCs. These results are consistent with the recent study which showed that biogenic secondary aerosol formation can be promoted by anthropogenic influences (Froyd et al., 2010; Zhang et al., 2009).

The present-day forests in Northern Michigan are largely composed of tree species such as bigtooth aspen with small contribution by white pine, red maple, red oak and paper birch (Ortega et al., 2007). However, about 70% of aspen trees in the northern Michigan forest are ~50 years old and the forest average age is also greater than other mixed deciduous forests in the Great Lake region, thus beyond peak biomass production (Gough et al., 2007). This suggests a widespread change in forest structure and composition, for example, shifting from aspen trees (isoprene emitter) to pine trees (MT

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and SQT emitter), and the subsequent changes in carbon cycling dynamics (Bergen and Dronova, 2007). Indeed, an observation study (Mielke et al., 2010) showed that the MT concentrations have been increasing at this site over the past decade. When switching from bigtooth aspen to white pine tree species, R can be reduced to less than 1 (Ortega et al., 2007). As a result, one should expect a substantial increase in NPF events in the coming decade, thus increasing the aerosol cooling effect over forests. A recent study using a coupled global atmosphere-land model suggested an increase in isoprene (22%) and MT (18%) by 2100, as a result of the increased temperature (1.8 °C) (Heald et al., 2008), but this temperature increase alone may not affect the R values on a global scale. However, little is known about the adaptation of isoprene and MT emitters to long-term changes in temperature. Isoprene and MT emissions may react very differently to other factors, such as increasing CO₂ concentrations, which could lead to a much lower R value in many regions (Heald et al., 2009). Many forests, including some in the Michigan (Bergen and Dronova, 2007), are experiencing rapid changes in environmental conditions as a result of forest succession, land-use change, human activities, and climate change and their radiative effects need to be incorporated in global aerosol models.

Supplement related to this article is available online at:
[http://www.atmos-chem-phys-discuss.net/11/11039/2011/
acpd-11-11039-2011-supplement.pdf](http://www.atmos-chem-phys-discuss.net/11/11039/2011/acpd-11-11039-2011-supplement.pdf).

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free use of SCIAMACHY, onboard European ENVISAT spacecraft, tropospheric NO₂ data (<http://www.temis.nl>), NOAA ARL HYSPLIT transport model data (<http://ready.arl.noaa.gov>), and Environmental Protection Agency (EPA) SO₂ and NO_x data under the Acid Rain Program (<http://camddataandmaps.epa.gov/gdm/>).

5 References

Andreae, M. O. and Andreae, T. W.: The cycle of biogenic sulfur-compounds over the Amazon basin: 1. Dry season, *J. Geophys. Res.*, 93(D2), 1487–1497, doi:10.1029/JD093ID02P01487, 1988.

10 Apel, E. C., Riemer, D. D., Hills, A., Baugh, W., Orlando, J., Faloon, I., Tan, D., Brune, W., Lamb, B., Westberg, H., Carroll, M. A., Thornberry, T., and Geron, C. D.: Measurement and interpretation of isoprene fluxes and isoprene, methacrolein, and methyl vinyl ketone mixing ratios at the prophet site during the 1998 intensive, *J. Geophys. Res.*, 107(D3), 4034, doi:10.1029/2000JD000225, 2002.

15 Ball, S. M., Hanson, D. R., Eisele, F. L., and McMurry, P. H.: Laboratory studies of particle nucleation: Initial results for H₂SO₄, H₂O, and NH₃ vapors, *J. Geophys. Res.*, 104(D19), 23709–23718, doi:10.1029/1999JD900411, 1999.

Barket Jr., D., Hurst, J., Couch, T., Colorado, A., Shepson, P., Riemer, D., Hills, A., Apel, E., Hafer, R., Lamb, B., Westberg, H., Farmer, C., Stabenau, E., and Zika, R.: Intercomparison of automated methodologies for determination of ambient isoprene during the prophet 1998 summer campaign, *J. Geophys. Res.*, 106(D20), 24301–24313, doi:10.1029/2000JD900562, 2001.

20 Benson, D. R., Young, L. H., Kameel, R., and Lee, S.-H.: Laboratory-measured sulfuric acid and water homogeneous nucleation rates from the SO₂+OH reaction, *Geophys. Res. Lett.*, 35, L11801, doi:10.1029/2008GL033387, 2008.

25 Benson, D. R., Erupe, M. E., and Lee, S.-H.: Laboratory-measured H₂SO₄-H₂O-NH₃ ternary homogeneous nucleation rates: Initial observations, *Geophys. Res. Lett.*, 36, L15818, doi:10.1029/2009GL038728, 2009.

30 Benson, D. R., Al-Refai, M., and Lee, S.-H.: Chemical ionization mass spectrometer (CIMS) for ambient measurements of ammonia, *Atmos. Meas. Techn.*, 3, 1075–1087, doi:10.5194/amt-3-1075-2010, 2010.

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- Bergen, K. M. and Dronova, I.: A remote sensing-ecosystem approach to observing succession on aspen-dominated landscapes, *Landscape Ecol.*, 22, 1395–1410, 2007.
- Bonn, B., and Moortgat, G. K.: Sesquiterpene ozonolysis: Origin of atmospheric new particle formation from biogenic hydrocarbons, *Geophys. Res. Lett.*, 30(11), 1585, doi:10.1029/2003GL017000, 2003.
- Bonn, B., Kulmala, M., Riipinen, I., Sihto, S.-L., and Ruuskanen, T. M.: How biogenic terpenes govern the correlation between sulfuric acid concentrations and new particle formation, *J. Geophys. Res.*, 113, D12209, doi:10.1029/2007JD009327, 2008.
- Bovensmann, H., Burrows, J. P., Buchwitz, M., Frerick, J., Noël, S., Rozanov, V. V., Chance, K. V., and Goede, A. P. H.: SCIAMACHY- mission objectives and measurement modes, *J. Atmos. Sci.*, 56, 121–150, 1999.
- Boy, M., Kazil, J., Lovejoy, E. R., Guenther, A., and Kulmala, M.: Relevance of ion-induced nucleation of sulfuric acid and water in the lower troposphere over the boreal forest at northern latitudes, *Atmos. Res.*, 90, 151–158, 2008.
- Brock, C. A., Hudson, P. K., Lovejoy, E. R., Sullivan, A., Nowak, J. B., Huey, L. G., Cooper, O. R., Cziczo, D. J., Gouw, J., Fehsenfeld, F. C., Holloway, J. S., Hübler, G., Lafleur, B. G., Murphy, D. M., Neuman, J. A., Nicks Jr., D. K., Orsini, D. A., Parrish, D. D., Ryerson, T. B., Tanner, D. J., Warneke, C., Weber, R. J., and Wilson, J. C.: Particle characteristics following cloud-modified transport from Asia to north America, *J. Geophys. Res.*, 109, D23S26, doi:10.1029/2003JD004198, 2004.
- Burkholder, J. B., Baynard, T., Ravishankara, A. R., and Lovejoy, E. R.: Particle nucleation following the O₃ and OH initiated oxidation of α -pinene and b-pinene between 278 and 320 K, *J. Geophys. Res.*, 112, D10216, doi:10.1029/2006JD007783, 2007.
- Carroll, M. A., Bertman, S. B., and Shepson, P. B.: Overview of the Program for Research on Oxidants: PHotochemistry, Emissions, and Transport (PROPHET) summer 1998 measurements intensive, *J. Geophys. Res.*, 106(D20), 24275–24288, doi:10.1029/2001JD900189, 2001.
- Claeys, M., Graham, B., Vas, G., Wang, W., Vermeylen, R., Pashynska, V., Cafmeyer, J., Guyon, P., Andreae, M. O., Artaxo, P., and Maenhaut, W.: Formation of secondary organic aerosols through photooxidation of isoprene, *Science*, 303, 1173–1176, 2004.
- Cooper, O. R., Moody, J. L., Thornberry, T. D., Town, M. S., and Carroll, M. A.: PROPHET 1998 meteorological overview and air-mass classification, *J. Geophys. Res.*, 106(D20), 24289–24299, doi:10.1029/2000JD900409, 2001.

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- de Gouw, J. and Warneke, C.: Measurements of volatile organic compounds in the earth's atmosphere using proton-transfer-reaction mass spectrometry, *Mass Spectrom. Rev.*, 26, 223–257, 2007.
- Delia, A. E.: Real-time measurements of non-refractory particle composition and interactions at forested sites, Ph D Thesis, Department of Astrophysical, Planetary and Atmospheric Sciences, University of Colorado, USA, 2004.
- 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.
- Draxler, R. R., and Rolph, G. D.: HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) model access via NOAA ARL ready website (<http://ready.arl.noaa.gov/hysplit.php>), NOAA Air Resources Laboratory, Silver Spring, MD, USA, 2010.
- Dusanter, S., Vimal, D., Stevens, P. S., Volkamer, R., and Molina, L.: Measurements of OH and HO₂ concentrations during the MCMA-2006 field campaign: Part 1 - deployment of the Indiana University laser-induced fluorescence instrument, *Atmos. Chem. Phys.*, 9, 1665–1685, doi:10.5194/acp-9-1665-2009, 2009.
- Erupe, M. E., Benson, D. R., Li, J., Young, L.-H., Verheggen, B., Al-Refai, M., Tahboub, O., Cunningham, V., Frimpong, F., Viggiano, A. A., and Lee, S.-H.: Correlation of aerosol nucleation rate with sulfuric acid and ammonia in Kent Ohio: An atmospheric observation, 115, D23216, doi:10.1029/2010JD013942, 2010.
- Finlayson-Pitts, B. J., and Pitts, J. N.: Chemistry of the upper and lower atmosphere: Theory, experiments, and applications, Academic Press, San Diego, CA, USA, 191–196, 2000.
- Froyd, K. D. and Lovejoy, E. R.: Experimental thermodynamics of cluster ions composed of H₂SO₄ and H₂O: 1. Positive ions, *J. Phys. Chem. A*, 107, 9800–9811, 2003.
- Froyd, K. D., Murphy, S. M., Murphy, D. M., de Gouw, J. A., Eddingsaas, N. C., and Wennberg, P. O.: Contribution of isoprene-derived organosulfates to free tropospheric aerosol mass, *Proc. Natl. Acad. Sci., USA*, 107, 21360–21365, 2010.
- Goldstein, A. H. and Galbally, I. E.: Known and unexplored organic constituents in the earth's atmosphere, *Environ. Sci. Technol.*, 41, 1514–1521, 2007.
- Gough, C. M., Vogel, C. S., Harrold, K. H., George, K., and Curtis, P. S.: The legacy of harvest and fire on ecosystem carbon storage in a north temperate forest, *Global Change Biol.*, 13, 1935–1949, 2007.
- Greenberg, J., Guenther, A., Petron, G., Wiedinmyer, C., Vega, O., Gatti, L. V., Tota, J.,

- and Fisch, G.: Biogenic voc emissions from forested Amazonian landscapes, *Global Biogeochem. Cy.*, 10, 651–662, 2004.
- Guenther, A., Karl, T., Harley, P., Wiedinmyer, C., Palmer, P. I., and Geron, C.: Estimates of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and Aerosols from Nature), *Atmos. Chem. Phys.*, 6, 3181–3210, doi:10.5194/acp-6-3181-2006, 2006.
- Guenther, A. B., Hewitt, C. N., Erickson, D., Fall, R., Geron, C., Graedel, T., Harley, P., Klinger, L., Lerdau, M., McKay, W. A., Pierce, T., Scholes, B., Steinbrecher, R., Tallamraju, R., and Zimmerman, P.: A global model of natural volatile organic compound emissions, *J. Geophys. Res.*, 100(D5), 8873–8892, doi:10.1029/94JD02950, 1995.
- Hallquist, M., Wenger, J. C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., Dommen, J., Donahue, N. M., George, C., Goldstein, A. H., Hamilton, J. F., Herrmann, H., Hoffmann, T., Iinuma, Y., Jang, M., Jenkin, M. E., Jimenez, J. L., Kiendler-Scharr, A., Maenhaut, W., McFiggans, G., Mentel, T. F., Monod, A., Prévôt, A. S. H., Seinfeld, J. H., Surratt, J. D., Szmigielski, R., and Wildt, J.: The formation, properties and impact of secondary organic aerosol: Current and emerging issues, *Atmos. Chem. Phys.*, 9, 5155–5236, doi:10.5194/acp-9-5155-2009, 2009.
- Heald, C. L., Henze, D. K., Horowitz, L. W., Feddesma, J., Lamarque, J.-F., Guenther, A., Hess, P. G., Vitt, F., Seinfeld, J. H., Goldstein, A. H., and Fung, I.: Predicted change in global secondary organic aerosol concentrations in response to future climate, emissions, and land use change, *J. Geophys. Res.*, 113, D05211, doi:10.1029/2007JD009092, 2008.
- Heald, C. L., Wilkinson, M. J., Monson, R. K., Alo, C. A., Wang, G., and Guenther, A.: Response of isoprene emission to ambient CO₂ changes and implications for global budgets, *Global Change Biol.*, 15, 1127–1140, 2009.
- Held, A., Nowak, A., Birmili, W., Wiedensohler, A., Forkel, R., and Klemm, O.: Observations of particle formation and growth in a mountainous forest region in central Europe, *J. Geophys. Res.*, 109, D23204, doi:10.1029/2004JD005346, 2004.
- Henze, D. K. and Seinfeld, J. H.: Global secondary organic aerosol from isoprene oxidation, *Geophys. Res. Lett.*, 33, L09812, doi:10.1029/2006GL025976, 2006.
- Hoffmann, T., Bandur, R., Marggraf, U., and Linscheid, M.: Molecular composition of organic aerosols formed in the α -pinene/O₃ reaction: Implications for new particle formation processes, *J. Geophys. Res.*, 103(D19), 25569–25578, doi:10.1029/98JD01816, 1998.
- Junninen, H., Hulkkonen, M., Riipinen, I., Nieminen, T., Hirsikko, A., Suni, T., Boy, M., Lee,

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S.-H., Vana, M., Tammet, H., and Kulmala, M.: Observations on night time growth of atmospheric clusters, *Tellus B*, 60B, 365–371, 2008.

Kanamitsu, M.: Description of the NMC global data assimilation and forecast system, *Weather Forecast*, 4, 335–342, 1989.

5 Kanawade, V. P. and Tripathi, S. N.: Evidence for the role of ion-induced particle formation during an atmospheric nucleation event observed in TOPSE, *J. Geophys. Res.*, 111, D02209, doi:10.1029/2005JD006366, 2006.

Kesselmeier, J., Kuhn, U., Rottenberger, S., Biesenthal, T., Wolf, A., Schebeske, G., Andreae, M. O., Ciccioli, P., Brancaleoni, E., Frattoni, M., Oliva, S. T., Botelho, M. L., Silva, C. M. A.,
10 and Tavares, T. M.: Concentrations and species composition of atmospheric volatile organic compounds (VOCs) as observed during the wet and dry season in Rondonia (Amazonia), *J. Geophys. Res.*, 107(D20), 8053, doi:10.1029/2000JD000267, 2002.

Kiendler-Scharr, A., Wildt, J., Dal Maso, M., Hohaus, T., Kleist, E., Mente, T. F., Tillmann, R., Uerlings, R., Schurr, U., and Wahner, A.: New particle formation in forests inhibited by
15 isoprene emissions, *Nature Lett.*, 461, 381–384, 2009.

Kim, S., Karl, T., Helmig, D., Daly, R., Rasmussen, R., and Guenther, G.: Measurement of atmospheric sesquiterpenes by proton transfer reaction-mass spectrometry (PTR-MS), *Atmos. Meas. Tech.*, 2, 99–112, doi:10.5194/amt-2-99-2009, 2009.

20 Kuang, C., McMurry, P. H., McCormick, A. V., and Eisele, F. L.: Dependence of nucleation rates on sulfuric acid vapor concentration in diverse atmospheric locations, *J. Geophys. Res.*, 113, D10209, doi:10.1029/2007JD009253, 2008.

Kulmala, M., dal Maso, M., Makela, J. M., Pirjola, L., Vakeva, M., Aalto, P., Mikkulainen, P., Hameri, K., and O'Dowd, C. D.: On the formation, growth, and composition of nucleation
mode particles, *Tellus* 53B, 479–490, 2001.

25 Kulmala, M., Vehkamäki, H., Petaja, T., dal Maso, M., Lauri, A., Kerminen, V. M., Birmili, W. H., and McMurry, P. H.: Formation and growth rates of ultrafine atmospheric particles: A review of observations, *J. Aerosol Sci.*, 35, 143–176, 2004.

Kunhikrishnan, T., Lawrence, M. G., Kuhlmann, R. V., Richter, A., Ladstätter-Weißenmayer, A., and Burrows, J. P.: Analysis of tropospheric NO_x over Asia using the model of atmospheric
30 transport and chemistry (MATCH-MPIC) and GOME-satellite observations, *Atmos. Environ.*, 38, 581–596, 2004.

Laakso, L., Laakso, H., Aalto, P. P., Keronen, P., Petäjä, T., Nieminen, T., Pohja, T., Siivola, E., Kulmala, M., Kgabi, N., Molefe, M., Mabaso, D., Phalatse, D., Pienaar, K., and Kerminen,

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V.-M.: Basic characteristics of atmospheric particles, trace gases and meteorology in a relatively clean Southern African Savannah environment, *Atmos. Chem. Phys.*, 8, 4823–4839, doi:10.5194/acp-8-4823-2008, 2008.

Lee, S.-H., Reeves, J. M., Wilson, J. C., Hunton, D. E., Viggiano, A. A., Miller, T. M., Ballenthin, J. O., and Lait, L. R.: Particle formation by ion nucleation in the upper troposphere and lower stratosphere, *Science*, 301, 1886–1889, 2003.

Lindinger, W., Hansel, A., and Jordan, A.: On-line monitoring of volatile organic compounds at pptv levels by means of proton-transfer-reaction mass spectrometry (PTRM-MS) – medical applications, food control, and environmental research, *Int. J. Mass. Spectrom.*, 173, 191–241, 1998.

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

Makela, J. M., Alto, P., Jokinen, V., Pohja, T., Nissenin, A., Palmroth, S., Markkanen, T., Seitsonen, K., and Kulmala, M.: Observations of ultrafine aerosol particle formation and growth in boreal forest, *Geophys. Res. Lett.*, 24(10), 1219–1222, doi:10.1029/97GL00920, 1997.

Martin, S. T., Andreae, M. O., Artaxo, P., Baumgardner, D., Chen, Q., Goldstein, A. H., Guenther, A., Heald, C. L., Mayol-Bracero, O. L., McMurry, P. H., Pauliquevis, T., Pöschl, U., Prather, K. A., Roberts, G. C., Saleska, S. R., Silva Dias, M. A., Spracklen, D. V., Swietlicki, E., and Trebs, I.: Sources and properties of Amazonian aerosol particles, *Rev. Geophys.*, 48, RG2002, doi:10.1029/2008RG000280, 2010.

Martinez, M., Harder, H., Kubistin, D., Rudolf, M., Bozem, H., Eerdeken, G., Fischer, H., Klupfel, T., Gurk, C., Konigstedt, R., Parchatka, U., Schiller, C. L., Stickler, A., Williams, J., and Lelieveld, J.: Hydroxyl radicals in the tropical troposphere over the Suriname rainforest: Airborne measurements, *Atmos. Chem. Phys.*, 10, 3759–3773, doi:10.5194/acp-10-3759-2010, 2010.

McMurry, P. H., Fink, M., Sakuri, H., Stolzenburg, M., Mauldin III, R. L., Smith, J., Eisele, F. L., Moore, K., Sjostedt, S., Tanner, D., Huey, L. G., Nowak, J. B., Edgerton, E., and Voisin, D.: A criterion for new particle formation in the sulfur-rich Atlanta atmosphere, *J. Geophys. Res.*, 110, D22S02, doi:10.1029/2005JD005901, 2005.

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.

Metzger, A., Verheggen, B., Dommen, J., Duplissy, J., Prévôt, A. S. H., Weingartner, E., Riip-

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inen, I., Kulmala, M., Spracklen, D. V., Carslaw, K. S., and Baltensperger, U.: Evidence for the role of organics in aerosol particle formation under atmospheric conditions, *Proc. Natl. Acad. Sci., USA*, 107, 6646–6651, 2010.

Mielke, L. H., Pratt, K. A., Shepson, P. B., McLuckey, S. A., Wisthaler, A., and Hansel, A.: Quantitative determination of biogenic volatile organic compounds in the atmosphere using proton-transfer reaction linear ion trap mass spectrometry, *Anal. Chem.*, 82, 7952–7957, 2010.

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, D19205, doi:10.1029/2004JD005475, 2005.

Nowak, J. B., Huey, L. G., Russell, A. G., Tian, D., Neuman, J. A., Orsini, D., Sjostedt, S. J., Sullivan, A. P., Tanner, D. J., Weber, R. J., Nenes, A., Edgerton, E., and Fehsenfeld, F. C.: Analysis of urban gas phase ammonia measurements from the 2002 Atlanta aerosol nucleation and real-time characterization experiment (ANARCHE), *J. Geophys. Res.*, 111, D17308, doi:10.1029/2006JD007113, 2006.

O'Dowd, C. D., Aalto, P., Hameri, K., Kulmala, M., and Hoffmann, M. R.: Atmospheric particles from organic vapors, *Nature*, 416, 497–498, 2002.

Ortega, J., Helmig, D., Guenther, A., Harley, P., Pressley, S., and Vogel, C.: Flux estimates and oh reaction potential of reactive biogenic volatile organic compounds (BVOCs) from a mixed northern hardwood forest, *Atmos. Environ.*, 41, 5479–5495, 2007.

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.

Pearsall, D. R.: Landscape ecosystems of the University of Michigan biological station: Ecosystem diversity and ground-cover diversity, Ph D Thesis, School of Natural Resources and Environment, University of Michigan, USA, 1995.

Petaja, T., Mauldin, R. L., III, Kosciuch, E., McGrath, J., Nieminen, T., Paasonen, P., Boy, M., Adamov, A., Kotiaho, T., and Kulmala, M.: Sulfuric acid and oh concentrations in a boreal forest site, *Atmos. Chem. Phys.*, 9, 7435–7448, doi:10.5194/acp-9-7435-2009, 2009.

Pham, M., Muller, J. F., Brasseur, G., Granier, C., and Megie, G.: A three-dimensional study of the tropospheric sulfur cycle, *J. Geophys. Res.*, 100(D12), 26061–26092, doi:10.1029/95JD02095, 1995.

Pöschl, U., Martin, S. T., Sinha, B., Chen, Q., Gunthe, S. S., Huffman, J. A., Borrmann, S.,

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Farmer, D. K., Garland, R. M., Helas, G., Jimenez, J. L., King, S. M., Manzi, A., Mikhailov, E., Pauliquevis, T., Petters, M. D., Prenni, A. J., Roldin, P., Rose, D., Schneider, J., Su, H., Zorn, S. R., Artaxo, P., and O., A. M.: Rainforest aerosols as biogenic nuclei of clouds and precipitation in the Amazon, *Science*, 329, 1513–1516, 2010.

5 Pressley, S., Lamb, B., Westberg, H., Flaherty, J., Chen, J., and Vogel, C.: Long-term isoprene flux measurements above a northern hardwood forest, *J. Geophys. Res.*, 110, D07301, doi:10.1029/2004JD005523, 2005.

Pressley, S., Lamb, B., Westberg, H., and Vogel, C.: Relationships among canopy scale energy fluxes and isoprene flux derived from long-term, seasonal eddy covariance measurements over a hardwood forest, *Agr. Forest Meteorol.*, 136, 188–202, 2006.

10 Pryor, S. C., Barthelmie, R. J., Sørensen, L. L., McGrath, J. G., Hopke, P., and Petaja, T.: Spatial and vertical extent of nucleation events in the Midwestern USA: Insights from the nucleation in forests (NIFTy) experiment, *Atmos. Chem. Phys.*, 11, 1641–1657, doi:10.5194/acp-11-1641-2011, 2011.

15 Richter, A., Burrows, J. P., Nues, H., Granier, C., and Niemeijer, U.: Increase in tropospheric nitrogen dioxide over China observed from space, *Nature*, 437, 129–130, 2005.

Rinne, H. J. I., Guenther, A. B., Greenberg, J. P., and Harley, P. C.: Isoprene and monoterpene fluxes measured above Amazonian rainforest and their dependence on light and temperature, *Atmos. Environ.*, 36, 2421–2426, 2002.

20 Rizzo, L. V., Artaxo, P., Karl, T., Guenther, A. B., and Greenberg, J.: Aerosol properties, in-canopy gradients, turbulent fluxes and VOC concentrations at a pristine forest site in Amazonia, *Atmos. Environ.*, 44, 503–511, 2010.

Rosen, J. M., Hoffmann, D. J., and Gringel, W.: Measurements of ion mobility to 30 km, *J. Geophys. Res.*, 90(D4), 5876–5884, doi:10.1029/JD090iD04p05876, 1985.

25 Sakulyanontvittaya, T., Duhl, T., Wiedinmyer, C., Helmig, D., Matsunaga, S., Potosnak, M., Milford, J., and Guenther, A.: Monoterpene and sesquiterpene emission estimates for the united states, *Environ. Sci. Technol.*, 42, 1623–1629, 2008.

Schmid, H. P., Su, H.-B., Vogel, C. S., and Curtis, C. S.: Ecosystem-atmosphere exchange of carbon dioxide over a mixed hardwood forest in northern lower Michigan, *J. Geophys. Res.*, 108(D14), 4417, doi:10.1029/2002JD003011, 2003.

30 Sellegri, K., Hanke, M., Umann, B., Arnold, F., and Kulmala, M.: Measurements of organic gases during aerosol formation events in the boreal forest atmosphere during QUEST, *Atmos. Chem. Phys.*, 5, 373–384, doi:10.5194/acp-5-373-2005, 2005.

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- Sihto, S.-L., Kulmala, M., Kerminen, V.-M., Dal Maso, M., Petäjä, T., Riipinen, I., Korhonen, H., Arnold, F., Janson, R., Boy, M., Laaksonen, A., and Lehtinen, K. E. J.: Atmospheric sulfuric acid and aerosol formation: Implications from atmospheric measurements for nucleation and early growth mechanisms, *Atmos. Chem. Phys.*, 6, 4079–4091, doi:10.5194/acp-6-4079-2006, 2006.
- 5 Sipila, M., Berndt, T., Petaja, T., Brus, D., Vanhanen, J., Stratmann, F., Patokoski, J., Mauldin III, R. L., Hyvarinen, A.-P., Lihavainen, H., and Kulmala, M.: The role of sulfuric acid in atmospheric nucleation, *Science*, 327, 1243–1246, 2010.
- Slade, J. H., VanReken, T. M., Mwaniki, G. R., Bertman, S., Stirm, B., and Shepson, P. B.: Aerosol production from the surface of the Great lakes, *Geophys. Res. Lett.*, 37, L18807, doi:10.1029/2010GL043852, 2010.
- 10 Smith, J. N., Barsanti, K. C., Friedli, H. R., Ehn, M., Kulmala, M., Collins, D. R., Scheckman, J. H., Williams, B. J., and McMurry, P. H.: Observations of aminium salts in atmospheric nanoparticles and possible climatic implications, *Proc. Natl. Acad. Sci. USA*, 107, 6634–6639, 2009.
- 15 Sorooshian, A., Varutbangkul, V., Brechtel, F. J., Ervens, B., Feingold, G., Bahreini, R., Murphy, S. M., Holloway, J. S., Atlas, E. L., Buzorius, G., Jonsson, H., Flagan, R. C., and Seinfeld, J. H.: Oxalic acid in clear and cloudy atmospheres: Analysis of data from International Consortium for Atmospheric Research on Transport and Transformation 2004, *J. Geophys. Res.*, 111, D23S45, doi:10.1029/2005JD006880, 2006.
- 20 Spirig, C., Guenther, A., Greenberg, J. P., Calanca, P., and Tarvainen, V.: Tethered balloon measurements of biogenic volatile organic compounds at a boreal forest site, *Atmos. Chem. Phys.*, 4, 215–229, doi:10.5194/acp-4-215-2004, 2004.
- Spracklen, D. V., Carslaw, K. S., Kulmala, M., Kerminen, V.-M., Sihto, S.-L., Riipinen, I., Merikanto, J., Mann, G. W., Chipperfield, M. P., Wiedensohler, A., Birmili, W., and Lihavainen, H.: Contribution of particle formation to global cloud condensation nuclei concentrations, *Geophys. Res. Lett.*, 35, L06808, doi:10.1029/2007GL033038, 2008.
- 25 Suni, T., Rinne, J., Reissell, A., Altimir, N., Keronen, P., Rannik, U., Dal Maso, M., Kulmala, M., and Vesala, T.: Long-term measurements of surface fluxes above a Scots pine forest in Hyytiälä, Southern Finland, 1996–2001, *Boreal Environ. Res.*, 8, 287–301, 2003.
- 30 Suni, T., Kulmala, M., Hirsikko, A., Bergman, T., Laakso, L., Aalto, P. P., Leuning, R., Cleugh, H., Zegelin, S., Hughes, D., van Gorsel, E., Kitchen, M., Vana, M., Horrak, U., Mirme, S., Mirme, A., Sevanto, S., Twining, J., and Tadros, C.: Formation and characteristics of ions

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and charged aerosol particles in a native Australian eucalypt forest, *Atmos. Chem. Phys.*, 8, 129–139, doi:10.5194/acp-8-129-2008, 2008.

Suni, T., Sogacheva, L., Lauros, J., Hakola, H., Back, J., Kurten, T., Cleugh, H., van Gorsel, E., Briggs, P., Sevanto, S., and Kulmala, M.: Cold oceans enhance terrestrial new-particle formation in near-coastal forests, *Atmos. Chem. Phys.*, 9, 13093–13122, doi:10.5194/acp-9-13093-2009, 2009.

Surratt, J. D., Chan, A. W. H., Eddingsaas, H. E., Chan, M., Loza, C. L., Kwan, A. J., Hersey, S. S., Flagan, R. C., Wennberg, P. O., and Seinfeld, J. H.: Reactive intermediates revealed in secondary organic aerosol formation from isoprene, *Proc. Natl. Acad. Sci. USA*, 107, 6640–6645, 2010.

Tanner, D. J. and Eisele, F. L.: Present oh measurement limits and associated uncertainties, *J. Geophys. Res.*, 100(D2), 2883–2892, doi:10.1029/94JD02609, 1995.

Tunved, P., Hansson, H.-C., Kerminen, V.-M., Ström, J., Dal Maso, M., Lihavainen, H., Viisanen, Y., Aalto, P. P., Komppula, M., and Kulmala, M.: High natural aerosol loading over boreal forests, *Science*, 312, 261–263, 2006.

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(D22), 4622, doi:10.1029/2002JD002184, 2002.

Westberg, H., Lamb, B., Hafer, R., Hills, A., Shepson, P. B., and Vogel, C.: Measurement of isoprene fluxes at the PROPHET site, *J. Geophys. Res.*, 106(D20), 24347–24358, doi:10.1029/2000JD900735, 2001.

Young, L. H., Benson, D. R., Rifkha, F., Pierce, J. R., Junninen, H., Kulmala, M., and Lee, S.-H.: Laboratory studies of sulfuric acid and water binary homogeneous nucleation: Evaluation of laboratory setup and preliminary results, *Atmos. Chem. Phys.*, 8, 1–20, doi:10.5194/acp-8-1-2008, 2008.

Yu, F., and Turco, R. P.: The role of ions in the formation and evolution of particles in aircraft plumes, *Geophys. Res. Lett.*, 24(15), 1927–1930, doi:10.1029/97GL01822, 1997.

Zhang, R., Suh, J., Zhao, J., Zhang, D., Fortner, E. C., Tie, X., Molina, M. T., and Molina, M., J.: Atmospheric new particle formation enhanced by organic acids, *Science*, 304, 1487–1490, 2004.

Zhang, R., Wang, L., Khalizov, A. F., Zhao, J., Zheng, J., McGraw, R. L., and Molina, L. T.: Formation of nanoparticles of blue haze enhanced by anthropogenic pollution, *Proc. Natl.*

Acad. Sci., USA, 106, 17560–17654, 2009.
Zhou, J. C., Swietlicki, E., Hansson, H. C., and Artaxo, P.: Submicrometer aerosol particle size distribution and hygroscopic growth measured in the Amazon rain forest during the wet season, J. Geophys. Res., 107(D20), 8055, doi:10.1029/2000JD000203, 2002.

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Table 1. The ratio of emitted isoprene carbon to MT carbon, OH, H₂SO₄ and CS in the Michigan, Amazon, and Finland forests. Refer to Table S1 for overview of emission fluxes and concentrations of isoprene, and MT and corresponding *R* values.

Parameters	Michigan forest ^a	Amazon forest ^b	Finland forest
<i>R</i>	26.4±4.5	15.2, Greenberg et al. (2004)	0.18, Spirig et al. (2004)
OH (cm ⁻³) ^c	1.2–1.5×10 ⁶	5.5×10 ⁶ , Martinez et al. (2010)	7.7×10 ⁵ , Petaja et al. (2009)
H ₂ SO ₄ (cm ⁻³) ^c	2.6×10 ⁶	1-5×10 ^{5d}	1.4×10 ⁶ , Petaja et al. (2009)
CS (s ⁻¹) ^c	1.5×10 ⁻³	0.9±0.3, Zhou et al. (2002) ^e	4.2×10 ⁻³ , Kulmala et al. (2001)

^a this study. ^b data from wet season only. ^c noontime peak values. ^d calculated H₂SO₄ from the measured SO₂ of the order of 0.02–0.03 ppbv (Andreae and Andreae, 1988) and OH of 5.5×10⁶ cm⁻³ (Martinez et al., 2010) over Amazon basin. ^e calculated total CS from statistical data (number concentration, geometric mean diameter and geometric standard deviation) for particle size distributions measured during March–April 1998 (Zhou et al., 2002).

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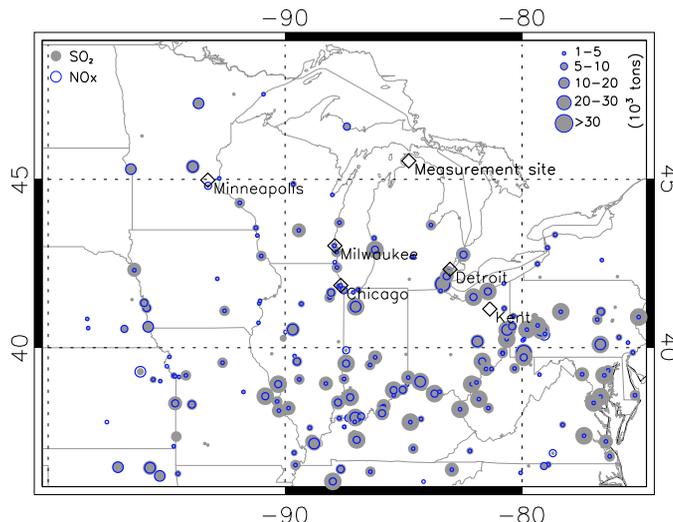


Fig. 1. A regional map showing the location of the Michigan forest measurement site (UMBS) as well as major urban centers (open diamonds), such as Minneapolis, Chicago, and Detroit, in addition to Kent. Both the SO₂ (gray dots) and NO_x (open blue circles) point sources (>10³ tons) for 2009 are also shown. The size of the dot and circle is proportional to the strength of the facility SO₂ and NO_x emission strength. The emissions data are obtained from the US Environmental Protection Agency (EPA) Office of Air and Radiation website (<http://www.epa.gov/air/data/geosel.html>) under Acid Rain Program.

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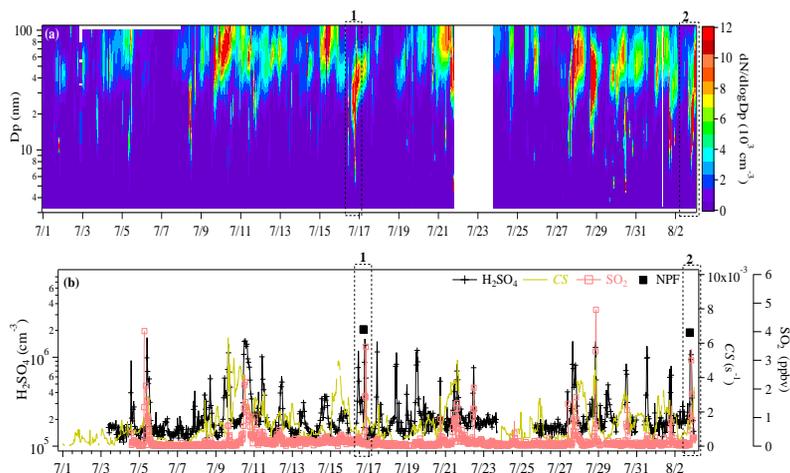


Fig. 2. (a) Particle size distributions in the size range from 3–109 nm measured by during 1 July–3 August 2009 in the Michigan forest. There were no NDMA measurements from 22–24 July. (b) The measured H_2SO_4 (line with black plus signs), SO_2 (light red open squares), and CS (yellow solid line) during 1 July–3 August 2009 at the same site. The two filled black squares show the observed early evening NPF events (Box 1 and 2 for 16 July and 2 August event, respectively). As mentioned in the main text, there were no conventional NPF events at noontime at all during the summer of 2009. Sharp spikes in particle number size distributions were seen at noontime (e.g. 8 July), but these particles did not grow enough to show aerosol size distributions with a typical “banana shape”.

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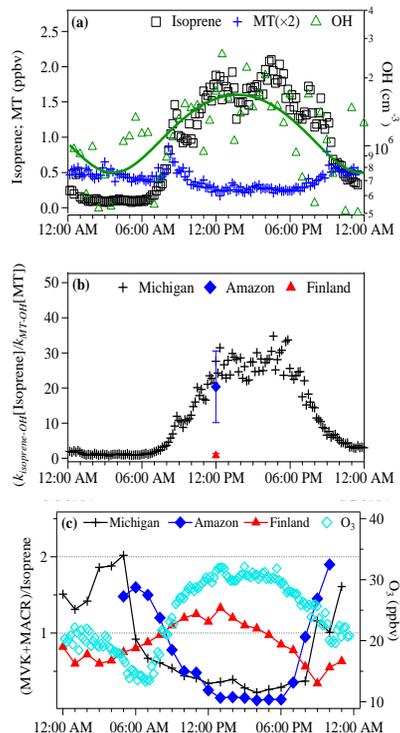


Fig. 3. (a) The average diurnal variation of isoprene (black open squares), MT (blue plus signs) and OH (open green triangles; green line shows the fitting of OH data) measured in the Michigan forest. (b) The diurnal variation of $(k_{\text{isoprene-OH}}[\text{Isoprene}]) / (k_{\text{MT-OH}}[\text{MT}])$ ratio averaged from 8–16 July in the Michigan forest. Gas Chromatography-Mass Spectrometry (GC-MS) measurements for MT speciation show that α -pinene was the most abundant MT, comprising 80% of the total MT mixing ratios. The reaction rate constants used in ratio calculation were $k_{\alpha\text{-pinene-OH}} = 53.6 \times 10^{-12} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ and $k_{\text{isoprene-OH}} = 101 \times 10^{-12} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ (Finlayson-Pitts and Pitts, 2000). In comparison, ratio values in Amazon (Kesselmeier et al., 2002) (blue diamond) and Finland boreal forests (Sellegrì et al., 2005) (red triangle) are also included here; vertical lines indicate one standard deviation in the ratio. (c) The ratios of (MVK+MACR)/isoprene for the Michigan forest (this study) (black line with plus signs), Amazon forests (Kesselmeier et al., 2002) (blue line with filled diamonds) and Finland boreal forests (Rinne et al., 2002) (red line with filled triangles). The measured O₃ (cyan open diamonds) in the Michigan forest are also shown.

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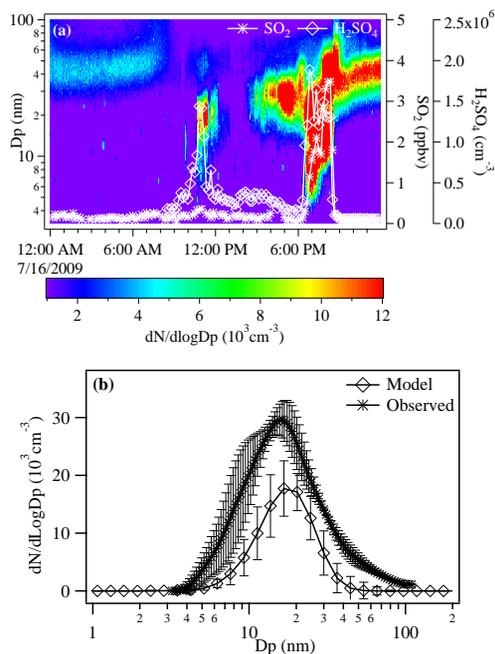


Fig. 4. (a) Particle number size distributions, SO_2 (white asterisks) and H_2SO_4 (white open diamonds) measured on 16 July 2009. The 2 August evening event also showed a strikingly similar feature as here. (b) The size distributions predicted from the model at the end of 35 h simulation (line with open diamonds) and that measured at the forest site at 19:00 LT (line with asterisks). The vertical bars indicate one standard deviation values. Considering uncertainties in measurements and modeling simulations, this is a very good agreement. IIN simulations for the 2 August event also showed very similar results.

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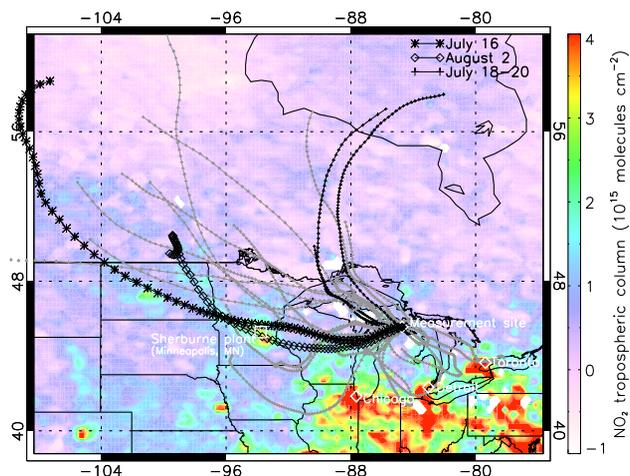


Fig. 5. The SCIAMACHY-retrieved 0.25 degree gridded tropospheric NO_2 column data from June–August 2009. The locations of the UMBS site and the nearby large urban centers are shown by white open diamonds. The white open square shows the location of the SPP, which was ranked 29th in US Environmental Protection Agency (EPA) region 5 (IL, IN, MI, MN, OH and WI) in 2009 for SO_2 emissions (24 015.8 tons) and 6th by NO_x (13 873.7 tons) under Acid Rain Program (ARP) sources (<http://camdataandmaps.epa.gov/gdm/>). The HYSPLIT-calculated 3-day backward trajectories starting at 10 m at 19:00 LT from 8 July–2 August are also shown, highlighting the two early evening NPF events on 16 July (black line with stars) and 2 August (black line with open diamonds) and very clean non-event days (18–20 July) (black line with plus sign).

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