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$PM_{2.5}$ chemical composition in five European Mediterranean cities: A 1-year study

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ABSTRACT

The seasonal and spatial characteristics of $PM_{2.5}$ and its chemical composition in the Mediterranean Basin have been studied over a 1-year period (2011–2012) in five European Mediterranean cities: Barcelona (BCN), Marseille (MRS), Genoa (GEN), Venice (VEN), and Thessaloniki (THE). During the year under study, PM_{10} annual mean concentration ranged from 23 to 46 μg m^{-3}, while the respective $PM_{2.5}$ ranged from 14 to 37 μg m^{-3}, with the highest concentrations observed in THE and VEN. Both cities presented an elevated number of exceedances of the PM_{10} daily limit value, as 32% and 20% of the days exceeded 50 μg m^{-3}, respectively. Similarly, exceedances of the WHO guidelines for daily $PM_{2.5}$ concentrations (25 μg m^{-3}) were also more frequent in THE with 78% of the days during the period, followed by VEN with 39%. The lowest PM levels were measured in GEN. $PM_{2.5}$ exhibited significant seasonal variability, with much higher winter concentrations for VEN and MRS, in fall for THE and in spring for BCN. $PM_{2.5}$ chemical composition was markedly different even for similar $PM_{2.5}$ levels. On annual average, $PM_{2.5}$ was dominated by OM except in THE. OM contribution was higher in Marseille (42%), while mineral matter was the most abundant constituent in THE (32%). Moreover, $PM_{2.5}$ relative mean composition during pollution episodes ($PM_{2.5}$ > 25 μg m^{-3}) as well as the origins of the exceedances were also investigated. Results outline mainly the effect of NO_3^- being the most important driver and highlight the non-negligible impact of atmospheric mixing and aging processes during pollution episodes.

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1. Introduction

Atmospheric particulate matter (PM) is nowadays one of the most challenging environmental issues, mainly because of its adverse effects on human health and its key role in atmospheric processes and climate change (IPCC, 2007; WHO, 2006a). Numerous studies including the Mediterranean region have found that both short- and long-term exposures to ambient $PM_{2.5}$ are associated with increased risk of mortality as well as respiratory illness, lung cancer, asthma and heart disease (Corbett et al., 2007; Dockery, 2009; Perez et al., 2009; Pope and Dockery, 2006; Samoli et al., 2014) and their effects depend on particle size and composition. In order to limit these adverse impacts and to develop efficient strategies for air quality control, the knowledge of $PM_{2.5}$ chemical composition is necessary.

The Mediterranean Sea is bordered by 21 countries, overall accounting for more than 400 million of inhabitants in 2011, ~6–7% of the total World population. These values rank the Mediterranean basin among the most populous regions in the World, akin to the population density found in the Indian subcontinent or in the South–East of China. Moreover, the population is predicted to reach 529 million by 2025 (UNEP/MAP, 2012). The Mediterranean region's population is also concentrated near the coasts. The population of the coastal regions grew from 95 million in 1979 to 143 million in 2000 and could reach 174 million by 2025 (UNEP/MAP, 2012). Furthermore, the Mediterranean Basin has experienced a rapid growth in urbanization (urban population—towns with more than 10,000 inhabitants—increased 1.9% per year during the period 1970–2010, from 152 million to 315 million). The high atmospheric PM loadings in many Mediterranean cities reflect this important urban expansion (Andreae et al., 2002; Gerasopoulos et al., 2011; Güllü et al., 2005; Kanakidou et al., 2011; Querol et al., 2004a; Rodríguez et al., 2001; Saliba et al., 2007).

Atmospherically, the Mediterranean Basin is a crossroad of air masses coming from Europe, Asia and Africa (Lelieveld et al., 2002). Delimited to the north by the populated and highly industrialized area of southern Europe and to the south by the northern Africa continent, aerosol particle loading is therefore largely affected by a number of natural and anthropogenic sources: Saharan dust (Moulin et al., 1998; Ganor et al., 2010; Israelevich et al., 2012; Querol et al., 2009; Pey et al., 2013b), marine aerosols (Piazzola and Despiau, 1997; Viana et al., 2014b), and anthropogenic emissions from the various urban activities (vehicular traffic, biomass burning, fossil fuel combustion, cooking activities) (El Haddad et al., 2011a,b; Minguillón et al., 2011; Mohr et al., 2012; Pandolfi et al., 2014; Reche et al., 2012), from industries and from the increasing maritime traffic (Eyring et al., 2010; Marmer and Langmann, 2005; Mueller et al., 2011; Pey et al., 2013a; Viana et al., 2014a). Shipping emissions are a significant and growing contributor to air quality degradation in coastal areas. Thereby, emissions of exhaust gases and particles from the oceangoing ships affect the chemical composition of the atmosphere, climate and regional air quality (Eyring et al., 2005). On average, shipping emissions contribute with 1–7% to PM_{10}, 1–20% to $PM_{2.5}$, and with 8–11% to PM_1 in coastal European areas with a maximal contribution in the Mediterranean basin and the North Sea (Viana et al., 2009, 2014a). Furthermore, Pey et al. (2013a) have found that, within shipping emissions, aged products dominated over primary ones even in the vicinity of the source. Forest fires are also a major issue in the Mediterranean area, where an average of 40,000 fires occur per year (period 2000–2009) representing about 300,000 ha of damaged forest each year for, only, France, Spain, Italy and Greece (Schmuck et al., 2013).

The Mediterranean basin is also characterized by a complex meteorology, which favors polluted air masses aging (Artíñano et al., 2001; Millán et al., 1997). During the cold season, atmospheric dynamics in the Mediterranean basin reflect the influence of synoptic conditions characterized by the prevalence of westerly winds. On the contrary, mesoscale processes play a dominant role during the warm season: a) recirculation of air masses in the western side of the basin (Millán et al., 1997; Pey et al., 2009) and b) the prevalence NE winds over the eastern side (Tyrlis et al., 2012). Moreover, as discussed in Querol et al. (2009), Pey et al. (2013b) and Israelevich et al. (2012) Saharan dust outbreaks occur in different seasons in the west (frequently in summer) and in the east (more concentrated in autumn and spring).

With this in mind, the Mediterranean basin is particularly impacted by photo-oxidants. Lelieveld et al. (2002) forecasted summer O_3 concentrations in the Mediterranean planetary boundary layer (PBL) around three times higher than in the northern hemisphere background PBL. In their study, they also pointed out the remarkably high tropospheric concentrations of formaldehyde, methanol and acetone leading to a large in situ production of peroxy radicals. Ozone measurements performed all around the Mediterranean Basin in the last decade have confirmed that the entire Mediterranean region is characterized not only by photochemical episodes in urban pollution plumes, but also by high background ozone concentrations (EEA, 2013). The oxidative capacity of the Mediterranean atmosphere seems also to play an important role in terms of aerosol formation and aging. Hildebrandt et al. (2010, 2011) underlined the high degree of oxidation of the organic aerosol based on Aerosol Mass Spectrometer (AMS) measurements performed in the remote coastal site of Finokalia (island of Crete, Greece) during late summer and winter, respectively. In Mediterranean cities, high contributions of oxygenated organic aerosol (proxy of secondary organic aerosol, SOA) were also observed in Barcelona and Marseille (El Haddad et al., 2013; Minguillón et al., 2011; Mohr et al., 2012). In Marseille, the SOA contribution during summer 2008 was estimated to account for ~80% of the total organic aerosol concentrations (El Haddad et al., 2011b, 2013), with around 80% of such SOA non-fossil in origin despite extensive industrial and urban emissions. The prevalence of non-fossil carbon in the SOA is also observed in Barcelona (February to March 2009), where about 60% of the secondary organic carbon was found to be originated from non-fossil origin (Minguillón et al., 2011). These unexpected results are inextricably linked to the prevalence of regional sources over local anthropogenic emissions.

As part of the APICE project (Common Mediterranean strategy and local practical Actions for the mitigation of Port, Industries, and Cities Emissions; http://www.apice-project.eu/), 1-year monitoring campaigns have been simultaneously organized in five European Mediterranean cities: Barcelona (Spain), Marseille (France), Genoa (Italy), Venice (Italy), and Thessaloniki (Greece). From these long monitoring periods, a detailed characterization of $PM_{2.5}$ in terms of chemical