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Dynamic and chemical controls on new particle formation occurrence and characteristics from in situ and satellite-based measurements

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HIGHLIGHTS

- There is potential for satellite-based proxies of nucleation occurrence/intensity.
- LAIxT$_{max}$, NO_2, HCHO, UV, AODxAE, u_*, and H differ on event vs. non-event days.
- However, they exhibit modest skill in explaining variability of J_6, GR, and SP.

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ABSTRACT

We analyze the association between satellite-based measurements of chemical conditions (sulfur dioxide (SO_2), nitrogen dioxide (NO_2), and formaldehyde (HCHO) concentrations), insolation (UV), and aerosol particle properties (aerosol optical depth (AOD) and Ångström exponent (AE)); and the occurrence of new particle formation (NPF), formation rates (J_6), growth rates (GR), and survival probabilities (SP) using particle size distribution measurements taken during two extended field campaigns at a forested location in southern Indiana. When conditionally sampled by event occurrence and non-occurrence the satellite-derived parameters exhibit significant differences and also show some degree of skill in predicting NPF though logistic regression analysis. During leaf-on measurement periods, NPF occurrence exhibits strong seasonality (NPF is more frequent in spring vs. summer) and is associated with a low condensational sink, while leaf-off NPF occurrence is associated with high near-surface UV receipt. Multiple linear regression equations of J_6, GR, and SP using the chemical conditions as predictors exhibit some significant r^2 values ($p < 0.1$), but are relatively unstable and many of the regression coefficients do not differ significantly from zero.

1. Introduction

New particle formation (NPF) events enhance aerosol particle (hereafter particles) concentrations (Kulmala et al., 2004) and occur on regional scales (Crippa and Pryor, 2013). They thus have the potential to impact regional and possibly global climate (Merikanto et al., 2009). For newly formed particles (~1–3 nm) to become climate relevant, they must survive and grow to sufficient diameters to act as cloud condensation nuclei (~100 nm). NPF events have been estimated to contribute up to 50% of particles >100 nm on a regional scale over northeastern North America (Pierce et al., 2014), but this contribution is likely to vary regionally (Kulmala et al., 2004; Westervelt et al., 2013) and such estimates are sensitive to the data analysis and model assumptions. The climate impact of NPF events is determined by factors such as the in situ particle population, frequency of NPF events, nucleation rate (i.e. how many new particles form, described here using the formation rate of 6–30 nm particles, J_6), growth rates (GRs), and survival probabilities (SPs, i.e. percentage of new particles that grow to climate relevant size). Herein we use statistical analyses of in situ and remote sensing data to diagnose the dependence of NPF occurrence, J_6, GR, and SP on parameters known, or thought, to play a key role in dictating each of those variables. These conditions are not necessarily mutually inclusive, i.e. conditions conducive to NPF event occurrence may be unfavorable for high formation rates and/or GR. For example, low condensational sink (CS) was found to be conducive to NPF occurrence and high J_6, while high CS was associated with high GR in the Yangtze River Delta in China (Qi et al.,

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2015). Clean air masses are also conducive to NPF in northeastern North America, but polluted air masses are associated with higher J_{10} (Pierce et al., 2014).

Specific objectives of the analyses herein are to characterize:

1. Chemical and physical regimes associated with NPF occurrence.
2. The association between different chemical regimes and J_6, GR, and SP of NPF events.

We develop a framework that can be uniformly applied to all in situ observational data sets of ultrafine particle size distributions (PSDs). As in situ trace gas measurements are not always available, we draw predictor variables from satellite-borne radiometers. It is acknowledged that these observations are associated with larger uncertainty than in situ measurements, and are typically not continuous through time. However, they provide consistent information about atmospheric composition across a range of spatial scales, and are uniformly available at least at low- and mid-latitudes. Further, they quantify columnar conditions and thus may be more strongly linked to regional-scale NPF than point measurements made at/or near the surface.

2. Methods

2.1. Data sets

PSD measurements used to describe the occurrence and characteristics of NPF events were taken during two extended field campaigns at a forested location in southern Indiana (in the Morgan Monroe State Forest, MMSF; 39.317°N, 86.417°W; Fig. 1) (Pryor et al., 2014, 2010):

- Data collected during Jan. 2007–Apr. 2009 using a Scanning Mobility Particle Sizer (SMPS comprised of an Electrostatic Classifier, nano-DMA, and Condensation Particle Counter) (Pryor et al., 2010). The measurements were taken sequentially every ~2.5 min for 10 min out of every half hour at 2 m, 34 m, and 46 m for a particle diameter range of 3.22–105.5 nm (due to low tubing penetration efficiencies, only the 81 bins > 6 nm are used here).
- Data collected during Mar. 2012–Dec. 2013 using a TSI Fast Mobility Particle Sizer (FMPS 3091; 32 logarithmically spaced bins 6–520 nm) (Pryor et al., 2014). Measurements were taken sequentially for 10 min out of every half hour at each of three sample heights: 12 m, 20 m, and 28 m. The FMPS reports at 1 Hz, but the data have been averaged to 2 min.

Analyses presented here employ predictands derived using PSD measurements from 34 m for 2007–2009 and 28 m for 2012–2013; both heights are above the canopy, but represent near surface concentrations.

The selection of predictor variables was based on the following reasoning:

- While uncertainty remains regarding the relative importance of different nucleation mechanisms (Boy et al., 2007) (e.g. cluster activation (Kulmala et al., 2006), kinetic (McMurry, 1980), ion mediated (Yu and Turco, 2000), binary (Jaecker-Voirol and Mirabel, 1989), or ternary nucleation (Kulmala et al., 2000)), most studies indicate a key role for sulfuric acid (H_2SO_4) with either ammonia (NH_3) or organic molecules contributing to the critical clusters (Almeida et al., 2013; O'Dowd et al., 2002; Sipilä et al., 2010). Although not uniformly observed, our further expectation is that NPF likelihood and intensity will tend to be reduced under conditions of a high CS, and that near-surface detection of NPF will be enhanced under conditions of high turbulence intensity (since there is some evidence that nucleation is concentrated aloft from the surface (Crippa et al., 2012; Pryor et al., 2011)).
- The relative contribution of different species to particle growth may vary over the course of an event. Prior research at MMSF has indicated initial particle growth is dominated by ammonium and sulfate although later growth exhibited evidence of some contribution from organics (Pryor et al., 2011). In Pittsburg H_2SO_4 also dominated formation and initial growth, followed by growth from ammonium, and organics contributing to particle growth later in the event (Zhang et al., 2004).
- A newly formed particle can grow to climate relevant size, given there are sufficient condensable vapors present and that it does not coagulate with other particles. Thus SP may be increased in conditions favorable for high GR and reduced under high CS or in conditions favorable for high J_6 and thus greater coagulation loss.

Based on the above, statistical models of NPF occurrence and properties (predictands are NPF occurrence, J_6, GR, and SP) are built using the following predictor variables:

- LAI × T_{max} (where T_{max} is the daily maximum hourly air temperature and LAI is the leaf area index as measured every sixth day at MMSF). LAI and T_{max} used here are from in situ measurements, but proxies of both (e.g. skin temperature and LAI) are available from the Moderate Resolution Imaging Spectroradiometer (MODIS)) (Huete et al., 1999; Wan, 1999). LAI × T_{max} is used as a proxy for biogenic volatile organic compound (BVOC) emissions (Guenther et al., 1993), the oxidation products of which may be involved in nucleation and/or growth of freshly nucleated particles (Laaksonen et al., 2008). This variable is thus anticipated to have a positive association with NPF occurrence, J_6, GR, and SP.
- Formaldehyde (HCHO). Although satellite retrievals of HCHO are highly uncertain (Barkley et al., 2013), HCHO is one of very few products of VOC oxidation that is detected by satellite-borne radiometers, and while it is not directly relevant to NPF or ultrafine particle growth, satellite-derived HCHO concentrations are used as an index of the abundance of relatively low-volatility oxidized organics of both anthropogenic and biogenic origin (Chance et al., 2000; Henze and Seinfeld, 2006). Given contradictory evidence that high isoprene concentrations may either suppress (Kiendler-Scharr et al., 2009) or participate in NPF (Surratt et al., 2006) and that yields of HCHO from isoprene oxidation are non-linearly dependent on NO_x (Wolfe et al., 2015), it is difficult to assert an a priori expectation of the relationship between HCHO and NPF occurrence or intensity. Since HCHO is a product of oxidation of a wide array of VOCs and generation of less volatile products it is anticipated to have a positive association with GR and SP.
- Sulfur dioxide (SO_2). SO_2 is used here as a proxy for H_2SO_4, a key NPF precursor (Sipilä et al., 2010) and a key component of condensational growth (Pryor et al., 2011). It is thus anticipated to have a positive association with NPF occurrence, J_6, GR, and SP.
- Nitrogen dioxide (NO_2). NO_2 is used as a proxy for anthropogenic gas and particle emissions (Russell et al., 2012). Given NO_x emissions are associated with both increased CS (due to co-emitted particles) and possible enhancement of condensable vapors (e.g. collocation of NO_2 and SO_2 from major industrial complexes) it is anticipated to have a negative association with NPF occurrence and positive association with J_6, GR, and SP.