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Geochemistry and carbon isotopic ratio for assessment of PM_{10} composition, source and seasonal trends in urban environment☆

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ABSTRACT

Investigating the nature of PM_{10} is crucial to differentiate sources and their relative contributions. In this study we compared the levels, and the chemical and mineralogical properties of PM_{10} particles sampled in different seasons at monitoring stations representative of urban background, urban traffic and sub-urban traffic areas of Naples city. The aims were to relate the PM_{10} load and characteristics to the location of the monitoring stations, to investigate the different sources contributing to PM_{10} and to highlight PM_{10} seasonal variability. Bulk analyses of chemical species in the PM_{10} fraction included total carbon and nitrogen, $\delta^{13}C$ and other 20 elements. Both natural and anthropogenic sources were found to contribute to the exceedances of the EU PM_{10} limit values. The natural contribution was mainly related to marine aerosols and soil dust, as highlighted by X-ray diffractometry and SEM-EDS microscopy. The percentage of total carbon suggested a higher contribution of biogenic components to PM_{10} in spring. However, this result was not supported by the $\delta^{13}C$ values which were seasonally homogeneous and not sufficient to extract single emission sources. No significant differences, in terms of PM_{10} load and chemistry, were observed between monitoring stations with different locations, suggesting a homogeneous distribution of PM_{10} on the studied area in all seasons. The anthropogenic contribution to PM_{10} seemed to dominate in all sites and seasons with vehicular traffic acting as a main source mostly by generation of non-exhaust emissions Our findings reinforce the need to focus more on the analysis of PM_{10} in terms of quality than of load, to reconsider the criteria for the classification and the spatial distribution of the monitoring stations within urban and suburban areas, with a special attention to the background location, and to emphasize all the policies promoting sustainable mobility and reduction of both exhaust and not-exhaust traffic-related emissions.

1. Introduction

The improvement of air quality through adoption of effective strategies for mitigation of air pollutant emissions still represents one of the most pressing environmental issues. For decades, several efforts from national and international legislations and policies (e.g. the UNECE Long-range Transboundary Air Pollution Convention) were directed toward monitoring the atmospheric composition, at local and global scale, to safeguard the whole environment and human health.

According to the World Health Organization (WHO, 2013), airborne particulate matter (PM), along with nitrogen dioxide and ground-level ozone, is among the chemicals of major public health concern, classified as carcinogenic by the International Agency for Research on Cancer (IARC, 2013). Emissions from road traffic, stationary sources (i.e. power plants, metal industries, mines and quarries), sea salts, wind-blown dust and chemical reactions in the atmosphere (oxidation of SO_2, NO_x and volatile organic compounds – VOCs -) are the main anthropic and natural source contributors of primary and secondary PM (EEA, 2012a).

Current ambient air quality standards are prevalently mass-based and restricted to PM_{10} and $PM_{2.5}$ fractions, namely inhalable particles, mostly of the coarse mode, with aerodynamic

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diameters equal or smaller than 10 and 2.5 μm (EEA, 2016; EPA, 2016; Morawska et al., 2008). Atmospheric pollution by PM has become particularly problematic in urban environments, in parallel with rapid and progressive population growth and urbanization phenomena over the past 300 years (USEPA, 2001). Between 2000 and 2014, from 16 to 42% of the European urban population was estimated to be exposed to PM_{10} with concentration levels above the limits set by the EU 2008 Air Quality Directive (50 μg m^{-3} for more than 35 days a year) (EEA, 2016). In urban environments, the measurement of PM concentrations in relation to the legal limits and target values (EU, 2008) are provided throughout Europe by monitoring/sampling stations placed at traffic-oriented and background (i.e. non-traffic) sites.

In the last decade, despite improvements of Earth observational strategies, there is a consensus in the atmospheric science community that well documented observations of the atmospheric chemical composition are needed i) to implement current legislation; ii) to improve our understanding of atmospheric processes; iii) to provide inputs to forecasting models, thus predicting accurately future atmospheric states. Despite the development of cost-effective abatement policies, recent evidence shows that PM_{10} concentrations, as well as major primary and secondary components, are relatively constant (Harrison et al., 2008). Improvements are required to address the issue of PM control in the air to allow the population to live in a cleaner environment and to ensure projected health benefits. A contribution to this issue might come from a better knowledge of the nature and properties of PM. Atmospheric particles have a complex and variable chemical composition, depending on their sources and the transformation processes of gaseous pollutants (SO_2, NO_x, NH_3 and VOCs) contributing to particle formation. Minerals of different origin (e.g. quartz, muscovite, kaolinite, iron oxides, carbonates), road dust (e.g. non-exhaust traffic-related particles), sea-salt aerosols (e.g. gypsum and halite), biogenic organic particles (e.g. pollen, spores and plant fragments) and carbonaceous particles originating mostly during incomplete combustion of fossil fuels and biomass are important constituent of PM (Sýkorová et al., 2016; Viana et al., 2008). The relative contribution of different particles affects PM geochemical characteristics, which may provide good indication of geogenic and anthropogenic sources.

Carbonaceous materials, consisting of both elemental carbon (EC) and organic carbon (OC), constitute a large but highly variable fraction of atmospheric aerosols. The ratio of elemental to total carbon (TC = EC + OC) strongly depends on the sources (mainly biomass and fossil fuel burning). However, it is still challenging to estimate the relative contribution of different emission sources of carbonaceous aerosols and their transformation and transport mechanisms in the atmosphere. Moreover, the monitoring of PM organic components is generally addressed only for harmful compounds or for those considered tracers of specific PM emission sources (Kosztowniak et al., 2016). In this context, the analysis of the stable carbon isotopic composition ($^{13}C/^{12}C$) of the carbon fraction in PM could be applied as source-identification method since the $^{13}C/^{12}C$ ratio is highly dependent on the origin of carbonaceous aerosol (Bird et al., 2015; Cachier, 1989; Ceburnis et al., 2011; Kosztowniak et al., 2016; Menon, 2004; Widory et al., 2004). The application of carbon isotopic ratio is used in various fields and can potentially provide information on both EC and OC carbon fractions in PM (e.g. Guillon et al., 2013; O'Brien, 2015; Schmidt and Jochmann, 2015).

This study focuses on the levels and geochemistry of atmospheric particulate matter PM_{10} collected at four monitoring stations in the city of Naples (south Italy). The monitoring stations were classified according to their location and EUROAIRNET Criteria (EEA, 1999), as urban traffic (i.e., near busy roads in the city center), suburban traffic (i.e., near busy roads in the suburban areas) and urban background (i.e., in urban area but away from emissions sources). PM_{10} filters were sampled for 1 year and analyzed for PM_{10} concentration, elemental composition, including carbon, nitrogen and sulphur content, mineralogy and morphological traits. Our main aims were to relate the PM_{10} load and characteristics to the location/classification of the monitoring stations, to investigate the various sources contributing to PM_{10} and to highlight PM_{10} seasonal variability. The different source types (not strength) of carbonaceous particles contributing to PM were investigated analyzing the filters for the isotopic ratio of C.

2. Materials and methods

2.1. Study area

The investigated area is part of the city limits of Naples (Campania Region, southern Italy). The city rises at an elevation of 17 m a.s.l. and lies in a coastal plain between two major volcanic systems, the Phlegrean Fields and Mount Vesuvius, such that the yellow tuff is the most widespread pyroclastic product characterizing the morphology of the Naples urban area. Naples is one of the most urbanized and densely populated of Italy's major cities, with approximately 8.151 people km^{-2} on a surface of 119.02 km^2. In 2015, the Metropolitan City of Naples with a population of 3.115.320 was the 9th-most populous urban area in the European Union, with around 975.260 people living within the city administrative limits (ISTAT, 2017). Naples is served by several major motorways (e.g. the A1 - known as "Autostrada del Sole", and the A3 Napoli – Salerno) and has an extensive public transport network, including a large harbor (i.e. Naples Harbor) and the largest airport in southern Italy (i.e. Naples Capodichino International Airport, about 4 km distant from Naples city center). The urban area of Naples is also affected by the presence of a big port, which runs several public services available both to the Campania coast and to destinations further afield. Heavy and slow-moving vehicular traffic characterize the city and its province, crossed every day, on average, by 529.000 automobiles (data from Naples City Council, 2015). Above ground fuel storage tanks and, in the past, also oil refineries and an iron-steel industry located at the eastern and western periphery of the city, contributed to air pollutant emissions as well.

During the study period (April 2008–May 2009), the main meteorological parameters (i.e. wind speed and direction, air temperature, precipitations and relative humidity) from the Naples Capodichino Weather Station (40°53′03.72″ N - 14°17′00.99″ E) were recorded (Fig. S1). According to the climatic diagram in Fig. S1, the climate of Naples city is Mediterranean, with a summer drought thatlasts from June to August. Temperature ranged between 12.7 and 21.6 °C (mean minimum and maximum), with an average value of 17.0 °C. The total rainfall was of 1109 mm (mostly concentrated in autumn and winter). Prevailing winds had a mean hourly speed of 6.2 km h^{-1} and an absolute maximum of 9.3 km h^{-1} in December 2008 with a prevailing direction from S (during spring and summer) and N-NE (in autumn and winter).

2.2. PM_{10} sampling and measurement

The PM_{10} was measured and sampled for one year (April 2008–May 2009) at four air pollution monitoring automated stations (namely, NA01, NA05, NA07, NA09) located in the urban and suburban territory of Naples city and managed by the Regional Environmental Protection Agency (ARPA-Campania). According to European legislation (EEA, 1999), the monitoring stations are representative of urban background (NA01, located in the Naples