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Sources and distribution of tracer elements in road dust: The Venice mainland case of study

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ABSTRACT

Road dust is an important non-exhaust traffic source of atmospheric particulate matter, from re-suspension of finer particles carried out by wind and traffic flow. Particles of road dust have both natural and anthropogenic origin; the latter is characterized by higher concentrations of several pollutants and are significantly emitted by other non-exhaust traffic source such as the brake and road wear process. Therefore the discrimination between atmospheric particles directly emitted from abrasion process and those related to re-suspension is currently an open issue.

Unlike the exhaust sources related to the fuel combustion, the non-exhaust emissions are not regulated by Communitarian Directives, although their percentage contribution is becoming more relevant due to the recent technological upgrades in the automotive field, focused on the reduction of exhaust emissions.

In this work we studied the morphology and the chemical composition of road dust particles collected on urban, sub-urban and rural roads of Venice mainland (Northern Italy) in August 2013. Results of SEM-EDS and ICP-OES were processed with statistical tools (i.e., enrichment factors and principal components analysis) in order to identify the main pollutant sources affecting the monitored areas. Peculiar associations among Cr, Mn, Zn, Cu, Fe suggested brake pads and tires wear as the dominant source of these elements, whereas the presence of Pb, Co, Ba, Ti was attributed to the tear of the painted horizontal signals. Moreover, the presence of particles originated from the latter source was also confirmed by the presence of glass beads with diameters ranging from 20 μm to 250 μm.

1. Introduction

Air quality is one of the major issues for human health in urbanized and industrial areas. In this regard the European Union drew attention on air quality promoting new quality standards and new objectives (Directive 2008/50/EC).

Road traffic is an important pollutant source in the abovementioned areas, indeed its emission contribute significantly to atmospheric particulate matter(PM) (e.g., Thorpe and Harrison, 2008; Wik and Dave, 2009; Franco et al., 2013; Kumar et al., 2013; Pant and Harrison, 2013; Amato et al., 2014a). This peculiar source includes exhaust and non-exhaust emissions. The former are due to the tailpipe emissions; the latter are related to the wear of vehicle parts (e.g., brake pads and tires), road surface abrasion and re-suspension of Road Dust (RD) finer particles.

In the last few years, stringent regulations promoted intensive study of exhaust emissions that have led to a sensitive decrease of tailpipe emissions in atmospheric PM (European Environment Agency, 2014; Thorpe and Harrison, 2008). Accordingly, the increase of engine technologies and of new low impact engines such as electrics and hybrids have resulted in an increase of percentage contribution of non-exhaust sources. Indeed, Rexeis and Hausberger (2009) suggested that, if the non-exhaust levels will not change in the next few years, the PM non-exhaust percentage contribution will increase up to 80–90% by the end of the next decade.

Among the abovementioned non-exhaust emission sources, the re-suspension of finer RD particles gives an important contribution to atmospheric PM with aerodynamic diameter <10 μm (PM_{10}) (Amato et al., 2014a; Rogge et al., 1993; Taylor and Robertson, 2009; Tervahattu et al., 2006). RD is a complex matrix made of natural and anthropogenic materials that accumulates on the road surface mainly close to the pavements (Pant and Harrison, 2013, and references therein). Specifically, the coarser particles are mainly mineral aggregates and, in addition to the deposition of crustal aerosol, there is a significant contribution deriving from materials used to build the road. The surface of the road is usually covered by a layer of asphalt concrete, i.e., a composite material of mineral aggregate and bitumen. Carbonate rocks like limestone and dolostone (composed of $CaCO_3$ and Ca, $Mg(CO_3)_2$, respectively) are commonly used for their gripping ability with bitumen. The main sources of heavy metals in road dust are tires and brake linings (Apeagyei et al., 2011). Road paints are also a possible source of Pb, Cr

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and Ti in road dust (Adachi and Tainosho, 2004; Fukuzaki et al., 1986). Although Pb was gradually removed in gasoline (definitively banned in Italy at the beginning of 2001 in DPCM, 2000) since the introduction of catalytic converters, it is still present in yellow paint as $PbCrO_4$, commonly used in road surface markings. Possible sources of Ti and Cr particles are also brake linings as reported by Wåhlin et al. (2006) in PM and observed by Kwak et al. (2013) in road dust. When rain events do not occur for long time, especially on summer, the contribution of road dust to PM increases considerably as reported by Amato et al. (2014b). Accordingly, since this matrix is also composed by anthropogenic particles previously emitted by other non-exhaust traffic sources such as processes involving the brake and road wear, the discrimination between atmospheric particles directly emitted from abrasion process and those related to re-suspension is currently an open issue (Amato et al., 2014b).

Venice mainland and in general the Po valley (northern Italy) have been intensively studied in the last decades for what concerns atmospheric pollution (e.g., Masiol et al., 2014; Valotto et al., 2014), being the most industrialized district of Italy with a dense road network, characterized by particular geographical and meteorological features that promote the pollutants concentration. The air quality is therefore continuously monitored by Environmental Regional Agency (ARPA) but the pollutants examined are mainly those selected by environmental legislation (including PM_{10} and $PM_{2.5}$). To date, there are few studies focused on the non-exhaust emission sources in the Po valley and in particular in the Venetian territory. Specifically, to the best of our knowledge, the RD was characterized only in a restricted area, namely, along the bridge that connects Venice with the mainland (Valotto et al., 2015). In order to fill this gap of information, in this work we examine the morphological and the elemental composition of RD sampled on different areas of the Venice mainland. Since the aim of this paper is at providing comprehensive and useful information for the future identification and quantification of this particular source in PM samples, RD samples were collected in urban, suburban and rural areas and in different driving situations (e.g., braking zones near a crossing, high speed sections on straight roads) in order to investigate the variation of this matrix as a function of the driving conditions. Samples where probed with Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) and Scanning Electron Microscopy-Energy Dispersive Spectroscopy (SEM-EDS) analyses, and results were processed with statistical approaches (Enrichment Factors—EF and Principal Components Analysis—PCA) to identify the main pollutant sources affecting the different monitored areas.

2. Materials and methods

2.1. Study area

RD samples were collected in August 2013, along urban, suburban and rural paved roads of two cities belonging to the Venice mainland (Mestre and Marghera), northern Italy. Mestre is one of the most populated city of Venice mainland (ISTAT, 2013) and is characterized by a dense road network with sites where the traffic flux many times exceeds 10,000 vehicles day^{-1}. Marghera is one of the widest industrial areas of Italy and is characterized by a high heavy duty vehicles traffic. 19 samples were collected after 7 days of absence of rain events. Sampling site locations are shown in Fig. 1. For further details, refer to "Road_dust_sampling_sites.kml" file in supplementary data.

Three kinds of roads were monitored: urban, suburban and rural. Urban roads are characterized by high traffic flux of light duty vehicles, slow speed (between 10 and 50 km h^{-1}) and intense phases of acceleration and braking. Instead, both light and heavy duty vehicles travel on

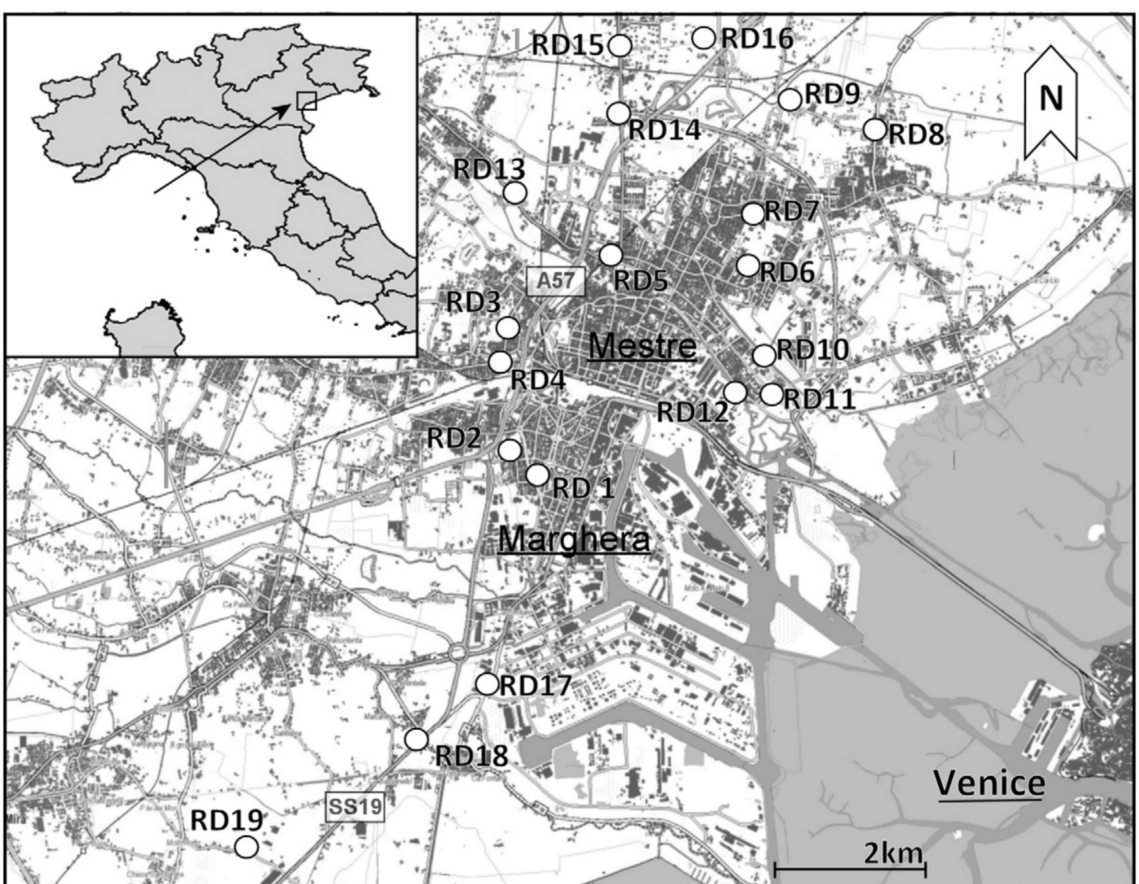

Fig. 1. Monitored area (Venice mainland, northern Italy) and sampling sites in Mestre - Marghera cities.