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Spatial variability of fine and coarse particle composition and sources in Cyprus

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ABSTRACT

Southern and Eastern European countries exceed WHO and EU air quality standards very often, and are influenced by both local and external sources from Europe, Asia and Africa. However, there are limited data on particle composition and source profiles. We collected $PM_{2.5}$ and PM_{10} samples (particulate matter with aerodynamic diameter less than 2.5 and 10 μm, respectively) in four cities in Cyprus using Harvard Impactors. Measurements were conducted between January 2012 and January 2013. We analyzed these samples for mass concentration and chemical composition, and conducted a source apportionment analysis using Positive Matrix Factorization (PMF).

All sites complied with $PM_{2.5}$ and PM_{10} WHO daily standards for most of the days. As in other Eastern European countries, we found higher sulfate contribution and less organic carbon than in the Western and central Europe. For $PM_{2.5}$, seven source types were identified including regional sulfur, traffic emissions, biomass, re-suspended soil, oil combustion, road dust, and sea salt. In all four sites, regional sulfur was the predominant source (>30%). High inter-site correlations were observed for both $PM_{2.5}$ component concentrations and source contributions, may be because a large fraction of $PM_{2.5}$ is transported. Finally, for $PM_{10-2.5}$ (coarse particles with aerodynamic diameter between 2.5 and 10 μm) three sources were identified, which include road dust, soil, and sea salt. Significant inter-site correlations were also observed for coarse particles. All dust storm samples, except one, had PM levels below the daily standard. However, mineral dust, defined as the total mass of crustal metal oxides, increased up to ten times during the dust events.

1. Introduction

Particulate matter (PM) and ground-level ozone (O_3) are the most significant environmental health risk factors in the European Union (EU) region (EEA, 2014). More than 80% of the population in the area live in cities with PM levels exceeding WHO (World Health Organization) Air Quality Guidelines (WHO, 2013). Particle pollution comprises mostly of inhalable particles (PM_{10}; particulate matter with aerodynamic diameter ≤10 μm), and fine particles ($PM_{2.5}$; particulate matter with aerodynamic diameter ≤2.5 μm). Short and long-term exposures to $PM_{2.5}$ and PM_{10} have been associated with respiratory and cardiovascular mortality (Filleul et al., 2005; Brook et al., 2010; Lepeule et al., 2012; Katsouyanni et al., 2009; Dominici et al., 2006). Recent studies are suggesting effects on diabetes, neurological development in children and neurological disorders in adults (Krämer et al., 2010; Rückerl et al., 2011; Andersen et al., 2012; Raaschou-Nielsen et al., 2013).

Particles exhibit considerable variability in their composition, which reflects the diversity of their sources and atmospheric formation processes. For this reason, epidemiological and toxicological studies are now studying the PM health effects using either chemical components as source indicators or source apportionment techniques (Medeiros et al., 2004; Rohr et al., 2014).

WHO-Europe has recently published a report titled "Review of evidence on health aspects of air pollution – REVIHAAP" that summarizes health effects of particle components (WHO, 2013). Black (BC) and organic carbon (OC) have been associated with short-term cardiovascular and respiratory diseases (Delfino et al., 2010; Janssen et al., 2012; Kim et al., 2012). Secondary inorganic aerosols (nitrate, NO_3^- and sulfate, SO_4^{2-}) have been recently associated with short-term effects on cardiovascular (Zanobetti et al., 2009; Ito et al., 2011) and respiratory health (Ostro et al., 2009; Atkinson et al., 2010; Kim et al., 2012; Son et al.,

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2012) hospital admissions. In addition, metals have been associated with different outcomes, for example: nickel with cardiovascular hospital admissions (Bell et al., 2009; Mostofsky et al., 2012) and cardiac function changes (Lippmann et al., 2006); zinc with oxidative stress and inflammation (Gilmour et al., 2006; Hatzis et al., 2006; Charrier and Anastasio, 2011), and; water soluble zinc and copper with cardiac oxidative stress (Gottipolu et al., 2008).

Traffic-related $PM_{2.5}$ that are composed of exhaust (combustion) particles and road dust (wear of road surfaces, brakes, clutches and tire dust) were associated with cardiovascular hospital admissions (Gent et al., 2009; Lall et al., 2011), daily all-cause mortality (Ostro et al., 2011), low birth weight (Bell et al., 2010; Wilhelm et al., 2012; Pereira et al., 2014) and preterm birth (Wilhelm et al., 2012). Similar cardiovascular effects such as cardiovascular and respiratory admissions, and cardiovascular mortality were found for biomass combustion (Mar et al., 2006; Andersen et al., 2007; Sarnat et al., 2008). Some studies have reported respiratory and cardiovascular effects from oil combustion (Andersen et al., 2007; Franklin et al., 2008; Ostro et al., 2011), particularly from vanadium and nickel (de Hartog et al., 2009; Zanobetti et al., 2009; Bell et al, 2010). Industrial emissions from nickel and/or copper smelters were reported to be associated with cardiovascular mortality (Pasanen et al., 2012), and emissions from point sources were associated with small children asthma (Clark et al., 2010). Desert dust, one of the main PM natural sources, was found to be associated with respiratory and cardiovascular mortality and hospitalizations (Middleton et al., 2008; Perez et al., 2009; Chan and Ng, 2011; Tam et al., 2012; Neophytou et al., 2013) and it is believed to be partly mixed with anthropogenic PM enhanced during outbreaks.

Although PM_{10} and $PM_{2.5}$ health effects have been well studied, recent epidemiological studies have focused on coarse particles ($PM_{10-2.5}$; particulate matter with aerodynamic diameter between 2.5 and 10 μm). Short-term exposure to coarse particles has been associated with cardiovascular (Atkinson et al., 2010; Mallone et al., 2011) and respiratory (Chen et al., 2011) effects, as well as total mortality (Tobías et al., 2011; Meister et al., 2012). Endotoxin, found in Gram-negative bacteria cell walls, has been associated with the inflammatory role of both fine and coarse particles (Behbod et al., 2013). Although the composition of coarse particles varies across cities, very little is known about the effects of their chemical particle components.

Many air pollution studies across Western and central Europe have focused on physical and chemical characteristics of $PM_{2.5}$ and/or PM_{10} (Putaud et al., 2010). The Eastern EU member countries are having difficulties in meeting EU air quality standards, partly due to contributions from external sources. More specifically, the Eastern Mediterranean (EM) countries experience high particulate matter because of mass advection from Europe, Asia and frequent desert dust storms (Querol et al., 2009a, 2009b; Achilleos et al., 2014). Hence, the aerosol chemistry of the EM is very important for both epidemiological and regulatory purposes. However, there are limited data on PM chemical composition and sources in urban areas in East Europe and Mediterranean. We therefore, aim to study the composition and sources of fine and coarse particles in the EM region. Toward this end, we set up four urban monitoring sites across the island of Cyprus, a European Union member country located in the Eastern Mediterranean sea, to sample PM mass, to analyze it to determine elemental and organic carbon, nitrate, sulfate and elemental concentrations and conduct a source apportionment analysis.

2. Materials and methods

2.1. Study design

2.1.1. Sampling sites

We collected $PM_{2.5}$ and PM_{10} samples in the four main cities of Cyprus. Specifically, the urban sites were located in Limassol (LIM: 34°40′ N, 33°2′ E; 10 m above sea level (asl)), Nicosia (NIC: 35°10′ N, 33°22′ E; 136 m asl), Larnaca (LCA: 34°55′ N, 33°37′ E; 10 m asl), and Paphos (PAF: 34°46′ N, 32°25′ E; 47 m asl) (Fig. 1). The samplers were located on the rooftops of institutional buildings with an approximate height of 10 m and collected particles during the period between January 2012 and January 2013. The selected sites were located away from point sources such as factories, power plants, or traffic.

In Nicosia, Cyprus' capital and largest city, the sampling site was located in a residential area, approximately 3 km northeast of downtown Nicosia and 140 m from a main road. In Limassol, the biggest industrial center in Cyprus, the site was located in downtown, 170 m from a busy street, ~600 m from the small port, and a few kilometers from the main port of high commercial and passenger traffic flow. Larnaca is the city on the southeastern coast of the island. The site was located in a residential area, 700 m from the marina and ~5 km from Larnaca International airport and a sea salt lake. Finally, Paphos is the smallest coastal city and the site is located ~1.5 km from the sea and ~9 km from Paphos International Airport.

The climate in Cyprus is characterized by long, hot, and dry summers and mild winters. The winds over the island are quite variable in strength and direction and are influenced by: a) the depression over southwest Asia in the summer; b) the eastward moving anticyclones from Eurasia and low pressure over North Africa in the winter; c) topography that is dominated by two mountainous areas and the central Mesaoria plain, and; d) sea and land breezes. For each city, the Cyprus Meteorological Service provided daily meteorological data for the year 2012. Weather parameters including mean temperature, precipitation, dew point, wind speed and direction, are summarized in Table 1. The coastal cities experienced a warmer winter than inland Nicosia. Winter was the rainy season with the lowest precipitation in Nicosia. Summer was cooler on the coastline and more humid than the inland. Larnaca and Paphos were windier than Limassol and Nicosia. The prevailing wind directions were West, and Southwest (Limassol, Nicosia, Larnaca) or Northwest (Paphos). South or Southwest winds are more common during the day and Northwest or Northeast winds during the night (Paschardes and Christofides, 1995).

2.1.2. Sample collection

Integrated 24 h PM samples were collected every 6 days except in Limassol, where sampling was conducted every 3 days. All samples were collected on a 37-mm filter using Harvard Impactors (Marple et al, 1987). At each site, four impactors were simultaneously running every sampling day. The parameters measured include: $PM_{2.5}$ mass, black carbon, trace elements, nitrate, sulfate, and EC-OC; and PM_{10} mass, black carbon and trace elements. One $PM_{2.5}$ Teflon membrane filter was used for mass, black carbon, and trace elements. PM_{10} was also collected on Teflon filters. Fine particle EC-OC samples were collected on pre-fired quartz fiber filters. Fine particle nitrate and sulfate were collected on sodium carbonate-coated glass fiber filters. Since nitrate is present in the air in gaseous form (as nitric acid, HNO_3) and particulate form (as ammonium nitrate, NH_4NO_3), nitric acid was removed from the air sample prior to particle collection. A sodium carbonate-coated aluminum honeycomb denuder was placed upstream of the impactor inlet and the particle nitrate was collected on the sodium carbonate-coated glass fiber filters (Appel et al., 1981; Ferm, 1986; Koutrakis et al., 1988). All $PM_{2.5}$ samples except that for particle nitrate were collected at a flow rate of 16.7 liters per minute (LPM). $PM_{2.5}$ samplers were operated with a size-selective inlet composed of two impactor stages in series with polyurethane foam (PUF) impaction substrates (Lee et al., 2005). Particle nitrate samples were collected at a flow rate of 4 LPM, using a size-selective inlet composed of two impactors in series with oiled porous stainless steel impaction substrates (Marple et al., 1987). PM_{10} particles were collected at a flow rate of 10 LPM, using a size-selective inlet with a single impactor stage with PUF substrate. Both types of impaction substrates were used to prevent particles larger than the cut-off diameter to bounce and re-entrain in the flowstream, and therefore positive bias of the measured mass (Lee et al., 2005). Co-located (duplicate) samples and field blanks were collected for