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Authors

Lawler, Michael J
Rissanen, Matti P
Ehn, Mikael
et al.

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Evidence for diverse biogeochemical drivers of boreal forest new particle formation

Michael J. Lawler[1], Matti P. Rissanen[2], Mikael Ehn[2], R. Lee Mauldin III[2,3], Nina Sarnela[2], Mikko Sipilä[2], and James N. Smith[1]

[1]University of California, Irvine, Department of Chemistry, Irvine, USA.

[2]University of Helsinki, Department of Physics, Helsinki, Finland.

[2]University of Colorado Department of Atmospheric and Ocean Sciences, Boulder, USA.

Corresponding author: Michael J. Lawler (mlawler@uci.edu)

Key Points:

- The roles of organic acids, amines, inorganic acids, and highly oxidized organics are analyzed for two new particle formation events using *in situ* observations.
- Saturated linear organic acids are the particulate species most associated with the appearance of new 20-50 nm particles.
- The event days were associated with rapid transport of marine air to the site.

Abstract

New particle formation (NPF) is an important contributor to particle number in many locations, but the chemical drivers for this process are not well-understood. Daytime NPF events occur regularly in the springtime Finnish boreal forest and strongly impact aerosol abundance. In April 2014 size-resolved chemical measurements of ambient nanoparticles were made using the Time-of-Flight Thermal Desorption Chemical Ionization Mass Spectrometer (TOF-TDCIMS), and we report results from two NPF events. While growth overall was dominated by terpene oxidation products, newly formed 20-70 nm particles showed enhancement in apparent alkanoic acids. The events occurred on days with rapid transport of marine air, which correlated with low background aerosol loading and higher gas phase methanesulfonic acid levels. These results are broadly consistent with previous studies on Nordic NPF but indicate that further attention should be given to the sources and role of non-terpenoid organics and the possible contribution of transported marine compounds in this process.

1 Introduction

Atmospheric particles are important for the climate system due to their direct interaction with radiation and their role in cloud formation. The majority of atmospheric particles are generated by new particle formation [*Spracklen et al.*, 2006; *Merikanto et al.*, 2009] which proceeds by homogeneous nucleation and subsequent growth due to net uptake of gas phase species [*McMurry*, 1983; *Kulmala et al.*, 2004; *Kuang et al.*, 2010; *Zhang et al.*, 2012]. However, the relative impact of new particle formation on global radiative forcing compared with directly emitted particles is less clear. This is due to uncertainties about the chemical mechanisms of nucleation and the efficiency with which newly-formed particles are able to grow to sizes at which they can directly interact with shortwave radiation and/or act as cloud condensation nuclei [*Spracklen et al.*, 2008, e.g.].

New particle formation has been a topic of intense study at the Hyytiälä field site in recent years, spurred in part by the development of new instruments capable of detecting ever smaller particles and chemically identifying their gas phase precursors [*Kulmala et al.*, 2013; *Schobesberger et al.*, 2013]. Sulfuric acid is thought to be an important NPF precursor here and in general [*Kuang et al.*, 2010; *Zhang et al.*, 2012, e.g.]. Sulfuric acid concentrations at Hyytiälä are higher during NPF event days, and increased ultrafine particle sulfate fractions were observed to increase at the start of an event [*Smith et al.*, 2010; *Bzdek et al.*, 2012; *Kulmala et al.*, 2013]. Organics correlated with Hyytiälä NPF events include short-chain (< C11) alkanoic acids detected in the aerosol phase [*Anttila et al.*, 2005], and organic highly oxygenated molecules generated from the ozonolysis and rapid autoxidation of biogenic terpenoids and detected in the gas phase [*Ehn et al.*, 2014; *Rissanen et al.*, 2014]. Mäkelä et al. [2001] also found enhancement of methanesulfonic acid (MSA) in the nucleation mode during NPF events, and much higher levels of dimethylamine (DMA) in ultrafine aerosol overall. Smith et al. [2010] found methylammonium to be the main aminium salt component in recently formed ultrafine particles. Overall, these observations imply that the condensation of low volatility highly oxygenated organics and sulfuric acid and the formation of organic and inorganic salts drive growth of newly formed particles at this site.

The correlation of the dimethylsulfide (DMS) oxidation product MSA with NPF suggests a role for marine air in this process. NPF events are more common in air with northwesterly trajectories, associated with transport over the relatively unpopulated northern Nordic region from the North Atlantic and Arctic Oceans [*Mäkelä et al.*, 2000; *Dal Maso et al.*, 2005; *Nilsson and Kulmala*, 2006]. The apparent marine effect may be due to a lower aerosol condensation sink for nucleating vapors compared with continental air masses, allowing a larger fraction of the available low volatility compounds to contribute to new particle formation. In addition, it is also possible that the marine atmosphere provides important chemical precursors. DMS may be one such precursor, leading to the formation of sulfuric acid as well as MSA, which can also undergo NPF reactions [*Chen et al.*, 2016].

In highly controlled laboratory experiments at CLOUD in CERN, the observation of stepwise molecular additions of well-identified precursor species to growing molecular clusters has informed our view of atmospheric nucleation, both for systems of sulfuric acid with gas phase bases and for oxidized organic molecules produced from common biogenic precursors [*Kirkby et al.*, 2011; *Almeida et al.*, 2013; *Schobesberger et al.*, 2013; *Tröstl et al.*, 2016]. However, molecular cluster measurements under ambient conditions are harder to interpret, making it difficult to infer NPF chemistry in the atmosphere [*Schobesberger et al.*, 2013].

We present observations of the chemical composition of recently formed ambient aerosol in the size range of about 20-70 nm made at Hyytiälä in the Finnish boreal forest. These observations have sufficient time resolution to identify changes over the course of individual NPF events, and sufficient chemical specificity to identify some of the key species involved. We use this unique data set to highlight some of the processes involved in new particle formation in this environment.

2 Materials and Methods

2.1 Field Site Conditions

The well-characterized Hyytiälä field station is located in a stand of Scots pine (*Pinus sylvestris*) at a lake in southwestern Finland (61.8475°N, 24.2950°E) [*Kulmala et al.*, 2000; *Hari and Kulmala*, 2005]. The nanoparticle observations reported here were made over a period from April 23 to May 1, 2014, during Biogenic Aerosols–Effects on Clouds and Climate (BAECC) [*Petäjä et al.*, 2016]. During this period the wind was predominantly from the northwest. Temperatures ranged from a nighttime minimum of - 4 °C to a 17 °C maximum in the afternoon. Conditions were mostly sunny from April 22-26, with increasing cloudiness afterwards, leading to rain on April 28th. Windspeeds ranged from 0.5 to 6.9 m s^{-1} (10 min averaged).

2.2. Instrument: TOF-TDCIMS

The Thermal Desorption Chemical Ionization Mass Spectrometer (TDCIMS) instrument and technique has been described in detail elsewhere [*Voisin et al.*, 2003; *Smith and Rathbone*, 2008; *Lawler et al.*, 2014]. Briefly, it can identify the organic and inorganic components present in recently formed ultrafine particles as small as ~ 10 nm by ionizing and size-selecting the particles, electrostatically precipitating them on a Pt filament, thermally volatilizing their constituents, and detecting the resultant gas phase molecules by chemical ionization via $(H_2O)_nH_3O^+$ or $(H_2O)_nO_2^-$ reagent ions. A regular cycle during these observations included 30 minutes of collection, then 30 minutes of background assessment of gas phase interferences, for each ion polarity, for a total cycle of roughly 2 hours. Backgrounds were assessed by turning off the filament high voltage. The collected particle sizes were assessed using a scanning mobility particle sizer (SMPS, TSI 3085 and TSI 3025) downstream of the TDCIMS collection wire by comparing collection and background period. A separate condensation particle counter (CPC, TSI 3025) also monitored the sample flow downstream of the TDCIMS collection wire to measure the total sampled particle number.

2.3 Supporting Observations

The Hyytiälä site supports several continuous observations which are available on the SMEAR website (http://avaa.tdata.fi/web/smart) [*Junninen et al.*, 2009]. From this database we used gas phase nitrogen oxides (NO_x: NO_2 + NO) and sulfur dioxide (SO_2), as well as wind speed and direction, and the particle size distribution as measured by a differential mobility particle sizer (DMPS) [*Aalto et al.*, 2001]. In addition, gas phase sulfuric acid (H_2SO_4) and methanesulfonic acid (MSA) were measured by nitrate addition chemical ionization mass spectrometry using an atmospheric pressure interface time-of-flight mass spectrometer (CI-APi-TOF, Aerodyne Research, Inc.) after the design of Eisele and Tanner [1993] and detailed in Jokinen et al. [2012].

3 Observational Results

3.1 Events and Air Mass Origins

Two intense new particle formation events lasting more than 12 hours were observed while the TDCIMS was fully operational, one on April 23 and one on April 29, 2014 (Figure 1.d.). Increased sub-10 nm particle number concentrations were apparent by late morning in both cases, typical of springtime new particle formation events at Hyytiälä [*Dal Maso et al.*, 2005]. The April 23 event was preceded by an event on the 22nd, while prior to the April 29 event the background particles were much larger and older. April 23 was characterized by northerly winds that reached about 5 m s^{-1} around midday. April 29 had the highest windspeeds of the campaign, about 6 m s^{-1} around midday (Figure S1.f.). The April 23 event was followed by a continuation of its growth mode during most of the subsequent 3 days and possibly longer (Figures 1.d and S1.d.). This implies that it was a very widespread regional event and also that the air flow conditions were less dynamic after the event. This is confirmed by a back trajectory analysis (next paragraph). A brief, intense new particle formation event occurred on the following day (April 24), concomitant with growth of the mode that began on April 23 (Figure 1.d.). This new nucleation mode decreased in number abruptly around 17:00 local time (UTC +2) on April 24, as the air mass histories transitioned away from rapid marine transport. Every day there was some particle number enhancement at sub-20 nm sizes (Figure S1.d.), but only days with a relatively low condensation sink (below about 1-2 x 10^{-3} s^{-1} for H_2SO_4) showed new particle formation events with growth beyond about 30 nm (the 23rd and 29th). The condensation sink was calculated after Dal Maso et al. [2002] for an H_2SO_4 diffusion coefficient of 0.075 cm^2 s^{-1} [*Brus et al.*, 2016]. Ultrafine particle number enhancement was strongly correlated with wind speed (Figure S8). Of eight clear NPF events (> 2000 cm^{-3} sub-20 nm particles) during the intensive period of April 14 – May 3, 2014, all included air masses that had been over the ocean within 1.5

days and half of them within 24 hours. The April 29 event lasted only about 21 hours, a more typical timescale for the Hyytiälä events than the lengthy April 23 event.

Four-day air mass back trajectories for air arriving at the site were calculated using the HYSPLIT online model with Reanalysis data (http://ready.arl.noaa.gov/HYSPLIT.php) [*Stein et al.*, 2015; *Rolph et al.*, 2017]. Trajectories were computed for air arriving at the site at 00:00, 06:00, 12:00, and 18:00 local time each day. For the events of the 23rd and 29th, as well as the brief 24th event, the 12:00 back trajectories showed that the air masses had been over the Atlantic Ocean within 1-2 days, as a result of the relatively high windspeeds (Figures 2 and S1.f.). For the days without strong events (April 25-28), the air masses spent more time circulating over the Scandinavian land mass and the Bay of Bothnia. The longevity of an individual new particle formation event appears to depend on the time the air mass spent over the continent. It seems likely that NPF occurs simultaneously over much of Fennoscandia, and that the growth mode from the events is observable at Hyytiälä as long as the air measured at the site had been over the continent after the onset of the regional new particle formation event. During the week of sampling, particles from apparent regional new particle formation events were observed when the sampled air had been over the ocean within the previous four days. After midday on April 30, the air mass origins shifted to the east, away from the ocean, and a clear NPF event was not observed until May 3, when the air mass back trajectories shifted to the North Atlantic.

3.2 TDCIMS Collected Particles

Ambient particle collections with well-resolved volume median diameters (VMD) as small as 25 nm were achieved during the new particle formation events (Figure 1.d. and 1.i.; Supplemental S1). By increasing the nano-DMA set points up to 30 nm, it was possible to collect well-defined, size-resolved nanoparticles up to a VMD of 58 nm [*McMurry et al.*, 2009]. At a nominal set point of 40 nm, the collected particle mass was dominated by particles larger than the ~80 nm size limit of the SMPS system (Figure S2). Collected masses for well-defined particle collections ranged from 0.03 - 0.82 ng, assuming a 1 g cm^{-3} density for simplicity. The TDCIMS sum detectable ion signal showed a strong linear correlation with the total mass collected for these well-defined mass collections (r^2= 0.82 for neg ions, r^2= 0.84 for pos ions). By extrapolation, collected masses at a nominal setpoint of 40 nm ranged from 0.13 - 2.4 ng.

3.3 TDCIMS Composition Observations

The TDCIMS composition results are presented as ion fractions of major classes of compound detected (Figure 1.a-h.). In both positive and negative ion mode, organics essentially always made up over 90% of the total signal. Ions consistent with linear carboxylic and dicarboxylic acids with 0-2 double bonds typically represented about 25% (and as much as 35%) of the negative ion signal. C_2-C_{11} species of this type were detected, with C_6 and C_8 alkanoic acids and a mono-unsaturated C_6 diacid showing large contributions (Supplemental Figure S3). About half of the apparent acid signal was represented by saturated linear acids (SatAcids). The SatAcids showed the largest relative increases of any identified group when newly formed particles were sampled, reaching up to 18% of the negative ion signal (Figure 1a.,f.). They were also the group showing the best correlation with number of ambient 4-50 nm particles (r^2=0.28, p=1.2 x 10^{-6} Figure S6.). No other identified chemical group showed a statistically significant correlation ($p=0.05$). Negative ions containing only C, H, and O atoms and having more than 5 O atoms were grouped into a highly oxidized organics category (OxOrgs). These represent both actual molecular ions of the species present in the particle phase and fragments that result from thermal or ionization-induced decomposition of the particle phase species. These species reached their highest signal fractions (up to 16%) in pre-existing aerosol at the beginning of the events (Figure 1.a. and 1.f.). The bulk of the organic ions are consistent with terpenoid oxidation products, based on their H:C ratios, carbon numbers, and their similarity with particles formed from known monoterpene precursors, but with an additional influence from the SatAcids (Figure 3).

Sulfate and sulfonate salts (S salts), identified by their decomposition to form SO_2^- and SO_3^- ions, represented only about 1% of the negative ion signal. These were higher than average during the half day following the events on the 23rd and 29th (and the 22nd), with a clear enhancement relative to background aerosol on the 29th. Molecular methanesulfonic acid (MSA) and its precursor methanesulfinic acid (MSIA) were observed at ion fractions less than 1% and were not always enhanced in newly formed particles. However, the brief event on April 24th was clearly associated with a sharp increase in these organic sulfur acids in the Aitken mode particle sampled (Figure 1b.).

While the collected particles early on April 23rd were primarily from the recently formed <100 nm mode from an event begun the previous day, the collected particles early on April 29th were primarily > 100 nm accumulation mode particles probably formed at least two days prior. These older, larger particles had a higher ammonium fraction and a lower carboxylic acid fraction than the smaller, more recently formed particles. The aminium fractions were comparable in the two particle modes.

4 Discussion

4.1 Salt formation

The slightly higher inorganic sulfur fraction in the newly formed particles indicates that sulfate and/or sulfonate salt formation played a larger role in the early growth of particles than later on. But these salts only represented a small fraction of the total particle signal. Pennington et al. [2013] found that sulfate dominated growth of 15-21 nm particles during NPF. The present results imply that there is a shift to organics-dominated growth above this size. Gas phase MSA reached its highest levels on the event days April 23 and 29, but was about two orders of magnitude lower in concentration than H_2SO_4 (Figure S1.e.).

Ammonium was often present at much greater fractions in the accumulation mode particles observed compared with the nucleation mode particles, as much as 18% of the positive ion signal (Figure S1). The alkylaminium:ammonium ratio in the observed particles was typically about 0.5 in recently formed small particles and was typically 0.1-0.25 in the larger particles (see Figure S1.c.). This indicates that the alkylamines had preferential uptake to form salts in the smallest observed particles, consistent with their higher basicities and greater enhancement of nucleation rates with respect to ammonia [*Barsanti et al.*, 2009; *Smith et al.*, 2010; *Almeida et al.*, 2013]. The aminium fractions in these measurements were lower than in the Smith et al. [2010] observations, likely due to both the ability to measure hundreds more organic ions with the more sensitive TOF mass analyzer and the collection of slightly larger particles [see *Riipinen et al.*, 2012].

There were no gas phase observations of amines during these observations. Previous measurements at this site are few and widely differing. Kieloaho et al. [2013] found small alkylamines at levels of tens of parts per trillion by volume (ppt). Sipilä et al. [2015] determined an upper limit for dimethylamine (DMA) of 0.15 ppt. The presence of as little as 5 ppt of DMA is enough to increase rates of new particle formation by about six orders of magnitude with respect to sulfuric acid and water alone [*Almeida et al.*, 2013]. Ambient gas phase ammonia levels are almost certainly higher than the DMA levels, and the presence of 5 ppt DMA may only increase nucleation rates by a factor of about 1000 with respect to sulfuric acid-ammonia-water nucleation, possibly with nonlinear enhancements when both ammonia and DMA are present [*Yu et al.*, 2012; *Almeida et al.*, 2013]. We estimate an equivalent of 0.1-0.7 ppt boundary layer DMA bound in ambient sub-100 nm particles, based on lab calibrations of dimethylammonium sulfate. If gas phase mixing ratios were at comparable or higher levels, it is likely that DMA acted to enhance the rates of new particle formation for the observed events.

4.2 Organics contributing to growth

It is clear from recent experiments that highly oxidized, very low volatility, particle-forming compounds can be formed from ozonolysis of unsaturated terpenoid precursors present in the boreal forest [*Zhao et al.*, 2013; *Ehn et al.*, 2014; *Rissanen et al.*, 2014]. Ehn et al. [2014] demonstrated that highly oxidized monoterpene ozonolysis products were present in the right gas phase concentration range to explain most of the growth of 5-50 nm particles during new particle formation at Hyytiälä. Vogel et al. [2016] showed relative enhancements in such very low volatility products, including sesquiterpene oxidation products, during new particle formation. These species are essentially nonvolatile and are likely thermally decomposed at least in part during analysis by TDCIMS. Our measurements do indicate a role for smaller organic acids, consistent with the particle phase measurements of Anttila et al. [2005]. To be clear, the molecular formulae of the species detected by TDCIMS are consistent with alkanoic acids, but we cannot exclude other molecules with identical formulae or the breakdown of larger molecules during analysis. In either case, the observed series of monocarboxylic acids is unlikely to arise from reactions of mono- or sesqui-terpenes, and in laboratory NPF experiments with monoterpene precursors we have not observed them (Fig. 3). Possible sources of linear chain organic acids to aerosol include leaf waxes and transport from the marine atmosphere [*Beri and Lemon*, 1970; *Tervahattu*, 2002, e.g.]. Kourtchev et al. [2013] reported the presence of fatty acids in total (not size-resolved) Hyytiälä aerosol only on days of clean marine air mass influence, suggesting either that these compounds are not sourced in the forest or they are destroyed under polluted conditions.

4.3 Ocean-Forest Interactions

The regional events observed here appear to be restricted to the continent, and the bulk of the material contributing to ultrafine particle growth is almost certainly composed of forest biogenic compounds and/or their oxidation products, based on both direct chemical observations and on the relationship between inferred biogenic emissions and particle growth [*Tunved et al.*, 2006]. However, several observations suggest a possible role of marine-derived compounds in new particle formation at this site, including the appearance of likely (MSA) and possible (amines, alkanoic acids) marine-derived compounds and the observation of strong events after rapid transport of marine air.

On April 23 and 24, smooth particle growth from undetectably small sizes was observed. Both of these days had back trajectories indicating rapid transport from the marine atmosphere. At 6 AM each day, the air had been over the ocean within about 1.5 days. For the April 29th NPF event, the classic "banana" growth profile was not observed, and new particles at sizes around 8 nm appeared around 11 AM without a clear preceding growth period. Back trajectories early on this day indicate that the sampled air mass had not recently been over the ocean (Figure S7). By noon, when the newly formed particles were apparent, the sampled air had been in the marine boundary layer within only about a day. While previous statistical studies have indicated that clean marine and Arctic air masses result in higher new particle formation probabilities [*Sogacheva et al.*, 2005, 2008], a possible enhancement of NPF likelihood due to rapid marine air transport has not been fully explored.

Marine air may provide important chemical species, such as organic sulfur compounds like dimethylsulfide (DMS). DMS is oxidized to form methanesulfinic acid, methanesulfonic acid, sulfur dioxide, and sulfuric acid and has a lifetime on the order of a day [*Lenschow et al.*, 1999, e.g. *von Glasow and Crutzen*, 2004]. Atmospheric DMS mixing ratios of hundreds of ppt are not uncommon over productive North Atlantic waters [*Marandino et al.*, 2008; *Bell et al.*, 2013, e.g.]. Therefore it is likely that at least tens of ppt of DMS may sometimes reach the Hyytiälä site given relatively rapid transport from the ocean, potentially representing a significant source of gas phase precursors for NPF. Similarly, transported marine carboxylic acids may be more likely to persist with rapid transport. The apparent daily photochemical production of MSA at the site indicates that some DMS is regularly present. The highest gas phase MSA mixing ratios were measured on the two event days, reaching 1 x10^5 cm^{-3}. These maxima likely result from a combination of rapid transport of marine air and very low condensation sinks. At these low levels, MSA did not likely compete with sulfuric acid in the nucleation or growth of new particles during this study. However, DMS oxidation upwind of the site may represent a significant source of SO_2, leading to sulfuric acid and new particle formation. At levels of 50-100 ppt DMS over the ocean, about 10-30 ppt of SO_2 can be produced daily [*von Glasow and Crutzen*, 2004], which would represent a substantial fraction of the SO_2 at Hyytiälä under clean conditions. We have argued that amines and alkanoic acids appear to be involved in NPF at this site, and these are both known to have marine as well as land sources [*Beri and Lemon*, 1970; *Facchini et al.*, 2008; *Decesari et al.*, 2011; *You et al.*, 2014, e.g.].

The annual cycle of NPF events is also suggestive of a marine influence, as it roughly matches the seasonal cycle of marine phytoplankton concentration near the Nordic coast, with spring and fall local maxima [*Colebrook*, 1979; *Dal Maso et al.*, 2005]. Furthermore, April is the month when DMS concentrations typically begin to increase in the Atlantic Subarctic region, as a result of the spring phytoplankton bloom [*Lana et al.*, 2011]. If the ocean provides NPF-relevant biogenic organic compounds, it seems likely that the greatest flux would be during bloom periods.

Recent global-scale modeling studies which include microphysical aerosol processes have indicated that marine DMS emissions do not exert a strong control on CCN and that changes in emission strength would have little impact on climate [*Woodhouse et al.*, 2010, 2013]. Woodhouse et al. [2013] estimate only a 1-2% increase in annually averaged CCN in the southern Finnish boreal forest when DMS emissions are included in the model. Their explanation for the small effect is that SO_2 produced from DMS oxidation is only inefficiently converted to H_2SO_4. This may be the case in many regions. However, NPF occurs frequently at Hyytiälä, it has been tied to H_2SO_4 formed in situ from SO_2 oxidation, and the newly formed particles have been demonstrated to result in CCN [*Kerminen et al.*, 2005]. We have presented inferential evidence that DMS may be a source of SO_2 and H_2SO_4 at Hyytiälä. If this is the case, it seems likely that DMS has an impact on CCN in at least some Nordic regions. High quality in situ measurements of DMS and SO_2 of sufficient length and precision to capture seasonal patterns and diel cycles are necessary to answer this question, and to isolate the influence of marine air from that of continental pollution.

5 Conclusions

We sampled and chemically analyzed recently formed, size-resolved ambient nanoparticles in the southwest Finnish boreal forest using TDCIMS. These observations indicate a possible enhancement of highly oxidized hydrocarbons and sulfur salts at the beginning of events, and showed that most growth to 20-70 nm sizes can likely be attributed to terpene oxidation products. However, newly formed particles in this size range were associated with higher fractions of non-terpene-derived saturated organics consistent with alkanoic acids. Alkylamines are likely important drivers of new particle formation in this environment, though their gas phase mixing ratios are uncertain. Some evidence points to a possible role for ocean-derived species in new particle formation events in the forest. We suggest that there should be new efforts to determine whether ocean emissions impact downwind boreal forest new particle formation, both through targeted precursor observations and further statistical analyses that consider marine air transport to the forest.

Acknowledgments and Data

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- TDCIMS nanoparticle and CI-APiTOF gas phase time series data are available at the Department of Energy ARM data website as part of the BAECC campaign.

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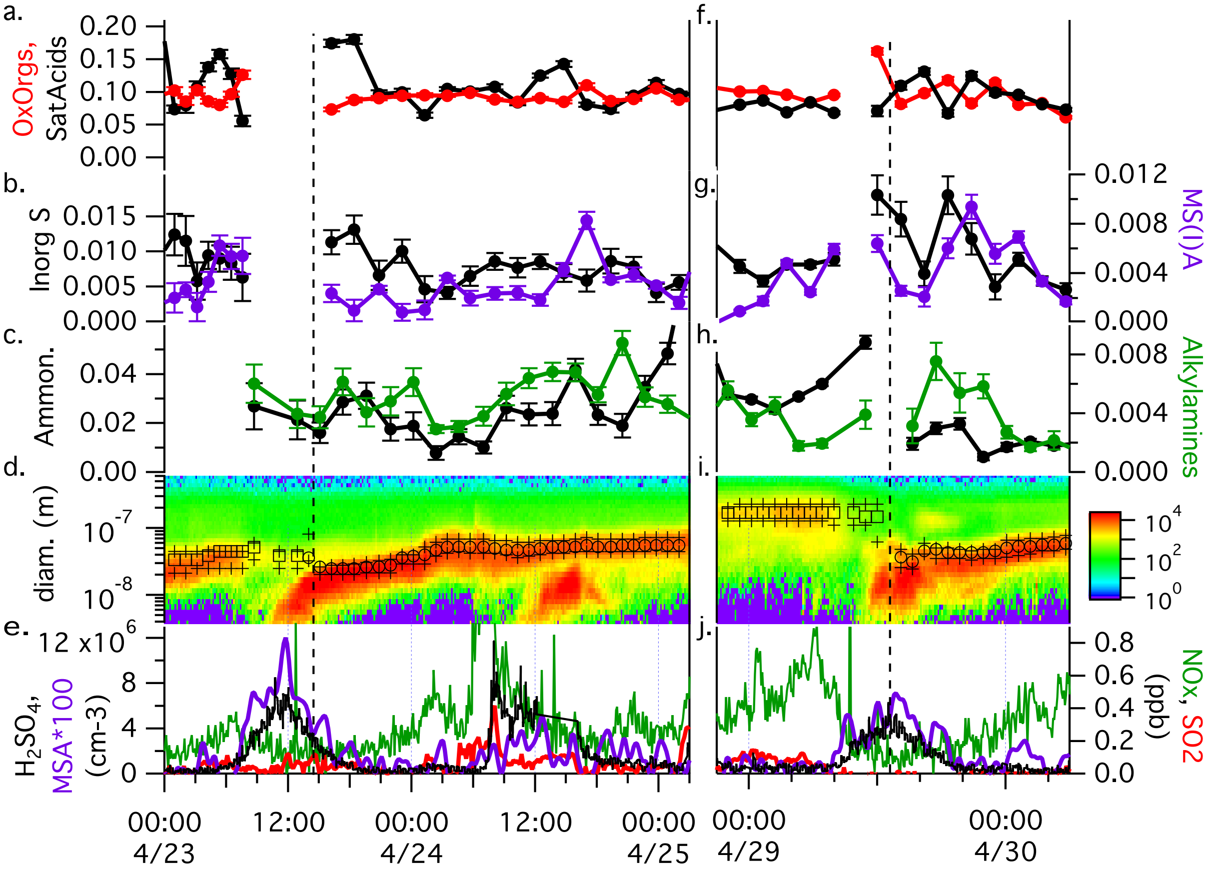

Figure 1. Particle and gas phase observations around the events of April 23 and 29. Particle measurements before the vertical dashed lines are primarily of pre-event aerosol. Particle phase negative ion fractions for (a., f.) oxidized hydrocarbons with greater than 5 oxygen atoms (OxOrgs), and the sum of alkanoic acids and linear, unsubstituted saturated dicarboxylic acids (SatAcids); and ion fractions for (b., g.) methanesulfonate and methanesulfinite (MS(I)A) and sulfur salts (Inorg S). Negative ion data for <70 pg collected mass were excluded due to low signal-to-noise. Positive mode ion fractions of (c., h.) ammonium (Ammon.) and alkylaminium (Alkylamines). (d., i.) Ambient aerosol size distribution (dN/dlogDp) and particle diameters collected for TDCIMS analysis. Circles are volume median diameter (VMD) of collected particles assessed by direct measurements. Squares are VMD as assessed by analysis of ambient size distributions and number concentration measured after the TDCIMS wire. Crosses represent the range of particle sizes composing 90% of the total collected mass. (e., j.) Gas phase observations of sulfuric acid (H_2SO_4), methanesulfonic acid (MSA), NO_x (NO_2 + NO), and sulfur dioxide (SO_2).

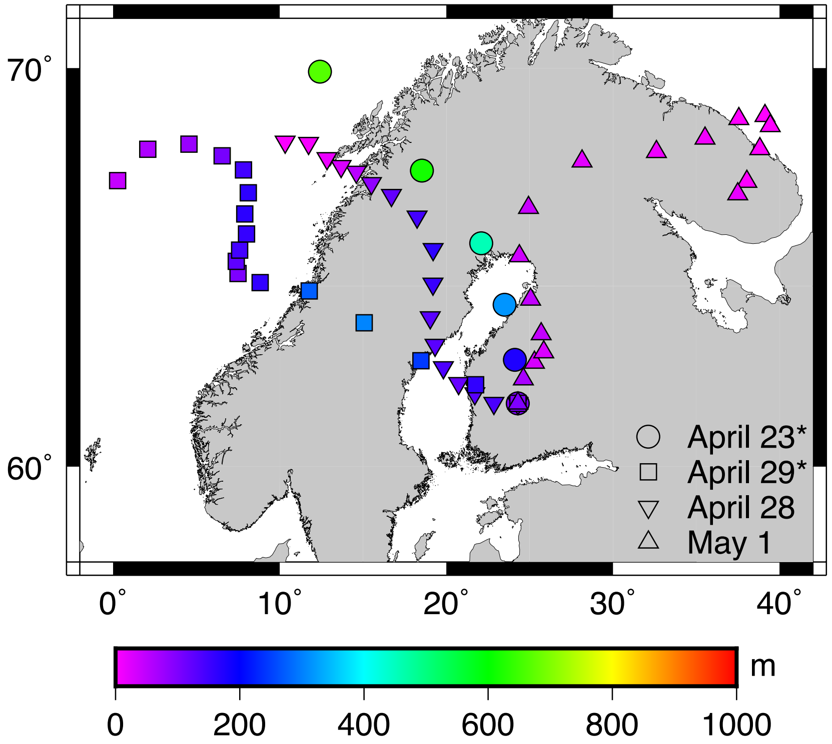

Figure 2. Air mass back trajectories arriving at the site in 2014 at 100 m elevation at 12:00 local time on the days of two events, April 23 (circle) and April 29 (squares), and on two non-event days, April 28 (downward triangles) and May 1 (upward triangles), calculated using the HYSPLIT model. The time between points for each trajectory is 6 hours. Complete four-day back trajectories are shown with the exception of the 23rd, which showed transport in the lower atmosphere from northern Greenland and was cropped for clarity. The two strong event days days are indicated by * in the legend.

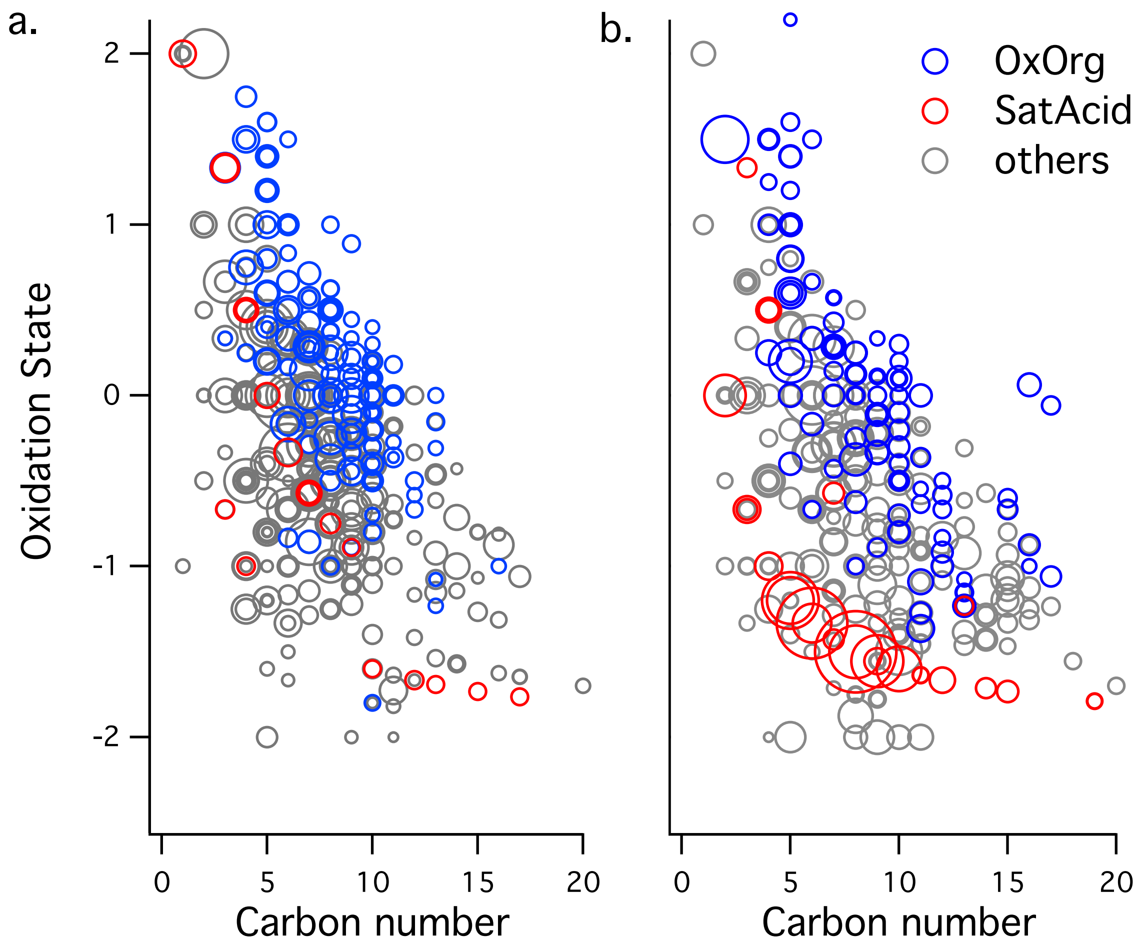

Figure 3. Carbon oxidation state of organic species detected by TDCIMS in negative ion mode for a.) a chamber NPF experiment with collected ~30 nm particles formed from oxidation products of alpha-pinene and delta-3-carene, and b.) recently formed ~25 nm particles at the Hyytiälä field site sampled from 15:42-16:12 local time on April 23, 2014. The area of the circles indicates relative signal intensity. The same high resolution ion peak list was used for both data sets. Colors indicate the ion type from Figure 1.a: OxOrg (blue), SatAcids (red), and others (gray).