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Case studies of new particle formation and evaporation processes in the western Mediterranean regional background

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HIGHLIGHTS

- Ultrafine aerosol processes in the Mediterranean regional background are presented.
- Specific cases of new particle formation are investigated.
- Nucleation events occur under clean and polluted atmospheric conditions.
- Effect of air mass mixing/transport is discussed.
- Particle shrinkage/evaporation important process for the region.

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ABSTRACT

Case studies of new particle formation (NPF), subsequent growth and possible particle shrinkage occurring in the western Mediterranean regional background are presented in this work. Owing to the mid-altitude height of the station (720 m.a.s.l.), aerosol processes were highly influenced by mixing layer height and development, and mountain breezes. Nucleation processes were observed to occur both under cold and warm conditions, when solar radiation and sulphuric acid concentrations were sufficiently high. Intense bursts of NPF were recorded when the station resided above the polluted mixing layer with little influence of upslope transport of pollution. NPF and growth was also observed to occur within polluted air masses residing over the site, owing to the probable abundance of anthropogenic and natural organic vapours promoting rapid particle growth after nucleation. Measurable growth rates for the NPF episodes ranged from 1.3 to 6.9 nm h^{-1}. Reductions in modal diameters, indicating particle shrinkage, were also observed and were attributed to the evaporation of semi-volatile species from the particulate phase to the gas phase. Particle shrinkage was observed both for pre-existing particles and for freshly formed particles. In the latter case, an "arch" formation was observed in the size distribution contour plot, as the nucleating particles grew and subsequently evaporated until the mode disappeared completely. In agreement with the few articles on particle shrinkage published to date, evaporation appears to be favoured under warm temperatures, high solar radiation, low relative humidity and atmospheric dilution, causing particle-to-gas transformations.

1. Introduction

Atmospheric NPF and growth has been the focus of intensive study for many decades. Understanding the processes behind the formation of nanoparticles in the atmosphere, both by primary and secondary formation processes, is important both for climate and epidemiology studies (Clarke and Kapustin, 2010; Nel, 2006).

Secondary NPF involves gas to particle processes whereby homogenous or ion-induced nucleation of ion or neutral clusters occurs. H_2SO_4, formed from the oxidation of SO_2, is believed to be the most important nucleating agent in the atmosphere (Sipilä et al., 2010). However, it has been shown that sulphuric acid cannot account for the observed growth rates of nucleation clusters and other condensable vapour precursors are believed to play an important role in subsequent growth (Tunved et al., 2006; Jimenez et al., 2009). Thus, when sulphuric acid and other condensable vapours such as low-volatile organics, ammonia and water are in

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sufficiently high concentrations in the atmosphere, gas to particle processes can occur and grow rapidly before being scavenged by pre-existing particles (Kulmala et al., 2013).

Recent publications have suggested that new particle growth can be reversible under certain atmospheric conditions. Yao et al. (2010) observed particle shrinkage following NPF in an urban environment in Hong Kong, and suggested that the observed shrinkage was a result of evaporation of organic compounds and ammonium nitrate. Young et al. (2013) presented several examples of particle shrinkage in Taiwan which occurred following NPF and growth. The authors in this case similarly propose that semi-volatile NH_4^+, NO_3^- and organics in the particle phase are the likely evaporating species. Finally, Backman et al. (2012) observed particle shrinkage in São Paulo and suggested that changes in atmospheric conditions resulting in a decrease in precursor vapour concentrations might cause condensed semi-volatile species to evaporate, resulting in a shrinking of particle sizes.

This current work presents case studies of NPF at a regional background mid-altitude site in the western Mediterranean basin. Each case study presents considerably different scenarios when NPF occurs, and a broad range of variables are presented and discussed in order to determine the main influential factors on NPF, thus helping to identify the favourable conditions leading to nucleation events. The influence of air mass mixing between polluted and non-polluted boundary layer air, and NPF at different stages of development within the same air mass, are presented. Finally, occasions whereby apparent particle shrinkage occurs are also presented and discussed.

2. Methodology

2.1. Observation site

This current article is intended as a companion piece to a previous publication by Cusack et al. (2013), within which full details of the measurement site, the specifications of the instruments used, the methods used and general meteorological conditions can be found. The Montseny (MSY) station is located 40 km to the N–NE of the metropolitan area of Barcelona, and 25 km from the Mediterranean Sea. The area is mountainous (site elevation of 720 m.a.s.l.) and densely forested, located in the Montseny natural park. The MSY station is a member of the ACTRIS network (Aerosols, Clouds, and Trace gases Research InfraStructure Network; formerly EUSAAR), a Europe wide network of aerosol monitoring supersites. The greater region is generally densely populated and industrialised, and regional pollution can affect the site regularly. Pey et al. (2010) and Pérez et al. (2008) have described the effect of meteorology and air mass origins on aerosols at the site. Owing to the sites eastern orientation, mountain breezes are activated early in the day by insolation, which advects anthropogenic and natural emissions from the urbanised valleys below MSY to the site. In winter MSY typically remains above the mixing layer, but injections of polluted mixing layer air can be brought to the site by the mountain breeze development. In contrast, during the warmer months the mountain breeze is still influential, but MSY also resides within the mixing layer for most of the day, regularly exposing the site to a broad range of both anthropogenic and natural emissions within the mixing layer, dilution processes and intense photochemical activity. Thus, the aerosol processes that occur at MSY are often complex, and the effect of air mass mixing between polluted and non-polluted boundary layer air gives rise to unusual particle number size distributions, as will be discussed anon. For in depth analysis on particle number size distributions, modality, seasonality and trends of particle number concentrations and various other parameters at the site, please see Cusack et al. (2013). In brief, it was concluded that during the colder months, NPF was usually observed to occur under clean air conditions, i.e. in the absence of the polluted mountain breeze and a significant CS. On the other hand, it was observed that during the warmer months increased concentrations of nucleation mode particles existed regardless of elevated pre-existing background particle concentrations, suggesting that with increased photochemistry and organic vapour concentrations, NPF can still occur.

2.2. Sampling and instrumentation

Particle number size distributions with mobility diameters between 9 and 825 nm were performed using a Scanning Mobility Particle Sizer (SMPS) operated in the scanning mode. The SMPS consists of a Differential Mobility Analyser (DMA) connected to a Condensation Particle Counter (CPC; TSI Model 3772). The system was designed by the Leibniz Institute for Tropospheric Research (IfT) in Leipzig, Germany in the framework of the ACTRIS project. Wiedensohler et al. (2012) has published the full specifications of the instrument, such as DMA dimensions, bipolar diffusion charger etc. The SMPS was set to provide size distribution data from an up and down scan every 5 min, with a sheath air flow of 5 lpm and an aerosol flow of 1 lpm. The sheath and sampled aerosol were both dried using a nafion dryer to maintain relative humidity below 40% in accordance with ACTRIS requirements. The case studies presented in this work were taken from a dataset from October 2010 to June 2011. Surface plots of the time series of the number size distributions were made and, according to the procedure described by Kulmala et al. (2012), the dataset was visually analysed in order to identify NPF events. These events were then classified according to the criteria outlined by Dal Maso et al. (2005), where a new mode appears in the nucleation mode and these particles grow in size over a number of hours. Furthermore, the growth rate was determined by using the log-normal distribution function method, as outlined by Kulmala et al. (2012). The shrinkage rate is calculated in the same way as the growth rate.

A Multi-Angle Absorption Photometer (MAAP, model 5012, Thermo) provided real time measurements of the cross section absorption coefficient, which was corrected according to Pandolfi et al. (2011) to provide equivalent Black Carbon (BC) concentrations. The sampling line and inlet for the SMPS and MAAP instruments reached 1.5 m above the roof of a climate controlled cabin, with a cut-off diameter of 10 μm. Pollutant gas concentrations (O_3, NO, NO_2, SO_2) were also measured on site and were provided by the Department of the Environment of the Autonomous Government of Catalonia. Meteorological data such as temperature, relative humidity, solar radiation, wind direction, wind speed and precipitation was recorded in real time on site. Absolute humidity (AH) was used as a tool to observe changes in the air mass over MSY.

The dry aerosol condensation sink (CS) was calculated according to Kulmala et al. (2001). A proxy for sulphuric acid, [H_2SO_4], was calculated using the method described by Mikkonen et al. (2011):

$$[H_2SO_4] = 8.21 \times 10^{-3} \cdot k \cdot \text{Radiation} \cdot [SO_2]^{0.62} (CS \cdot RH)^{-0.13} \quad (1)$$

where k is the reaction rate constant, CS is the condensation sink (s^{-1}) calculated from the SMPS measurements, [SO_2] is the measured SO_2 concentrations in molecules cm^{-3}, RH is the relative humidity (%) and Radiation is global radiation (W m^{-2}). The proxy is scaled by multiplying with 10^{12} (Wu et al., 2013). All times reported are in GMT.