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Estimation of the contributions of the sources driving $PM_{2.5}$ levels in a Central Mediterranean coastal town

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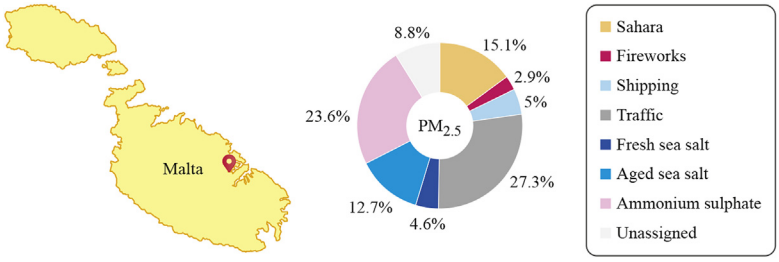
HIGHLIGHTS

- Seven sources were isolated for a traffic site in a coastal town in Malta.
- Traffic was the most significant contributor to ambient PM2,5 levels.
- A component due to letting of fireworks was also identified.
- Traffic should be targeted in order to reduce PM2,5 levels and achieve the WHO guidelines by 2020.
- In the long run the countries in the region should also curb emissions from shipping.

GRAPHICAL ABSTRACT



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ABSTRACT

Receptor modelling techniques are widely used in order to identify the main natural and anthropogenic processes driving aerosol levels at a receptor. In this work, Positive Matrix Factorization (PMF) was used to apportion $PM_{2.5}$ levels at a traffic site (Msida) located in a coastal town. 180 filters collected throughout a yearly sampling campaign conducted in 2016, were chemically characterized by light absorbance analysis, x-ray fluorescence and ion chromatography in order to determine the concentrations of black carbon, 17 elements and 5 ions, respectively. The resulting chemical data base was used in conjunction with PMF in order to identify the 7 components affecting the $PM_{2.5}$ levels at the receptor site. Six of these sources are considered to be typical of the atmospheric composition of coastal traffic sites: traffic (27.3%), ammonium sulfate (23.6%), Saharan dust (15%), aged sea salt (12.7%), shipping (5%) and fresh sea salt (4.6%). This is the first time that such a study was carried out in Malta and helps in understanding the aerosol pollution climate of the Central Mediterranean, which is still relatively understudied when compared to the Eastern and Western Mediterranean. Furthermore, we have isolated a factor exclusive to Malta: the fireworks component, which is responsible for 2.9% of the $PM_{2.5}$ and which has health implications due to its chemical composition. The results of this work should also serve to guide the policy

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makers in achieving the necessary emission reductions in order to achieve the WHO guideline for $PM_{2.5}$ by 2020.

1. Introduction

The fine fraction of airborne Particulate Matter (APM) or $PM_{2.5}$ is defined by ISO 7708 (1995) as particles which pass through a size-selective inlet with a 50% efficiency at the 2.5 μm aerodynamic diameter cut-off and is the metric that is considered to be the high-risk respirable convention. Current epidemiological evidence suggests that $PM_{2.5}$ plays a prominent role in the adverse health effects resulting from exposure to polluting levels of atmospheric PM (Pope and Dockery, 2006). These effects depend on the magnitude of the exposure concentration as well as on the duration of the exposure. Robust associations have been established between $PM_{2.5}$ and both daily mortality (e.g. Schwartz et al., 1996; Burnett et al., 2000; Simpson et al., 2005; Ostro et al., 2006; Perez et al., 2009) as well as long term mortality (e.g. Dockery et al., 1993; Pope et al., 1995; Pope et al., 2002; Pope et al., 2004; Laden et al., 2006). Cardiovascular, cerebrovascular and respiratory illnesses are the main causes of mortality due to acute and chronic exposures to $PM_{2.5}$. Correlations have also been established between long-term exposures to fine particulate matter and lung cancer e.g. (Dockery et al., 1993; McDonnell et al., 2000). The association between lung cancer and fine particulate matter is particularly significant for diesel exhaust due to the presence of elemental carbon-EC, (Attfield et al., 2012; Silverman et al., 2012), to the extent that IARC (2012) has classified diesel exhaust as a Group 1 carcinogen. Links have also been established between acute exposure to fine particulate matter and cardiovascular (Franchini and Mannucci, 2007; Miller et al., 2007) and respiratory morbidity (Atkinson et al., 2001; Ko et al., 2007). In southern Europe, increases in admissions due to cardiovascular and respiratory causes, with $PM_{2.5}$ levels, have been reported by e.g. Stafoggia et al. (2013). Furthermore, Lanki et al. (2006) and Penttinen et al. (2006) found that $PM_{2.5}$ exacerbated both peak respiratory flow and ischemic heart disease in adults with stable coronary heart disease.

In the European Union (EU-28) ambient levels of $PM_{2.5}$ are regulated by Directive 2008/50/EC, which sets an annual limit value of 25μg/m^3. This limit value is not considered to be sufficiently protective of human health, and in fact the World Health Organization (WHO) recommends an annual air quality guideline (AQG) of 10μg/m^3 and a daily guideline of 25μg/m^3, which can be exceeded 0.5% of the time, WHO (2006). According to the European Environment Agency (EEA, 2016), in the period running from 2012 to 2014, 85–91% of the urban populations in Europe were exposed to $PM_{2.5}$ levels higher than the WHO AQGs. Additionally, according to WHO (2013), the latest available research has highlighted associations between ambient levels of $PM_{2.5}$ and mortality levels at concentrations well below 10μg/m^3 (the current AQG).

$PM_{2.5}$ background levels in the Mediterranean countries tend to be rather high, due to both geographic (closeness to the African continent) as well as meteorological factors such as semi-aridity, modest precipitation rates, weak advection of air masses and the frequency of occurrence of local re-circulation patterns, Rodríguez et al. (2007). The meteorological factors favor higher residence times of particulate matter in the atmosphere, and in fact, the highest concentrations of $PM_{2.5}$ in Europe are measured in near-city, urban background and traffic sites in Southern countries, (Putaud et al., 2010). Closeness to the Saharan region results in a significant influence of Saharan episodes on the PM immissions in these countries, including on the $PM_{2.5}$ levels (Molinaroli et al., 1993; Kubilay et al., 2000; Viana et al., 2002; Almeida et al., 2005; Nicolás et al., 2011). In addition, a variety of regional and local sources contribute to the atmospheric levels of $PM_{2.5}$ in the region.

Secondary particulate formation through atmospheric chemical reactions is an important contributor to APM in the region. NO_2 and SO_2 emitted by anthropogenic processes such as fossil fuel combustion (by both land based and maritime sources) are converted by photo-oxidative processes into the respective acids. Particulate matter forms from the reaction of these acids with ammonia, sea salt or mineral dust, Galindo et al. (2013). The prevailing meteorological conditions in the Mediterranean, in particular the insolation rates and higher temperatures, favor the formation of the sulfate (which occurs mostly in the $PM_{2.5}$ fraction) rather than the thermally unstable nitrate.

Sea breezes enhance the troposphere in coastal areas with Na^+ and Mg^{2+}, giving rise to sea salt aerosol which can contribute from 1 to 6% of the $PM_{2.5}$ levels in Southern Europe (Amato et al., 2016a). The metal ions take part in neutralization reactions with nitric and sulfuric acids (particularly during spring and summer) to form nitrate (Nicolás et al., 2009) and sulfate salts of these ions.

Air quality in coastal areas is also adversely affected by maritime transport (Viana et al., 2014), especially due to the fact that 70% of the emissions occur close to the coast (Endresen et al., 2003). Emissions from shipping are still relatively under-regulated when compared to land-based sources (Viana et al., 2009). Particulates emitted by shipping occur mostly in the finer fraction and can be emitted as either primary emissions such as EC, Ni, V, etc. (Viana et al., 2014) or result from gas to particle reactions, (Reche et al., 2011). According to Viana et al. (2014), only 30–40% of the particulates from shipping are emitted as primary particles, while the remaining 60–70% are secondary particles.

Road traffic is widely recognized as one of the major (local) contributors to $PM_{2.5}$ levels in urban areas, (e.g. Viana et al., 2008; Belis et al., 2013), contributing up to a maximum of 49% (Amato et al., 2013) of the fine fraction of APM. Furthermore, in Southern Europe, $PM_{2.5}$ levels increase along the rural background-urban background-kerbside gradient, (Putaud et al. (2010)). Traffic derived atmospheric particulate matter may be divided into exhaust and non-exhaust fractions. Exhaust emissions include both primary and secondary particles. Primary particles are mainly composed of carbonaceous aerosol together with minor amounts of inorganic ions and of metals. Combustion of fuel and lubricant are responsible for the carbonaceous particles (El Haddad et al., 2009), while metal emissions result from engine corrosion (Lough et al., 2005; Sysalová et al., 2012; Varrica et al., 2013) and from the after-treatment systems (Pulles et al., 2012). Secondary particulates, are formed from gas to particle reactions involving the NO_x and VOCs (Amato et al., 2016a) but also SO_2, (Weinbruch et al., 2014). Re-suspended road dust and emissions from abrasion make up the non-exhaust component. The abrasion component results from friction at the brake lining – wheel interface, and at the tyre – road interface. It has been shown that a significant portion of these emissions occurs in the $PM_{2.5}$ fraction both for brake wear (Wåhlin et al., 2006; Iijima et al., 2007) and tyre wear