Sources of size-resolved Particle Number Concentrations at an urban location in Athens

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Ultrafine particles (UFP; diameter less than 100 nm) have attracted the attention both of the aerosol and health communities as a rising, effective pollutant crucial for both the humankind and the environment. They mainly originate from direct emissions or New Particle Formation (NPF) events. In urban areas, UFP mostly stem from combustion processes. Understanding the complex interaction between air quality and climate needs excessive information on aerosol particles (e.g. number concentration, size distribution, chemical composition). Useful knowledge can be acquired via modal analysis and statistical techniques (e.g. clustering, PMF) on particle number size distribution (PNSD) data. Modal analysis is used to identify the multiple modes (e.g. nucleation, Aitken, accumulation), while cluster analysis is applied to isolate groups with high PNSD similarity (*Beddows et al., 2015*). PNSD measurements can be additionally used in Positive Matrix Factorization (PMF) to quantify contributions of direct sources or atmospheric processes to size-resolved particle number concentrations (PNC) and related metrics (*Vu et al., 2016*).

The Greater Athens Area (GAA) is a region gathering the 50% of the population of Greece, and is appealing as an ideal testbed for such statistical applications, due to strong emissions of fresh particles by a variety of local sources, and also to the prevailing mesoscale meteorology and atmospheric dynamics that enhance secondary UFP formation (*Petäjä et al., 2007*).

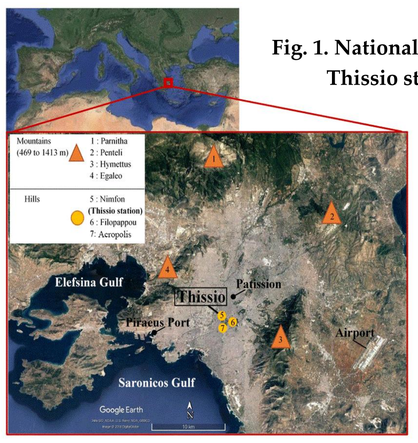
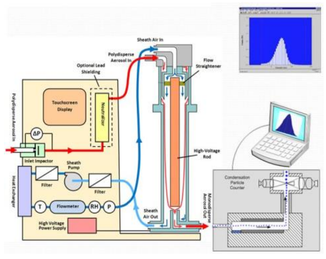
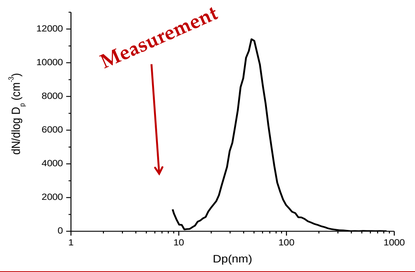


Fig. 1. National Observatory of Athens (NOA), Thissio station (37.97° N., 23.72° E.)

View from the sampling site

To quantitatively assess the impact of aerosol sources and formation processes to PNC, 5 min PNSD measurements between 10 and 487 nm were collected with a Scanning Mobility Particle Sizer (SMPS, TSI Model 3034) during *i*) a warm period (June to August 2017) and *ii*) a cold period (November 2017 to February 2018) at the National Observatory of Athens (NOA) Air Monitoring station, in Thissio, Central Athens (Fig. 1). Ancillary online measurements of regulatory pollutants (NO_x, CO, SO_2 O_3), aerosol composition (BC_{ff}, BC_{bb}, organics, sulfates, nitrates, ammonium) and meteorological parameters are also used for the validation of identified sources.





Modal Analysis

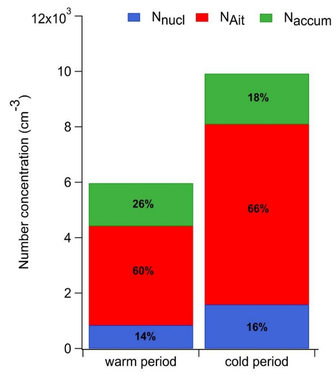


Fig. 2. Average PNC of the nucleation (N_{nucl}; blue bars), Aitken (N_{Ait}; red bars), and accumulation (N_{accum}; green bars) mode at Thissio, during summer 2017 (warm period), and winter 2017-2018 (cold period) at Thissio.

UFP dominated, and the PNC had a mode diameter in the Aitken region, between 58 to 63 nm. Total PNC (N_{total}) and number concentrations in other modes (e.g. nucleation; N_{nucl}, Aitken; N_{Ait}, accumulation; N_{accum}) in the cold period presented higher coefficients of hourly variation (54-86%) compared to the warm period (Fig. 2). This indicates a significant episodic character of PNC during the cold period, especially throughout evening hours, under the presence of strong heating and traffic emissions, in limited atmospheric dispersion conditions. The N_{total} in the warm period was significantly lower than in the cold period (48%). The N_{nucl} was comparable may due to conditions favorable for photochemical processing and NPF. Furthermore, in summer the share of N_{accum} was higher (26% vs. 18% in the winter), suggesting a larger contribution of aged aerosol (photochemical and/or heterogeneous processing) from regional transport, in the setting of declining of local UFP emissions.

The PNSD diurnal variation patterns (Fig. 3) show their origins and key influencing factors at a glance. Regardless the period, an enhancement of PNC in the early morning hours (7:00-10:00) is observed, reflective of go-to-work traffic, with the increment in the warm period being restricted as morning traffic in summer (includes also the vacation period of August) diminishes dramatically. PNC are highly augmented anew in nighttime until the early morning hours, because of the combined effects of evening traffic and especially of residential wood burning (RWB) during the cold period into a lower mixing layer. The fingerprint of evening traffic is evident in summer where RWB is absent. A noteworthy amount of UFP is also observed during midday, and this enhancement indicates atmospheric NPF, which contributes 50% to the total UFP.

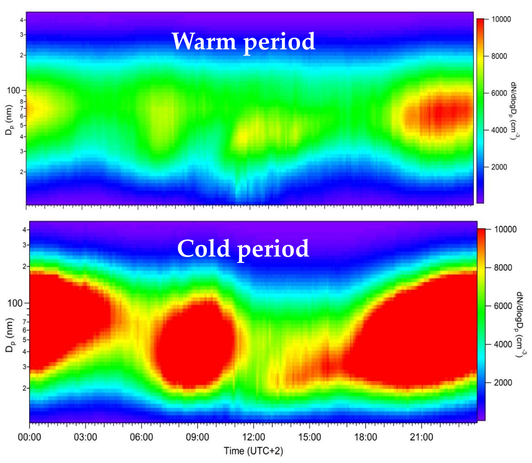
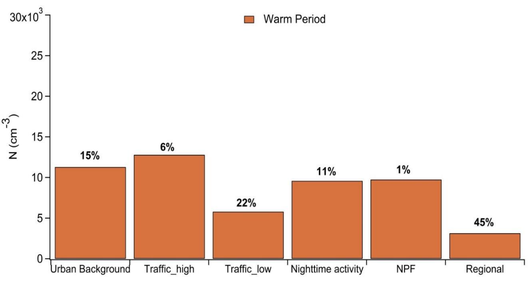


Fig. 3 Average diurnal evolution of the PNSD during summer 2017 (warm period), and winter 2017-2018 (cold period) at Thissio. Time is in (UTC+2).

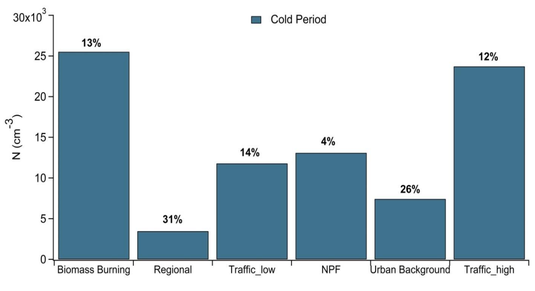
Cluster Analysis

Cluster analysis (*k*-means) was performed on hourly-averaged PNSD spectra and in conjunction to meteorological parameters, atmospheric pollutants, and PNC into the three modes (N_{nucl}, N_{Ait}, and N_{accum}), 5 clusters (Figures below) related to *i*) high- and *ii*) low-traffic, *iii*) nucleation, *iv*) urban background aerosol and *v*) regional aerosol, were identified for both periods, whilst 2 clusters were related to nighttime anthropogenic activity and occurred both in the warm (left Figure) and cold (right Figure) period, the latter linked with biomass burning (BB).



Clusters related to regional aerosol had the highest frequencies in both periods (30-45%) but low average PNC (≈ 3,500 cm^{-3}). NPF clusters accounted for the lowest number of observations for both cases (1-4%), however exhibited significant PNC (10,000 and 13,000 cm^{-3}), advocating the crucial role of NPF on N_{total}. Traffic clusters (high and low) were major contributors to PNC, collectively comprising the 25% of the N_{total} during the study period, with their PNC were significantly higher by 50% in the cold phase compared to warm phase. Urban background aerosol cluster had great percentage (the 2nd highest in cold period), burdening the Thissio's atmosphere with 1.5-fold more PNC during warm period compared to cold period (11,300 vs. 7,5000 cm^{-3}).

Cold-period BB had a considerable frequency (13%) and presented the highest PNC among clusters (≈ 25,500 cm^{-3}). Nighttime summer activity contributed 11% to the total PNSDs, with mean N_{total} 10,000 cm^{-3} being a comparable source on PNC like NPF and traffic.



PMF Analysis

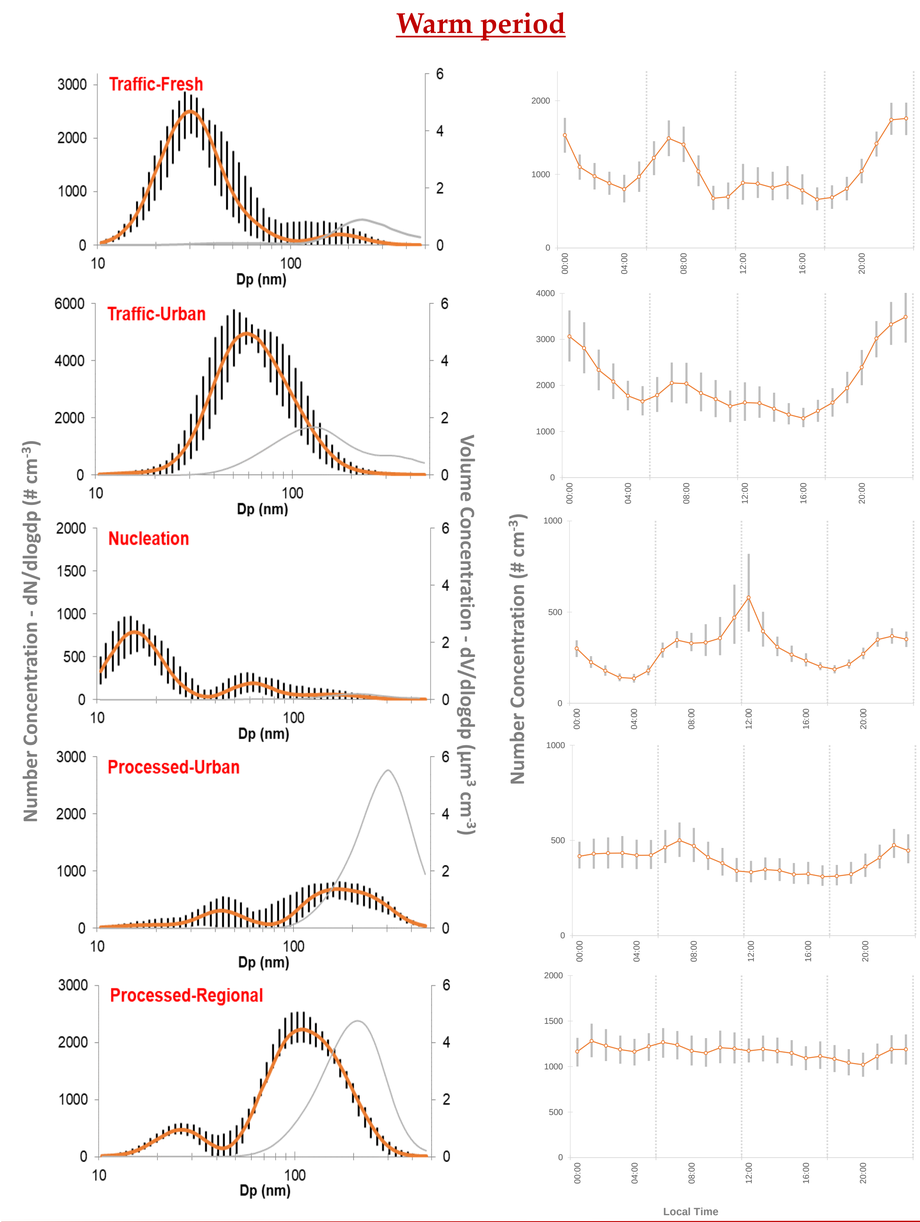
Five factors were identified by applying PMF to PNSDs and consisted of *i*) traffic-fresh, *ii*) traffic-urban, and *iii*) nucleation for both examined periods, while *iv*) BB-fresh and *v*) BB-processed are identified in cold period, and 2 factors (processed-urban and regional) related to secondary processes in summer.

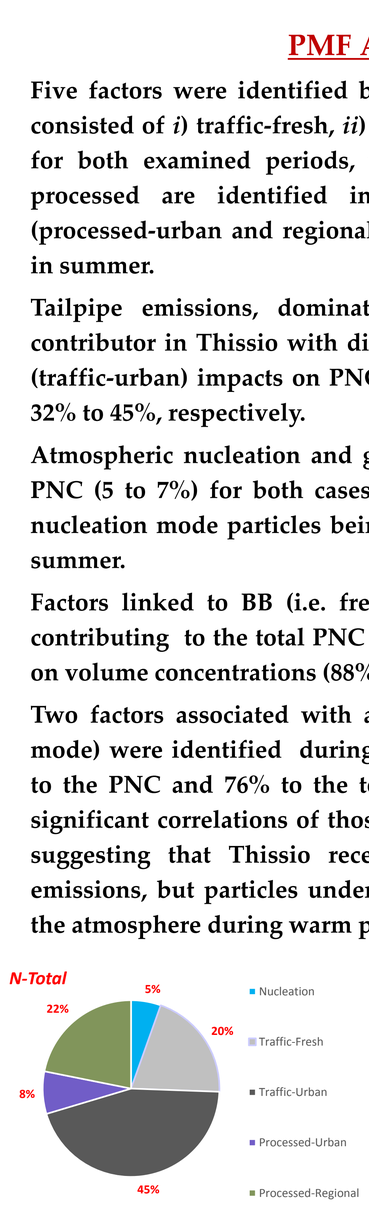
Tailpipe emissions, dominated by UFP, were the main contributor in Thissio with direct (traffic-fresh) and processed (traffic-urban) impacts on PNC ranging from 20% to 24%, and 32% to 45%, respectively.

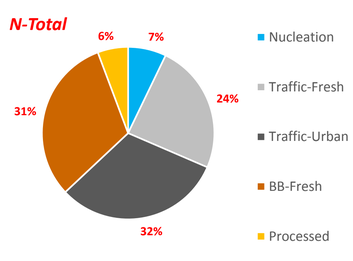
Atmospheric nucleation and growth had similar influence on PNC (5 to 7%) for both cases, however the concentrations of nucleation mode particles being higher in winter compared to summer.

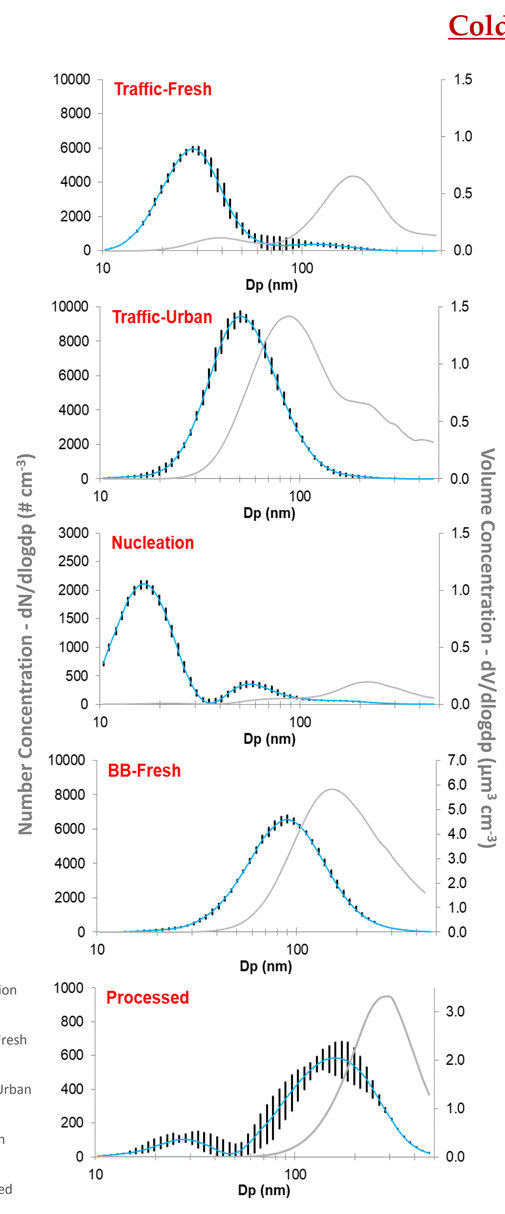
Factors linked to BB (i.e. fresh and processed) considerably contributing to the total PNC (38%), and had the greater effect on volume concentrations (88%) during the cold phase.

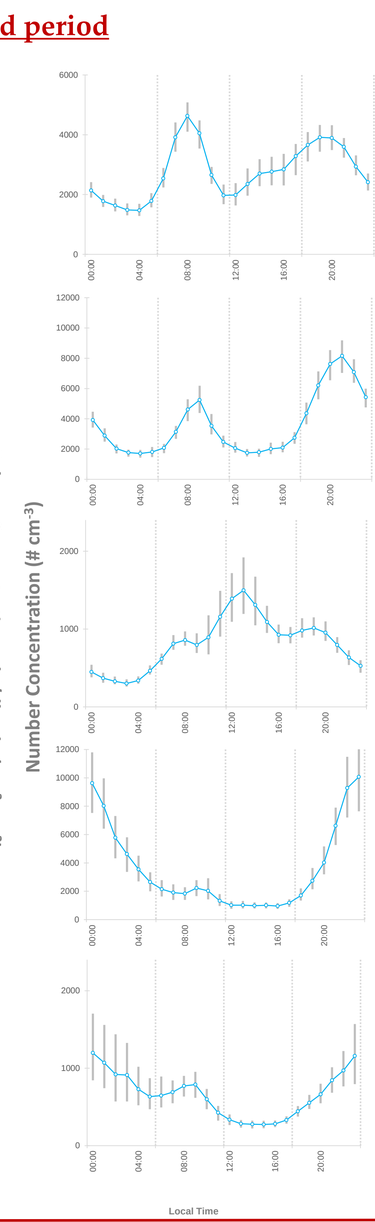
Two factors associated with aged particles (i.e. accumulation mode) were identified during warm period, contributing 30% to the PNC and 76% to the total volume concentrations. The significant correlations of those factors with SVOOA and SO_4, suggesting that Thissio receives particles not from direct emissions, but particles undergone processes and reactions in the atmosphere during warm period.











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