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Characterisation of the local topsoil contribution to airborne particulate matter in the area of Rome (Italy). Source profiles

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HIGHLIGHTS

▶ We report source profile of the PM₁₀ fraction of local natural topsoil in Rome area.

► Chamber resuspension and EDXRF technique were used for PM₁₀ collection and analysis.

▶ PM₁₀ differentiates from raw topsoil for its higher trace metals content.

► Our profiles were compared with literature signatures of African dust and road dust.

▶ Mg/Ca and Ti/Ca ratios separate Rome natural crustal PM₁₀, African dust and road dust.

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ABSTRACT

Elemental profiles of the local resuspended natural topsoil of Rome area have been studied. Relevant compositional differences were observed either among main geological domains and rock types of this area (volcanics, flysch, marlstone, travertine) or between the two considered dimensional fractions (50 μ m and PM₁₀ resuspended from the former). A significant enrichment in trace metals (especially Pb, Ni and Cr) has been observed in the PM₁₀ resuspended fraction of either volcanics or sedimentary outcropping rocks; volcanics show larger trace metals enrichment than sedimentary. Profiles of this study have been compared with signatures of natural crustal dust of African origin (collected either *in situ* or at European receptor sites, including Rome and other sites in the Latium region) and with signatures of road dust, properly selected from literature. This comparison was performed for source apportionment goals, with the aim of improving discrimination among signatures of local and non-local natural crustal materials.

Elemental ratios of major and trace elements of geochemical relevance were used for the comparative study. Mg/Ca and Ti/Ca ratios appear successful in separating, by dispersion diagram, the resuspended fraction of local Rome geological topsoil from road dust and from long-range transported dust from Africa.

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1. Introduction

The chemical composition of airborne particulate matter (PM) plays a key role in the potential noxious and polluting actions of PM at receptors in the lower boundary layer. The atmospheric fate of airborne particles is commonly investigated by dispersion-based or receptor-based modelling techniques of source apportionment (SA). Information provided by dispersion models (aerosols loads, formation, transport and deposition patterns) improve knowledge at

different temporal and spatial scales (daily to long-term forecasts on urban to regional resolutions) and allow obtaining scenario studies to evaluate the effectiveness of emission reduction measures (Viana et al., 2008; Fragkou et al., 2011).

However, the actual responsible of the effects on health, environment and cultural heritage at a given receptor are those particles and chemical species experimentally observed in airborne PM at the time of its collection (excluding sampling artifacts). These species are the result of the influence of atmospheric ageing processes acting on aerosols until they are collected (Lee et al., 2008).

In this view, receptor models are more useful since they allow the apportionment of PM mass on the basis of chemical and physical data directly referred to the receptor. This helps to





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understand to what extent the mixing of local sources, site variability and long-range transport events finally influenced the receptor during the PM sampling period. Besides PM chemical composition, the size distribution, individual particle analysis, meteorological conditions and knowledge of local stationary/ diffuse sources are key information in SA by receptor modelling (RM).

RM techniques provide estimates of source contributions to PM mass and of chemical profile of sources; reliability of estimates depends either on the overall accuracy of analytical determinations, or on the availability of chemical tracers (single or group of species, or concentration ratios) and of local source profiles (Pant and Harrison, 2012). The selectivity of a species towards a specific contribution and the availability of local source profiles are indeed crucial in receptor modelling, either when factor analysis (mostly PCA-APCS, PMF, UNMIX, ME) or chemical mass balance (CMB and hybrid models) approaches are used. Errors of estimate in CMB are frequently due either to site-specific compositional differences of local source signatures, with respect to profiles available from other regions (Marmur et al., 2007; Yatkin and Bayram, 2008), or to collinear sources, the latter affecting also outputs from factor analysis models (Shi et al., 2011; Pant and Harrison, 2012). These issues are particularly critical when related to elemental fingerprints of fuel, coal and biomass burning (Yin et al., 2010), building materials, road dust, desert sand, soil and wind-driven dust from topsoil (Shi et al., 2011; Viana et al., 2008; Lee et al., 2008). Nevertheless, main crustal-like contributions can be separated and apportioned in the PM mass when their profiles are clearly distinguishable, particularly concerning trace metals (Viana et al., 2008; Yin et al., 2010). In the case of resuspended crustal contributions, reaching this goal strictly depends on differentiating the natural mineral dust locally originated by rural topsoil from longrange transported desert dust and from crustal materials derived by urban activities.

A number of studies are available in literature which report elemental fingerprints of local desert sand, soil, road dust, wind blown topsoil and crustal fugitive dusts from African (Moreno et al., 2006; Eltayeb et al., 2001; Dia et al., 2006; Linke et al., 2006), Asian (Awadh, 2011; Ho et al., 2003; Bi et al., 2007; Cao et al., 2008; Kong et al., 2011), Australian (Moreno et al., 2009) and American regions (Vega et al., 2001; Gidhagen et al., 2002; Figueroa-Cisterna et al., 2011; Chow et al., 2003, 2004; Labban et al., 2004). However, up to now few studies report elemental signatures of local crustal materials contributions to airborne PM at European locations. Some of these concern road dust and urban works (Amato et al., 2009, 2011; Samara et al., 2003; Manoli et al., 2002; Jankowski et al., 2007; Wåhlin et al., 2006), while a smaller number concern the study of local geochemistry (Yatkin and Bayram, 2008; Samara et al., 2003; Prohaska et al., 2005; Dordevic et al., 2005; Coz et al., 2010). At present, similar studies have been reported for Italy only by Colombi et al. (2010) and by Cesari et al. (2012): the first one reports profiles of, among others, paved and unpaved road dust and of local topsoil from a rural site in the Lombardy region, while the second one characterizes the elemental signature of urban dust and rural topsoil in the Salentum peninsula of the Apulia region. The latter study outlines that element abundances can differ significantly between raw topsoil and PM₁₀ resuspended from the former, due either to a decreasing gradient of particles size along topsoil layers or to local soil variability with different outcropping lithotypes.

Recently, Canepari et al. (2008) published elemental fingerprints of road dust and other traffic-related sources in Rome. However, to our awareness, source profiles of the local natural topsoil in the area of Central Italy still represent a gap of knowledge, especially as far as the PM respirable fraction is concerned, although the stratigraphic succession of raw soil in Latium volcanic districts have been widely characterised by geochemistry and petrology by other Authors (Conticelli et al., 1997; Giordano et al., 2006; Marra et al., 2011; Cinti et al., 2011).

Where topsoil is not covered by vegetation, its finer fractions can be easily released to the atmosphere and may contribute to resuspended PM, as reported by Moreno et al. (2009). This is particularly expected in case of soil dryness and wind erosion conditions, which are frequently observed also in many semi-arid or arable areas of the southern Mediterranean basin (EMEP, 2010). The case of Rome is well included in this picture. Actually, its extended territory holds geological importance due to different outcropping lithological terms alternating in a restricted area (Cosentino et al., 2009). Crustal dust resuspended in Rome outskirts by wind-blowing of the rural topsoil can thus show different elemental signatures, depending on the type of rocks outcropping in the area where the dust resuspension was originated. This peculiar intra-regional variability of the mineral composition associated to outcropping rocks is combined with a large percentage of arable lands within the rural background and with a typical mediterranean climate mainly tuned by local land – sea breezes (Colacino and Lavagnini, 1982).

Within this picture, the load of local wind blown topsoil to airborne PM can be of main relevance for the city of Rome. In the years 2003-2005 many exceedances of the PM₁₀ daily limit of $50 \ \mu g \ m^{-3}$ have been recorded in Rome. Of these, considering the overall period averages, outbreaks of African dust contributed for about 27% at background sites and 20% at urban/traffic sites, while local sources affected exceedances at urban/traffic sites for about 25-40% (HEREPLUS, 2011). Among local sources, resuspension of road dust and of crustal materials largely contributes to PM₁₀ in the city of Rome (HEREPLUS, 2011). However, these two factors are currently estimated as total contribution of crustal matter to the PM₁₀ mass. In fact, their disaggregation would require profiles of the local geological topsoil, as well as of materials used in construction/demolition activities and urban works, to be used for source apportionment, which are still not available for Rome. Aim of this study is thus to partially fill this gap, by profiling the natural topsoil dust of local provenance. The research has been mainly focused on the respirable fraction of topsoil, in order to provide profiles suitable for the source apportionment of the airborne PM_{10} . Using these profiles, e.g. in receptor modelling, gives the possibility of disaggregating the local geological contribution from that of road dust and of African dust outbreaks, and of estimating each of them separately.

This study represents thus a first investigation towards the possibility of subtracting the natural dust contribution from the total PM_{10} mass in the air quality framework, when exceedances are recorded.

In this work we report elemental signatures of the geological Rome topsoil, and two profiles of paved road dust collected in correspondence of topsoil sampling points. Elemental abundances of the resuspended PM₁₀ fraction of main different lithological terms are discussed with respect either to the corresponding 50 µm sieved fraction, or to the Alban Hills and Sabatini Mountains stratigraphic geochemistry. A number of literature works reporting source profiles and elemental signatures of local topsoil, road dust, desert soil and desert airborne dust (collected at European receptor sites) have been also considered and element ratios from our profiles and from these works have been discussed in a comparative analysis. Finally, element ratios were evaluated in their capacity of locally separating signatures of main non-industrial dust sources (e.g. airborne desert dust, road dust and resuspended local topsoil) from each other and from the average signature of airborne PM₁₀ of the city of Rome.

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