Solar eclipse demonstrating the importance of photochemistry in new particle formation

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Solar eclipses provide unique possibilities to investigate atmospheric processes, such as new particle formation (NPF), important to the global aerosol load and radiative balance. The temporary absence of solar radiation gives particular insight into different oxidation and clustering processes leading to NPF. This is crucial because our mechanistic understanding on how NPF is related to photochemistry is still rather limited. During a partial solar eclipse over Finland in 2015, we found that this phenomenon had prominent effects on atmospheric on-going NPF. During the eclipse, the sources of aerosol precursor gases, such as sulphuric acid and nitrogen-containing highly oxidised organic compounds, decreased considerably, which was followed by a reduced formation of small clusters and nanoparticles and thus termination of NPF. After the eclipse, aerosol precursor molecule concentrations recovered and re-initiated NPF. Our results provide direct evidence on the key role of the photochemical production of sulphuric acid and highly oxidized organic compounds in maintaining atmospheric NPF. Our results also explain the rare occurrence of this phenomenon under dark conditions, as well as its seemingly weak connection with atmospheric ions.

Solar eclipses have provided fundamental opportunities for scientific research, the most profound outcomes of which include the verification of Einstein’s general theory of relativity1 and characterization of the Sun’s atmosphere2. Sun-induced photochemical reactions sustain life on Earth and play essential roles in atmospheric chemistry. Quantifying the chain of atmospheric processes initiated by photochemical reactions is crucial for our understanding on aerosol and cloud formation and climate change.

New particle formation (NPF) produces around half of atmospheric cloud condensation nuclei, being important to the radiative balance and climate3. In most locations, observed NPF and subsequent particle growth take place during daytime only4. Simultaneously, photochemical cycles control the concentrations of reactive oxidants such as OH-radical and ozone. Clustering seems to be taking place also in the dark but these clusters are rarely growing5–7. Sulphuric acid, the principal driver of atmospheric NPF, is formed mainly by reaction of sulphur dioxide with OH-radicals, and to some extent also by its reaction with Criegee intermediates8–10. The newly formed particles are suggested to grow bigger in size mainly by condensation of low-volatile, highly-oxidized multifunctional compounds (HOMs) from terpene oxidation11–14. Some HOMs have extremely low volatilities (ELVOC) and they are able to condense onto sub-2 to 3 nm clusters, thus being responsible for the initial growth of fresh-formed particles and also a large part of secondary organic aerosol (SOA)11,14,15. Despite very high O:C ratios, not all HOMs are ELVOCs16, although the terms have been used interchangeably in previous studies (see SI for more details)11.

In the presence of NOx, also nitrogen containing HOMs (N-HOMs) are formed, and they have been observed during NPF events17–19, but the exact contribution of N-HOMs vs. HOMs that do not contain nitrogen on NPF is...
not known. In general, very little is known about the detailed connection between atmospheric photochemistry, production and composition of different low-volatility compounds, cluster formation and atmospheric NPF.

We measured aerosol precursor molecules, clusters and nanoparticles during a partial solar eclipse (81% of the sun blocked) on 20 March 2015 at SMEAR II-station, Finland. Sudden changes in oxidant production during the eclipse gave us a unique opportunity to investigate the importance of photochemistry, especially OH-radical driven reactions, on the gas-to-particle conversion process. Similar boundary conditions are very difficult to find from any other kind of field measurement data. For example, daytime and night-time data differ from each other not only in terms of the strength of photochemistry, but also in terms of the chemical mixture of air pollutants and the presence of an additional oxidant (nitrate radical) during night time. Comparing data from clear-sky and cloudy days to each other would not allow isolating the effect of photochemistry either, as clear-sky and cloudy days tend to have different air mass properties. The closest analogy to a solar eclipse would be a transition between clear and cloudy skies. The problem with that data is that such transitions tend follow each other too rapidly to track the whole sequence of processes starting from atmospheric oxidation to the formation of growing nanoparticles.

**Results**

The eclipse day was a sunny, mostly clear-sky NPF event day with light winds (2–3 m/s). During the eclipse, we observed a drop in the UV-B radiation intensity and ambient temperature (Fig. 1A), but no apparent change in either wind speed or direction. A drop similar to the UV-B radiation is collaterally expected in the OH-radical concentration (Fig. S1) for which we applied a proxy calculation in lack of direct measurements. Previous studies have shown a high correlation (>85%) between the OH-radical concentration and its primary production from ozone photolysis, supporting the validity of our proxy calculation. After a notable decrease in the NOx concentration prior to eclipse, concentrations of both NO and NOx were low during the eclipse (Fig. S2). Also, the measured SO2 concentration remained low during the day (Fig. S2). The ozone concentration usually increases by about 10 ppb from morning to afternoon on springtime NPF event days at our measurement site. The eclipse stalled this ozone increase momentarily, but did not cause any ozone decline as reported in earlier studies conducted in semi-polluted environments. The lack of such decline in our measurements is probably related to the low NOx concentration, making the ozone concentration less susceptible to its local photochemical production than in more polluted sites. We also observed an instant decrease in photochemical energy conversion rates in the forest and, subsequently, reductions in transpiration and CO2 exchange rates (Fig. S3). Monoterpene concentration decreased under detectable levels after the eclipse (Fig. S4).

The concentration of gaseous sulphuric acid (H2SO4) and two nitrogen containing HOMs (C10H15O4N, 339.068 Th and C10H15O3N, 355.063 Th) whose concentration decreased the most during the eclipse. Panel C shows other measured (N-)HOMs that stayed more constant during the eclipse: C10H14O7 (308.062 Th), C10H14O9 (340.052 Th) and C10H15O8 (325.065 Th), C20H31O11N (523.178 Th), C20H31O13N (555.168 Th) and C20H28O15 (570.131 Th). All mentioned m/z contain the mass of the charger ion, NO3−. Vertical red line: maximum phase, dashed black lines: beginning and end time of the eclipse.
of the cluster formation with atmospheric photochemistry. Concentrations of <2 nm ions (cluster ions) were not affected by the eclipse as their primary production depends on ionizing radiation. Concentrations of 2−3 nm neutral particles and ions decreased by approximately the same factor, and their concentration minima were achieved a bit later than those of smaller particles. These features suggest that >2 nm particles originated mainly from the growth of sub-2 nm neutral clusters, and that ions in that size range originated from the charging of the neutral particles by cluster ions, consistent with earlier studies made at SMEAR II17,30. The concentration of 3–6 nm particles changed little during the eclipse, indicating that their formation rate was suppressed compared to regular NPF days at SMEAR II when their concentration usually increases rapidly around noon31,32. We did not observe any systematic change in the submicron aerosol mass concentration, or its bulk chemical composition, during the eclipse (Fig. S11).

Long-term observations at the SMEAR II-station show, on average, higher concentrations of sulphuric acid, N-HOM and several other HOM monomers during NPF event days compared with non-event days (Fig. 3).
During the eclipse, the formation rate of 1.5 nm particles, \( J_{1.5} \), was positively correlated with both sulphuric acid and 
N-HOM concentration, but not with the concentrations of other HOMs (Figs S12–15). Furthermore, \( J_{1.5} \) was 
positively correlated with the product of the \( \text{H}_2\text{SO}_4 \) concentration and concentration of any of the major 
HOMs. Correlations with the formation rate of 2 nm particles, \( J_2 \), were quantitatively similar but clearly weaker compared 
with \( J_{1.5} \) (Figs S16–18). While these observations do not prove any causality between NPF and sulphuric acid or 
(N-)HOMs, they definitely support the idea that both sulphuric acid and some subset of (N-)HOMs at large enough 
concentrations are needed for active NPF at this site.

During the recovery from the solar eclipse, sulphuric acid concentration increased rapidly (Fig. 1B), consistent 
with its UV-driven production during daytime (Figs S19 and S20). Concentrations of N-HOMs increased 
at a slower rate (Fig. 1B), since their production route requires the initiation of NO\(_x\) photolysis, VOC emissions 
and their oxidation to RO\(_2\) radicals via either OH-radical reactions or ozonolysis (Fig. S21). Concentrations of 
sub-3 nm clusters and particles recovered somewhat later than sulphuric acid and N-HOM, as one would expect 
if these compounds were important precursors for small clusters. The observed growth rate of 2–3 nm particles 
was ~1 nm/h during the recovery from eclipse (Fig. S22). While our data do not reveal which compounds actu-
ally contributed to the particle growth, it is interesting to note that sulphuric acid together with the two major 
N-HOM compounds had high enough concentrations so that their concomitant, irreversible condensation onto 
sub-3 nm particles could explain the observed growth.

In summary, we have shown that the decrease in UV-radiation during the solar eclipse decreases the source 
rates of sulphuric acid and some (N-)HOMs, which further leads to a decrease in clustering and initial growth 
of aerosol particles. Since the condensation sink is hardly affected by the eclipse, low-volatile vapours continue 
condensing and small clusters coagulating onto existing aerosol particles. Thus, the gas-phase concentrations of 
the low-volatile vapour originating mainly from photochemistry and photooxidation of the clusters made of 
these vapours decrease notably. During the recovery phase of the eclipse, OH-radical, sulphuric acid, 
(N-)HOM and cluster concentrations recover and re-initialize NPF.

Our observations might explain why the frequently-observed night-time sub-3 nm clusters do not grow 
into larger aerosol particles. We conclude that when ozonolysis is the prominent formation route of condensing 
vapours (like HOMs at night-time, Fig. 3), the resulting ozonolysis products alone cannot grow these sub-3 nm 
clusters further into new aerosol particles in a boreal forest atmosphere at least in the observed concentration lev-
els. Thus, extremely low-volatile reaction products from the OH-radical oxidation, especially sulphuric acid and 
a sub-set of (N-)HOMs, are the key compounds for cluster growth and observing NPF. Furthermore, the build-up 
of HOMs and their dimers in the morning, apparent prior to the eclipse (Figs 3 and S9) and during regular NPF 
event days compared with non-event days, may boost the particle growth.

We had a unique possibility to investigate atmospheric chemistry and clustering related to NPF during a 
partial solar eclipse at the SMEAR II-station using state-of-the-art instrumentation. Our results highlight the 
necessity of photochemistry in aerosol precursor formation and provide a plausible explanation of why NPF is 
observed almost solely during daytime in continental boundary layers. Our results confirm the crucial role of 
sulphuric acid in maintaining atmospheric NPF and show further that extremely low volatile organic compounds, 
potentially important to the initial steps of atmospheric NPF, are formed not only by ozone oxidation but also 
through photochemical reactions. Our results show that neutral pathways dominate the initial clustering and 
growth, at least at our measurement site. Such consistent observations, from the oxidation of precursor vapours 
to nanoparticles, have previously been achieved only in controlled laboratory experiments. Our results are an 
important step toward understanding the connections between atmospheric oxidation, NPF and secondary aer-
osol formation, which is needed for quantifying the complex interplay between future anthropogenic activities, 
air pollution and changing global climate.

Methods
All measurements were conducted at the SMEAR II-station, located in Hyytiälä (61°51′N, 24°17′E, 181 m a.s.l.), 
Southern Finland. The main instrumentation was a mass spectrometer, a particle size magnifier and an ion 
mobility spectrometer. The mass spectrometric measurements were conducted with a CI-API-TOF with nitrate 
based chemical ionization scheme in the negative ion mode for the detection of aerosol precursor molecules and 
clusters such as sulphuric acid and highly oxidized organic compounds. Low volatile compounds were detected 
after a proton transfer or clustering with the charger ions. The number concentration of freshly formed 1–3 nm 
particles and clusters were measured by a PSM used that used diethylene glycol to activate and grow particles to 
90 nm. After that, particles grow to detectable sizes by condensation of butanol inside a condensation particle 
counter. Neutral cluster and Aerosol Spectrometer (NAPS) is an ion mobility spectrometer that was used to 
detect the size distributions of ions between 0.8 nm and 42 nm (mobility equivalent diameter) and total particles, 
i.e. neutral and charged, between ~2 nm and 42 nm. More detailed information of instrumentation and other used 
methods can be found in the Supplementary material.

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Author Contributions
T.J. and V.-M.K. wrote the main manuscript text. T.J. and J. Ko. prepared the figures. T.J., J.Ko., K.L., H.E.M., J.A., A.P.-C., O.G., T.N., M.E., J.Ka., H.J., J.L., J.D., L.R.A., P.R., L.H., Č.Y. and M.S. collected and analysed data, D.R.W., J.B. T.P., V.-M.K. an M.K. designed measurements. All authors contributed by drafting, commenting and revising the manuscript.

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