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Mass size distributions of soluble sulfate, nitrate and ammonium in the Madrid urban aerosol

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ABSTRACT

This paper analyzes the mass size distribution of some inorganic species present in the atmospheric aerosol from a field campaign carried out in Madrid throughout a complete year (February 2007–February 2008). Samplings were performed by means of a micro-orifice uniform deposit impactor (MOUDI). Ambient air was sampled during consecutive nocturnal and diurnal periods, and diurnal/nocturnal behaviors were compared for the twenty night-day sampling pairs that were gathered. Annual and seasonal averages were obtained, and some case studies under specific atmospheric conditions are discussed in the paper.

Results have shown that the sulfate and ammonium mass was concentrated in the accumulation mode, between 0.18 and 0.56 μm, so that gas-phase and condensation processes for secondary aerosol formation prevailed during the sampling periods in this area. An exception to this behavior was found during a fog event when distributions for these two species were centered in the 0.56–1 and 1–1.8 μm size stages, corresponding to the droplet mode. In most of the samples, the ammonium mass measured in these size ranges was enough or almost enough to neutralize inorganic acidity by formation of ammonium sulfate and nitrate. However, a significant sulfate mass not neutralized by ammonium was found in the impactor backup quartz filter (aerodynamic diameter < 0.056 μm). The concentration of this sulfate and its contribution to the ultrafine fraction mass was higher under good dispersive conditions, prevailing in summer, when particle growth processes are not so favored due to the higher atmospheric dilution factors. The origin of this ultrafine sulfate has been attributed to direct emissions from traffic, associated to the nucleation mode.

Regarding the nitrate concentration, it was found higher in the coarse mode than in the accumulation mode on an annual basis. The highest concentrations were measured in winter episodic situations. The marked seasonal variability shown in the accumulation mode by this species is related to the volatility of ammonium nitrate. Among all the studied ions, nitrate also presented the highest differences between the diurnal and nocturnal concentrations in all size ranges. This is probably related to the short time scale required for its formation from gaseous precursors.

1. Introduction

Knowledge of the mass size distributions of ambient aerosol species can provide valuable information and evidence for the physical and chemical atmospheric processes that are taking place (Meng and Seinfeld, 1994; Kerminen and Wexler, 1995; Yao et al., 2002). Most available information on the mass size distributions of water-soluble inorganic and organic ions (Cabada et al., 2004; Zhao and Gao, 2008) is limited, and it is not still well understood how the mass size distributions of some of these aerosol species, such as nitrate, sulfate, ammonium, calcium, nitrite and others vary under different ambient conditions.

In urban areas, sulfate and nitrate are the dominant components of water-soluble ions, accounting for up to 69% of water-soluble inorganic ions in fine particles and 20–50% of the total mass of fine particles (Zhuang et al., 1999; He et al., 2001; Querol et al., 2008). These major water-soluble ions often exhibit different mass size distributions both spatially and temporally. Whitby (1978) observed that sulfur aerosols exhibited a bi-modal distribution, with both the accumulation and coarse modes in the size range 0.1–10 μm. Other researchers observed that sulfate showed two sub-modes in the accumulation mode, peaking in the

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condensation mode at 0.2 μm, and in the droplet mode at 0.7 μm (John et al., 1990; Zhuang et al., 1999; Cabada et al., 2004). Nitrate can be found in both the coarse and fine modes, and its size distribution depends heavily on location and weather conditions (John et al., 1990; Gao et al., 1996; Zhuang et al., 1999). Ammonium nitrate formed in fine particles has a high volatility, and therefore dissociates into gas-phase nitric acid and ammonia at ambient temperatures higher than 25 °C. Nitric acid can react with sodium chloride in coastal areas to form stable sodium nitrate in the coarse mode (Harrison and Pio, 1983) and also with soil particles to form other coarse mode nitrates (Wolff, 1984; Dasch and Cadle, 1990).

Recent studies of soluble ion mass size-distributions in urban areas have shown a significant fraction of ultrafine sulfate and nitrate (Moya et al., 2004; Lin et al., 2007). The increase of the diesel vehicular fleet in some countries in the last decade and the recent implementation of oxidative particle filters could be some of the reasons for the observed increase in ultrafine concentrations of these species (Maricq, 2007; Morawska et al., 2008) although there is still a lack of results from representative urban areas in Southern Europe. This increase is important from a health perspective, because toxicological studies have shown that ultrafine particles can have a much stronger physiological effect than coarse particles of the same mass (Donaldson et al., 1998; Wichmann et al., 2000). Aerosols also have an important impact on climate. IPCC (2007) estimates that the radiative forcing value for the sulfate aerosol is $-0.4\ \mathrm{W\,m^{-2}}$ and for the particulate nitrate $-0.1\ \mathrm{W\,m^{-2}}$. The uncertainties associated to these values are high, especially for the nitrate aerosol because of the scarce number of studies that have been still performed on these species, and it is accepted that the direct radiative forcing of the individual aerosol species is less certain than the total direct aerosol radiative forcing.

The development of cascade impactors in the last decades has allowed studying the chemical composition of different aerosol size ranges. The micro-orifice uniform deposit impactor (MOUDI) is one of the most complex ones, having 10 stages and classifying particles in the range 0.058 to 18 μm, so that being widely used in recent studies focused on ultrafine particles. However, only a few of these have investigated the seasonal and nocturnal–diurnal differences in the particle mass size-distributions. For instance, in Los Angeles, Sardar et al. (2005) sampled over a period of 2 weeks and in three different seasons using a MOUDI and a nanoMOUDI (stage cut-off diameters: 0.01, 0.018 and 0.032 μm). In Italy, in two short campaigns covering two different seasons, samples were taken during nocturnal and diurnal periods using the Berner impactor and a MOUDI (Carbone et al., 2010). Both works studied the soluble sulfate and nitrate aerosols showing not only the geographical variability in their ambient aerosol mass size distribution, but also their seasonal and night-day variations.

The present study is focused on the mass size distribution of sulfate, nitrate and ammonium obtained in an urban background site of the metropolitan Madrid area using a MOUDI instrument. Unlike other studies, this one, which comprises samplings performed during a year, includes the analysis of the nanoparticles collected in its backup filter stage. The samples gathered consisted of pairs of consecutive night-day periods. The averaged mass size-distributions, the nocturnal-diurnal and seasonal differences, as well as individual cases of interest, have been analyzed to evaluate different origins and processes that could explain the obtained distributions. Neutralization balances have been calculated to evaluate aerosol acidity. In addition, meteorology, gaseous pollutants and particle number distribution have been considered as complementary information in the interpretation of some particular results.

2. Measurement site, instrumentation and methods

The measurement site was located within the CIEMAT facilities in the northwestern area of the city of Madrid. This site can be considered as representative of urban background conditions, being located hundreds of meters away from streets or roads and is close to an urban park. As can be seen in Fig. 1, the site is placed downwind of the city in the clockwise directions from N to SW, while the SW to NW directions correspond to the outskirts of the city, a green area with a big urban park (Casa de Campo) and a Holm oak forest (Monte de El Pardo), although some traffic lines are also present in these direction sectors. The Madrid metropolitan area has a population of around 6 million people, and the major particle emission source is road traffic along with heating combustion devices in the cold months (Artiñano et al., 2004). The vehicular fleet has greatly increased and changed in the last ten years, with more diesel than gasoline-powered vehicles in the current passenger car fleet (a total of 4.5 million vehicles in 2008, 52% of which are diesel-powered). Emissions from light industry, cooking and domestic heating in winter contribute in a lesser proportion. Gas boilers are the predominant domestic heating devices, while fuel-oil and coal boilers are also present but in a much lower percentage. Long–range transport events of Saharan dust and local/regional resuspension are the origin of mineral particles. This last case is an important calcium carbonate source during summer, which will give rise to calcium nitrate in the coarse mode.

A micro-orifice uniform deposit impactor (MOUDI M110R, MSP Corporation, Marple et al., 1991) was placed at the experimental site to perform the aerosol measurements in ambient air. This sampler separates particulate matter in an effective way into 10 ranges, with the following equivalent cut-off diameters (at 50% efficiency): 10, 5.6, 3.2, 1.8, 1.0, 0.56, 0.32, 0.18, 0.1 and 0.056 μm. The substrates used in these ten size stages and the filter backup stage (<0.056 μm) were uncoated aluminum foils and quartz fiber filters respectively. After sampling, impactor substrates were sonicated for 30 min with 15 ml of distilled water prior to analysis using a Dionex 4500i and Dionex 500 ionic chromatographs. The columns used were Dionex IonPac AG12A, AS12A (4 × 250 mm) for ammonium and Dionex IonPac AG9, AS9 (4 × 250 mm) for sulfate and nitrate with flow rates of $1.20\ \mathrm{ml\,min^{-1}}$ (cations) and $1.0\ \mathrm{ml\,min^{-1}}$ (anions). The eluents were $20\ \mathrm{mmol\,l^{-1}}$ methanesulfonic acid for cations and 2 mM Na_2CO_3/0.75 mM $NaHCO_3$ for anions. The injection volume was 100 μl and detectors were CSRS Suppressed conductivity, Recycle Mode for ammonium and AMMS Suppressed conductivity for sulfate and nitrate. For the external calibration standards of 0.1–$1\ \mathrm{mg\,l^{-1}}$ concentration were used. In addition to nitrate, sulfate and ammonium, chloride and nitrite anions and potassium, magnesium and calcium cations were also analyzed, but very low concentrations were measured excepting calcium in the coarse range and in a few cases chloride in the fine range.

Two replicates for each sample and size range were analyzed and their concentration values averaged. Blank values for each ion and substrate material were subtracted. The lower limit detectable in the ionic chromatographic analysis was $0.01\ \mathrm{\mu g\,m^{-3}}$. The overall accuracy of the concentration determination for nitrate, sulfate and ammonium for the sampled period was estimated as $0.03\ \mathrm{\mu g\,m^{-3}}$, as obtained from the standard deviation of blank filter averages.

Potential artifacts in the MOUDI during the sampling have been discussed in previous studies. The discrepancy found between MOUDI and high-volume samplers for gravimetrically determined PM_{10} mass is probably due to losses to the walls of the impactor or bounce-off from the collecting surface. Cabada et al. (2004) observed coarse particle losses affecting the PM_{10} fraction (15–20%) but not the $PM_{2.5}$ one. Comparing MOUDI and TEOM measurements, it was found an underestimation of 5% of the first instrument that can not