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## Nucleation events at a coastal city during the warm period: Kerbside versus urban background measurements

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### HIGHLIGHTS

- We report particle size distributions at a kerbside and an urban background site.
- New particle formation events are observed 27–29% of the days.
- The nucleation bursts show a similar pattern at both sites.
- Nanoparticles observed at the urban site are formed locally.
- Nanoparticle observed at the urban background station are formed elsewhere.

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### ABSTRACT

Number size distributions of atmospheric aerosol particles were simultaneously measured at a kerbside and an urban background site in the city of Thessaloniki, Greece, from June to October 2009. New particle formation events were observed ca. 27% of the days at the urban kerbside site and 29% of the days at the urban background site. In almost all the cases the events started between 10:00 and 12:00, and continued for several hours. The total number concentration (TNC) of the particles having diameters from 10 to ca. 500 nm during the events increased from  $1.4 \times 10^4$  to  $6.5 \times 10^4$  #/cm<sup>3</sup> at the urban kerbside site, and from  $0.2 \times 10^4$  to  $2.4 \times 10^4$  #/cm<sup>3</sup> at the urban background site. At the urban kerbside site, 9% of the days exhibited class I events (i.e., events followed by a clear growth of the newly formed particles), 10% class II (i.e., events during which the concentration of nucleation mode particles were high but their growth was not continuous), 67% were characterised as non-event days, and 14% of the days exhibited no clear particle formation pattern (undefined). At the urban background site, 15% of the days were classified as class I, 5% as class II, 75% of the days showed no nucleation, whereas only 5% of the days were undefined. While the fraction of event days (both class I and class II) at both sites was similar (ca. 20%), the higher fraction of class I events observed at Eptapyrgio can be attributed to the cleaner environment of the urban background site that allows better identification of the particle concentration increase. The nucleation bursts show a similar pattern at both sites, with the newly formed particles reaching a final size of ca. 80–100 nm. A distinct difference between the two stations was that the smallest particles observed during the new-particle formation events had a diameter of ca. 10 nm (i.e., the smallest particles we could observe) at the kerbside site and ca. 20 nm at the urban background site. This is an indication that the new particles observed at the urban background station are formed elsewhere and are transported to the site. Estimated concentrations of H<sub>2</sub>SO<sub>4</sub> using a proxy model, suggest that these are high enough to explain the nucleation events despite that the available aerosol surface was high, especially at the urban kerbside site.

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## 1. Introduction

Nucleation is an important contributor to the particle number concentration observed in the atmosphere of urban and background environments (Stanier et al., 2004; Shi et al., 2001). Particles produced by nucleation can have adverse effects upon human health since they can penetrate deep into our respiratory system (Schwartz et al., 1996; Pope et al., 1995) and cause severe symptoms (Atkinson et al., 2010; Salma et al., 2015). In addition, due to their ability to enter the blood stream through the lung epithelium, they can also cause cardiovascular diseases (Oberdörster, 2001; Politis et al., 2008). Despite their small size, nucleation-mode particles can also have a great impact on climate and visibility. Freshly formed nanoparticles eventually grow to larger optically-active particles that can directly affect the radiative properties of the atmosphere (Bryant et al., 2006). The grown particles can also affect the climate of the Earth indirectly by providing seeds for cloud formation.

Particle nucleation has been observed in many different locations including urban, rural, coastal and arctic areas (Kulmala et al., 2004; Colbeck and Lazaridis, 2010; Giamarelou et al., 2016). In all cases the process is heteromolecular, involving two or more mutually interacting vapor species. The most common nucleating species is sulfuric acid, which is produced by the photooxidation of sulfur dioxide in the presence of oxygen and water vapor (Stanier et al., 2004; Zhang et al., 2004). Due to its low vapor pressure at typical atmospheric temperatures, sulfuric acid is believed to induce new particle formation at concentrations higher than  $10^5$  molecules  $\text{cm}^{-3}$  (Curtius, 2006). Recent studies, however, have shown that organic molecules (e.g., amines) play a crucial role in this process by providing the seeds for particle formation and growth (Metzger et al., 2010; Kurten et al., 2014). A number of other nucleating precursors, including atmospheric ions, ammonia, amines, organic acids, and iodine oxides, have been proposed to be involved in the formation of the critical nucleus under different ambient environments.

Unraveling the details of the mechanism leading to new particle formation events is challenging due to limitations of state-of-the-art instrumentation to probe the properties of the initial clusters before they grow to nanometer-sized particles. These limitations also hold for well-controlled laboratory studies aiming to simulate the atmospheric conditions leading to new particle formation events. Due to this difficulty, the majority of the studies try to correlate the concentration of a number of potential precursor gases with information on the meteorological conditions and the growth rates of the nucleation-mode particles. Additional information to these measurements can be provided by comparing simultaneous observations of nucleation events taking place at different locations where the conditions differ slightly (e.g., at an urban and a nearby suburban site). Analysis of these observations can provide good indication about the gaseous species leading to the formation of new particles as well their nucleation and growth mechanisms.

Here we identify and determine the conditions that lead to new particle formation events at an urban and suburban site during the warm period. The measurements were conducted from June to October 2009 in the city of Thessaloniki, Greece. The two monitoring stations of the Municipality of Thessaloniki that exhibit the maximum and minimum levels of  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  in the city (Pettrakakis et al., 2007), namely Venizelou (kerbside site) and Eptapyrgio (urban background site), were selected for the measurements. Gaseous pollutants and meteorological data were also collected and used to examine the conditions leading to the nucleation events.

## 2. Experimental

### 2.1. Sampling sites

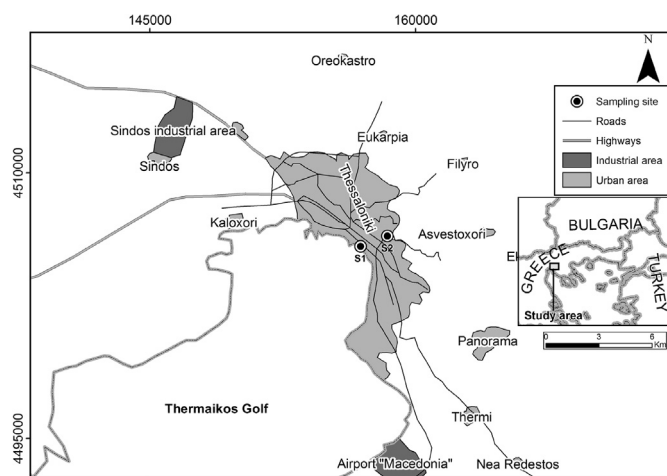
Thessaloniki is a densely populated ( $16,000$  inhabitants  $\text{km}^{-2}$ ) coastal city in Northern Greece. The city is located NE of Thermaikos Gulf, and is surrounded by residential communities and an industrial zone situated on the NW. The mean daily air temperature and relative humidity (RH) vary from  $5.5$  to  $28.1$  °C and from  $47$  to  $80\%$ , respectively. The prevailing winds have SW and NW directions ( $\sim 75\%$  of the cases) and are mainly weak, while the sea breeze (SW direction) has an important effect on the local ambient climate. Wind conditions are calm for the rest of the times ( $\sim 25\%$ ). Synoptic weather circulation, the spatial and temporal variation of mixing height, and the superimposed local land-sea breeze circulation influence the transport and dilution of atmospheric pollutants (Kassomenos et al., 2011).

Two stations of the Municipal Air Quality Network of Thessaloniki have been selected for the measurements (cf. Fig. 1). The first station (urban kerbside site) is located in the centre of the city on the highly busy Venizelou Street ( $40^\circ 38' 15''$  N,  $22^\circ 56' 30''$  E, and  $43.0$  m asl) indicated as S1 in Fig. 1. The second station (urban-background station), indicated as S2 in Fig. 1, is located on Agrafon Street at Eptapyrgio ( $40^\circ 38' 34''$  N,  $22^\circ 57' 38''$  E, and  $174.3$  m asl) next to a small residential area with a park on the West and the city ring road  $1$  km away on the East. Despite that the distance between the two stations is only  $2.5$  km, their characteristics are substantially different. The measurements presented in this paper were conducted for a period of  $130$  days, from  $5$  June to  $20$  October 2009.

### 2.2. Instrumentation

Number size distributions of particles having diameters from ca.  $10$  to  $500$  nm were measured simultaneously at the two stations with two identical Scanning Mobility Particle Sizers (SMPS; TSI, Model 3034). The instruments were housed in the air-pollution monitoring stations within which the temperature was maintained at  $20$  °C. Ambient air was sampled through conductive tubing (inner diameter  $5$  mm; length  $1.5$  m) from an inlet located  $2$  m above ground level. Size distribution measurements were recorded every  $3$  min.

Parallel to the particle size distributions, we collected



**Fig. 1.** Map of Thessaloniki and the surrounding area including the location of the two monitoring stations: S1 at Venizelou (kerbside site,  $43.0$  m asl) and S2 at Eptapyrgio (urban background site,  $174.3$  m asl). The distance between the two stations is  $2.5$  km.

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