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Integration of optical and chemical parameters to improve the particulate matter characterization

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ABSTRACT

Integrating nephelometer measurements have been combined with co-located in space and time PM10 and PM1 mass concentration measurements to highlight the benefits of integrating aerosol optical properties with the chemical speciation of PM1 and PM10 samples. Inorganic ions (SO_4^{2-}, NO_3^-, NH_4^+, Cl^-, Na^+, K^+, Mg^{2+}, and Ca^{2+}), metals (Fe, Al, Zn, Ti, Cu, V, Mn, and Cr), and the elemental and organic carbon (EC and OC, respectively) have been monitored to characterize the chemical composition of PM1 and PM10 samples, respectively. The scattering coefficient (σ_p) at 450 nm, the scattering Ångström coefficient ($\AA$) calculated at the 450–635 nm wavelength pair, and the scattering Ångström coefficient difference ($\Delta\AA$) retrieved from nephelometer measurements have been used to characterize the optical properties of the particles at the surface. The frequency distribution of the $\AA$ daily means during the one-year monitoring campaign, performed at a southeastern Italian site, has allowed identifying three main $\AA$ variability ranges: $\AA \leq 0.8$, $0.8 < \AA \leq 1.2$, and $\AA > 1.2$. We found that σ_p and $\Delta\AA$ mean values and the mean chemical composition of the PM1 and PM10 samples varied with the $\AA$ variability range. σ_p and $\Delta\AA$ reached the highest (149 Mm^{-1}) and the smallest (0.16) mean value, respectively, on the days characterized by $\AA > 1.2$. EC, SO_4^{2-}, and NH_4^+ mean mass percentages also reached the highest mean value on the $\AA > 1.2$ days, representing on average 8.4, 9.8, and 4.2%, respectively, of the sampled PM10 mass and 12.4, 10.6, and 7.7%, respectively, of the PM1 mass. Conversely, σ_p and $\Delta\AA$ mean values were equal to 85 Mm^{-1} and 0.55, respectively, on the days characterized by $\AA \leq 0.8$ and the EC, SO_4^{2-}, and NH_4^+ mean mass percentages reached smaller values on the $\AA \leq 0.8$ days, representing 4.5, 6.0, and 1.9% of the PM10 mass and 9.4, 7.3, and 5.8% of the PM1 mass, respectively. Primary and secondary OC (POC and SOC, respectively) contributions also varied with the $\AA$ variability range. POC and SOC mean mass percentages reached the highest and the smallest value, respectively, on the days characterized by $\AA > 1.2$. Conversely, POC and SOC mean mass percentages reached the smallest and the highest value, respectively, on the days characterized by $\AA \leq 0.8$. It has also been shown that the PM, OC, OC + EC, POC, and SOC mass scattering cross sections varied significantly with the $\AA$ variability range, because of the $\AA$ dependence on aerosol sources and/or emission, transport, and transformation mechanisms. Therefore, it has been shown that $\AA$ daily mean values can represent a good tool to better differentiate the chemical speciation of size-fractioned PM samples.

1. Introduction

The particulate matter (PM) has a large impact on climate, environment, and health, which depends on particle size, chemical composition, and optical properties (e.g. scattering and absorption coefficients). The PM properties are highly variable in time and space (Seinfeld and Pandis, 1998) because of their dependence on the local sources of pollution, the impact of the long-range transboundary air pollution, and the local meteorology (e.g. Perrone et al., 2013). Consequently, long-term measurements are regularly performed worldwide to obtain statistical significant data sets. The European Commission has strengthened the networking of different sites by founding, as an example, the ACTRIS (Aerosol, Cloud and Trace gases Research Infra-Structure networks) Project, to improve data quality and access (Collaud Coen et al., 2013). Size-fractioned PM samplings combined with elemental and chemical analyses are performed to characterize the mass concentration and chemical composition of different PM fractions (e.g. Perrone et al., 2014a). Multi-wavelength integrating nephelometers are instead used to characterize the PM optical properties by the scattering (σ_p) and hemispheric backscattering (β_p) coefficients and

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their respective dependence on wavelength. Pereira et al. (2011) reported the surface aerosol scattering properties measured during a period of seven years (2002–2008) at Évora, Portugal. They showed that both seasonal and daily cycles of the scattering and backscattering coefficients were related to the local production and the transport of particles from elsewhere. Integrating nephelometer measurements performed at different sites of Spain have provided similar results, according to Lyamani et al. (2010), Pandolfi et al. (2011, 2014), and Esteve et al. (2012). One year results of scattering and hemispheric backscattering coefficients, hemispheric backscattering fractions (β_p/σ_p) at three wavelengths (450, 525, and 635 nm), and scattering Ångström coefficients ($Å$) at different wavelength pairs have been reported by Perrone et al. (2014b). They combined multi-wavelength nephelometer measurements with PM10 sampling at a coastal site of southeastern Italy and found that σ_p, β_p, and their respective dependence on wavelength were strongly dependent on airflows. Therefore, β_p/σ_p, $Å$, and σ_p/PM10, which are intensive parameters, dependent on particle size and shape, also were strongly affected by airflows. More specifically, it was found that greater σ_p/PM10 mean values were associated with airflows responsible for the advection of fine mode particles. Perrone et al. (2016) have also shown that the scattering Ångström coefficient could represent an important tool to infer the advection of coarse mode particles at the surface during Sahara dust outbreaks. Moreover, Ealo et al. (2016) have demonstrated the potential of the intensive optical parameters obtained from nephelometer and aethalometer measurements for detecting specific air pollution scenarios in near real time. Wang et al. (2015) have characterized the evolution of the physical, chemical, and optical properties of urban aerosol particles during an extreme haze episode in Beijing, PRC, by in situ measurements. They found that an increasing relative amount of coarse particles could be deduced from the variations of backscattering ratios, asymmetry parameters, and scattering Ångström coefficients retrieved from nephelometer measurements. Moreover, light-scattering apportionment showed that organic, sulphate, ammonium nitrate, and ammonium chloride compounds contributed to light-scattering fractions by 54, 24, 12, and 10%, respectively, indicating that the organic component in the submicron aerosol played an important role in the visibility degradation during the analyzed haze episode in Beijing.

Multiwavelength integrating nephelometer measurements combined with simultaneous PM10 and PM1 mass concentration measurements, and chemical speciation analyses have been used in this study to investigate the relationships between aerosol optical properties and the chemical composition and mass concentration of PM10 and PM1 samples. The highlighting of the benefits of integrating aerosol optical properties with the PM chemical speciation represents the paper's main objective. Measurements have been performed from December 2011 to November 2012 at Lecce, a coastal site of southeastern Italy. Instruments and methods are described in Section 2. Sections 3 and 4 provide main results on the chemical speciation of PM1 and PM10 samples and on the mean optical properties of the ground level particles, respectively. Main results on the relationships between particle optical properties and the PM1 and PM10 chemical speciation are provided in Section 5. The dependence of the mean PM1 and PM10 chemical speciation on the $Å$ variability range is analyzed and discussed in Section 5. The impact of the long-range transported air masses on the $Å$ values is discussed in Section 6. Summary and conclusions are in Section 7.

2. Sampling site, instruments, and chemical analyses

2.1. Site description

Nephelometer measurements and PM samplings, in addition to particle size measurements, were simultaneously performed on the roof of the Mathematics and Physics Department of the University of Salento, at ~10 m above the ground level (agl) from December 2011 to November 2012. The monitoring site is in a flat peninsular area (40.33°N; 18.11°E), 6 km away from the town of Lecce (~95,000 inhabitants), and ~20 km away from both the Ionian and Adriatic Seas (Fig. 1). It can be categorised as rural background according to Larssen et al. (1999) and may be considered as representative of coastal sites of the Central Mediterranean away from large sources of local pollution (Perrone et al., 2013; Basart et al., 2009).

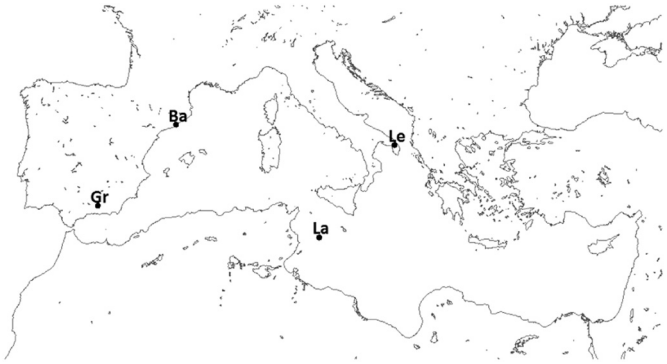

Fig. 1. Geographical location of Lecce (Le), Lampedusa (La), Barcelona (Ba), and Granada (Gr).

2.2. Sampling instruments

A low volume (2.3 $m^3 h^{-1}$) HYDRA-FAI dual sampler was used to simultaneously collect 24-h PM10 and PM1 samples on 47-mm-diameter quartz fibre filters, pre-heated for 1 h at 700 °C, at a mean rate of two daily samples per week. The filters were conditioned before and after sampling (25 °C and 50% humidity during 48 h), and PM mass concentrations were determined by the gravimetric measurements of the filters before and after sampling. Uncertainties on mass concentrations were lower than 5%.

Particle scattering and hemispheric backscattering coefficients at 450, 525, and 635 nm were measured by a LED-based integrating nephelometer (model Aurora 3000, ECOTECH, Knoxfield, Australia) at a temporal resolution of 5 min. A description of the main features of the Aurora 3000 nephelometer is given by Müller et al. (2011). Air sampling was obtained from the top of a stainless steel tube, 15 mm internal diameter and about 1.5 m length. The inlet was fitted with a funnel covered by a screen to prevent rain drops and insect from getting into the sample line. No aerosol size cut-off was applied to the sampled air, and a relative humidity threshold of 60% was set by a processor controlled automatic heater inside the nephelometer to prevent the hygroscopic effects that enhance the particle scattering. The nephelometer calibration procedure and the correction factors (Müller et al., 2011) applied to correct systematic uncertainties due to angular truncation and non-Lambertian illumination are reported in Perrone et al. (2014b).

An Aerodynamic Particle Sizer (APS) spectrometer (model 3321, TSI Inc., St. Paul, Minnesota, USA) was used to determine the number size distribution of ground-level particles in 51 channels of equal logarithmic width within the 0.5–20 μm range. The performance of the APS spectrometer has been documented in several papers (Baron et al., 2001; Pfeifer et al., 2016; and references therein).

2.3. Chemical analyses

Chemical analyses were performed on 86 PM1 and PM10 samples by selecting one or two samples per week during the monitoring campaign. Each analyzed filter was divided in four sections, three of which were used for the analysis of inorganic ions, metals, and organic and elemental carbon. Soluble ionic species (SO_4^{2-}, NO_3^-, NH_4^+, Cl^-, Na^+, K^+, Mg^{2+}, and Ca^{2+}) were analyzed via high-performance ion chromatography (HPIC, Dionex DX-500 System). Perrone et al. (2016)