Atmospheric Environment 178 (2018) 255–264

Contents lists available at ScienceDirect

Atmospheric Environment

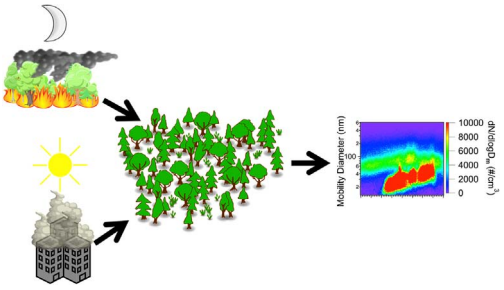
journal homepage: www.elsevier.com/locate/atmosenv

Particle growth in an isoprene-rich forest: Influences of urban, wildfire, and biogenic air masses

Matthew J. Gunsch[a], Stephanie A. Schmidt[b,f], Daniel J. Gardner[a], Amy L. Bondy[a], Nathaniel W. May[a], Steven B. Bertman[d], Kerri A. Pratt[a,c,**], Andrew P. Ault[a,e,*]

[a] Department of Chemistry, University of Michigan, Ann Arbor, MI, USA
[b] University of Michigan Biological Station, University of Michigan, Pellston, MI, USA
[c] Department of Earth and Environmental Science, University of Michigan, Ann Arbor, MI, USA
[d] Department of Chemistry, Western Michigan University, Kalamazoo, MI, USA
[e] Department of Environmental Health Sciences, University of Michigan, Ann Arbor, MI, USA
[f] Now at Department of Environmental Science and Policy, George Mason University, Fairfax, VA, USA

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Particle growth
Forest
Michigan
Wildfire
Remote

ABSTRACT

Growth of freshly nucleated particles is an important source of cloud condensation nuclei (CCN) and has been studied within a variety of environments around the world. However, there remains uncertainty regarding the sources of the precursor gases leading to particle growth, particularly in isoprene-rich forests. In this study, particle growth events were observed from the 14 total events (31% of days) during summer measurements (June 24 – August 2, 2014) at the Program for Research on Oxidants PHotochemistry, Emissions, and Transport (PROPHET) tower within the forested University of Michigan Biological Station located in northern Michigan. Growth events were observed within long-range transported air masses from urban areas, air masses impacted by wildfires, as well as stagnant, forested/regional air masses. Growth events observed during urban-influenced air masses were prevalent, with presumably high oxidant levels, and began midday during periods of high solar radiation. This suggests that increased oxidation of biogenic volatile organic compounds (BVOCs) likely contributed to the highest observed particle growth in this study ($8 \pm 2\,nm\,h^{-1}$). Growth events during wildfire-influenced air masses were observed primarily at night and had slower growth rates ($3 \pm 1\,nm\,h^{-1}$). These events were likely influenced by increased SO_2, O_3, and NO_2 transported within the smoke plumes, suggesting a role of NO_3 oxidation in the production of semi-volatile compounds. Forested/regional air mass growth events likely occurred due to the oxidation of regionally emitted BVOCs, including isoprene, monoterpenes, and sesquiterpenes, which facilitated multiday growth events also with slower rates ($3 \pm 2\,nm\,h^{-1}$). Intense sulfur, carbon, and oxygen signals in individual particles down to 20 nm, analyzed by transmission electron microscopy

* Corresponding author. Department of Environmental Health Sciences, University of Michigan, Ann Arbor, MI, USA.
** Corresponding author. Department of Chemistry, University of Michigan, Ann Arbor, MI, USA.
E-mail addresses: prattka@umich.edu (K.A. Pratt), aulta@umich.edu (A.P. Ault).

https://doi.org/10.1016/j.atmosenv.2018.01.058
Received 11 August 2017; Received in revised form 27 January 2018; Accepted 31 January 2018

with energy dispersive X-ray spectroscopy (TEM-EDX), suggest that H_2SO_4 and secondary organic aerosol contributed to particle growth. Overall, aerosol growth was frequently observed in a range of air masses (urban, wildfire, forested) and oxidant conditions (day vs. night), with rates ranging from 0.8 to 10.2 nm h^{-1}.

1. Introduction

New particle formation and growth (NPFG) has been identified as an important (Gordon et al., 2016; Jokinen et al., 2015; Kulmala et al., 2000, 2014), but uncertain (Pierce and Adams, 2007, 2009b), contributor to global aerosol concentrations. Growth events, where newly formed particles increase in size through condensation, impact climate by acting as cloud condensation nuclei (CCN) (Laaksonen et al., 2005; Merikanto et al., 2009; Pierce and Adams, 2009a; Sotiropoulou et al., 2006), thereby modifying cloud properties and leading to cooling through the indirect effect (Ruehl et al., 2016). Through model simulations, Gordon et al. (2016) suggested that biogenic NPFG events are the source of 50–100% of particles by number within 500 m of the surface over large swaths of North America, from interior Alaska to the northern Great Lakes region, with these particles increasing CCN concentrations by 3–40% and altering the cloud albedo effect by up to 0.5 W m^{-2}. Growth events have been observed in forested (e.g. Creamean et al., 2011; Dal Maso et al., 2005; Yu et al., 2015), urban (e.g. Salimi et al., 2017; Wang et al., 2013), marine (e.g. Allan et al., 2015; Sipilä et al., 2016), and polar regions (e.g. Weller et al., 2015; Willis et al., 2016), as well as in the free troposphere (e.g. Bianchi et al., 2016; Rose et al., 2015). However, there have been few studies in the upper Midwestern United States (Kanawade et al., 2011; Lee et al., 2008; Pierce et al., 2014; Twohy et al., 2002).

Nucleated particles are formed in-situ in the atmosphere from stable molecular clusters (Zhang, 2010), including a variety of chemical species, such as sulfuric acid (Sipilä et al., 2010; Zhang et al., 2004), low volatility oxidized biogenic gases (Jokinen et al., 2015; Tröstl et al., 2016), organic (including amine) salts (Barsanti et al., 2009; Jen et al., 2016; Smith et al., 2010), iodine-containing gases (Allan et al., 2015; Sipilä et al., 2016), and gaseous ions (Kirkby et al., 2016). In particular, low volatility oxidation products of biogenic volatile organic compounds (BVOCs), including monoterpenes and sesquiterpenes, are thought to play an important role in new particle formation due to the prevalence of events in forested regions (Laaksonen et al., 2008). Growth events have been observed in boreal forests (Mäkelä et al., 1997; Sellegri et al., 2005), European coniferous forests (Gonser et al., 2014; Manninen et al., 2010), African savanna forests (Laakso et al., 2008; Vakkari et al., 2011), and deciduous forests (Jung et al., 2013; Manninen et al., 2010; Pryor et al., 2011), all of which have significant concentrations of BVOCs. The oxidants present prior to and during growth events also impact the formation of low volatility species, with OH oxidation dominating during the day and NO_3 at night (Brown et al., 2006; Ziemann and Atkinson, 2012). In addition to precursor and oxidant concentrations, key factors determining whether a growth event will occur are background aerosol concentration (condensation sink) (Dal Maso et al., 2002), season (Kulmala et al., 2004), and radiation (George et al., 2015; Zhang et al., 2011). While the majority of growth events are observed during the daytime (Kulmala et al., 2004, 2014), some events have been measured at night (Lee et al., 2008; Salimi et al., 2017). Also, while most growth events have been observed during clean conditions in remote areas, growth events can also begin due to the influence of transported emissions from long-range sources, including urban areas (Chandra et al., 2016; Salma et al., 2016; Venzac et al., 2008; Yue et al., 2013) and wildfires (Bein et al., 2008). Given the wide range of chemical and atmospheric variables that can impact growth events, studies are needed that compare events that occur during different atmospheric conditions at the same location.

Growth rate is a key variable once particle growth is occurring, as this determines the time necessary for particles to reach a size where nucleated particles can act as CCN. While H_2SO_4 is a key gaseous precursor for NPF (Kulmala and Laaksonen, 1990; Kulmala et al., 2004; Sipilä et al., 2010), nucleation growth rates (J) are typically faster than can be explained by binary nucleation of H_2SO_4 and water vapor (Jokinen et al., 2015; Kulmala et al., 2014, 2012, 2004; Sipilä et al., 2016). In some locations, growth rates are seasonally dependent (Kulmala et al., 2004; Yu et al., 2015), but a great deal of uncertainty remains due to significant interannual variation (Kanawade et al., 2011; Yu et al., 2015). Growth rates are strongly related to the concentration and chemical form of low volatility materials present (Laaksonen et al., 2008). However, there are limited measurements of growth rates for growth events with different gaseous precursors and oxidants at the same site, particularly in northern portions of North America where growth events are expected to contribute substantially to CCN concentrations (Gordon et al., 2016).

A potential complicating factor for growth events in forested regions is that isoprene has been speculated to suppress growth events. For the summer of 2009 in northern Michigan, Kanawade et al. (2011) credited isoprene suppression leading to a lack of new particle formation events at the University of Michigan Biological Station (UMBS), though growth of ultrafine aerosol was observed on a few occasion from ~20 nm particles that were too small to have been regionally transported. This hypothesis was based on results from a laboratory chamber experiment, where a lack of nucleation was attributed to the high reactivity of isoprene with the hydroxyl radical, inhibiting nucleation (Kiendler-Scharr et al., 2009). However, many other studies (e.g. Jokinen et al., 2015; Kourtchev et al., 2005; Limbeck et al., 2003) have observed that isoprene could potentially enhance new particle formation and growth instead of inhibiting it. Therefore, it is important to investigate particle growth events in isoprene-rich environments.

At UMBS in northern Michigan, the Program for Research on Oxidants PHotochemistry, Emissions and Transport (PROPHET) tower is located within a temperate mixed-deciduous forest, dominated by isoprene emissions (Ortega et al., 2007), and representative of the north-central US and south-central Canada (Carroll et al., 2001; VanReken et al., 2015). Herein, frequent ultrafine particle growth events at UMBS during summer 2014 are reported. Particle size distributions, individual particle chemical composition, meteorological parameters, and air mass trajectories were examined from June 24 – August 2, 2014 to understand the conditions that led to particle growth. This paper highlights particle growth occurring during three unique air mass types within the same forest: transported urban air masses, transported wildfire-influenced air masses, and biogenic/stagnant local air masses from the surrounding isoprene-rich forest.

2. Methods

Atmospheric sampling was conducted between June 24 and August 2, 2014 at UMBS near Pellston, Michigan (45°33′31″N, 84°42′52″W). UMBS is a remote 40 km^2 research forest with little local pollution. The forest is dominated by aspen (61%), northern hardwoods (17%), and upland conifers (13%), with an average canopy height of 22.5 m (VanReken et al., 2015). Major nearby metropolitan areas include Milwaukee (370 km southwest), Detroit (385 km south-southeast), and Chicago (466 km south-southwest).

Instruments were located within the PROPHET laboratory adjacent to a 31 m tall outdoor tower. Above canopy air was sampled from 34 m (~12 m above the forest canopy) through an insulated 1.1 cm ID copper tubing inlet using a cylindrical sampling manifold with dedicated lines for each instrument. Sampled air had a residence time of