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Characterisation of the traffic sources of PM through size-segregated sampling, sequential leaching and ICP analysis

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ABSTRACT

A study of the elemental composition and size distribution of atmospheric particulate matter and of its spatial and temporal variability has been conducted at two traffic sites and one urban background site in the area of Rome, Italy. Chemical analysis included the fractionation of 22 elements (Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Na, Ni, Pb, S, Sb, Si, Sn, Sr, Ti, Tl, V) into a water-extractable and a residual fraction. Size distribution analysis included measurements of aerosols in twelve size classes in the range 0.03–10 μm. The simultaneous determination of PM_{10} and $PM_{2.5}$ at three sites during a 2-week study allowed the necessary evaluation of space and time concentration variations.

The application of a chemical fractionation procedure to size-segregated samples proved to be a valuable approach for the characterisation of PM and for discriminating different emission sources. Extractable and residual fractions of the elements showed in fact different size distributions: for almost all elements the extractable fraction was mainly distributed in the fine particle size, while the residual fraction was in general predominant in the coarse size range. For some elements (As, Cd, Sb, Sn, V) the dimensional separation between the extractable fraction, almost quantitatively present in the fine mode particles, and the residual fraction, mainly distributed in the coarse mode particles, was almost quantitative. Under these conditions, the application of the chemical fractionation procedure to PM_{10} samples allows a clear distinction between contributes originating from fine and coarse particle emission sources.

The results related to $PM_{(10-2.5)}$ and $PM_{2.5}$ daily samples confirmed that chemical fractionation analysis increases the selectivity of most elements as source tracers. Extractable and residual fractions of As, Mg, Ni, Pb, S, Sn, Tl, Sb, Cd and V showed different time patterns and different spatial and size distributions, clearly indicating that the two chemical fractions are provided by different emission sources.

The extractable fractions of As, Pb, Sn, S, Tl and V, in agreement to their dimensional distribution, were almost completely associated to $PM_{2.5}$ and showed the same time pattern at all three sites, revealing the presence of spatially homogeneous sources. On the other hand, for most elements the relevant increase of PM_{10} elemental concentration from background stations to traffic urban stations can be attributed almost completely to the residual fraction of coarse particles. Taking into account temporal and size variability, the residual fractions of all these elements showed a very consistent co-variation, which indicates a prevailing common source of coarse particles; this has been identified in non-tailpipe traffic source (road dust re-suspension, brake and tyre ware).

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1. Introduction

The identification of the sources of atmospheric particles constitutes one of the main objectives of the chemical and physical characterisation of PM. Any cost-effective air pollution control policy, in fact, cannot be planned without a robust knowledge of the main contributors to atmospheric aerosol concentration. The high number of possible sources and the fast variations of their relative contribution to the atmospheric aerosol make this goal attainable only if the highest possible number of information about particle dimension, shape and chemical composition, as well as of characteristics of the sampling sites and meteorological situation during the observation periods, are combined.

During the last few years, the scientific community has paid much attention to the study of atmospheric particle size distribution, as many processes occurring in the atmosphere (from climate forcing to cloud formation, as well as health effects) are dependent, besides chemical composition, also on particle size. Studies of the size distribution have been carried out for both PM mass and individual chemical components (ions, metals), and the existing relationship between particle formation pathways and particle dimensions has allowed the use of the size fractionation and chemical analysis, in combination with multivariate statistical techniques such as factor analysis, for the identification of some PM sources (e.g. local emission vs. long range transport) (Allen et al., 2001; Pakkanen et al., 2001, 2003; Singh et al., 2002; Harrison et al., 2003; Salma et al., 2005; Samara and Voutsa, 2005, among others).

From the point of view of the chemical analysis, the availability of multi-parametric analytical techniques for elements and the relative simplicity of sampling and pretreatment procedures have allowed a wide use of the elemental analysis for source apportionment studies. On the other hand, elements are scarcely selective tracers, since most of them are produced by a variety of processes and sources. The need for a deeper differentiation in the chemical analysis of elements has led to the application of sequential leaching methods to particulate matter samples. The real behaviour of a metal in the environment, its fate after mixing of the aerosol with water, its bio-availability, its geochemical cycle etc. depend, in fact, on its specific metallic form.

The development and application of chemical fractionation procedures for the analysis of trace metals in atmospheric particles have yielded many interesting results (Heal et al., 2005; Smichowski et al., 2005; Al-Masri et al., 2006; Birmili et al., 2006; Karthikeyan et al., 2006; Qureshi et al., 2006; Vasconcellos et al., 2007; Sato et al., 2008). In our laboratory, the recent application of a two-step chemical fractionation procedure to atmospheric particle samples has showed that the chemical fractionation noticeably increases the selectivity of some tracers of specific pollution sources (Canepari et al., 2006a). During the first stage of this procedure the collected particles are chemically fractionated for their solubility in a pH-buffered extracting solution; then the residue is mineralised. Among the most interesting results, the identification of magnesium as a responsive tracer of natural events (desert dust and sea-spray): a selective increase of the only mineralised residual fraction of Mg is observed in the case of desert dust, while during sea-spray events also the extractable fraction of Mg increases. In addition, it has been shown that the acetate extractable and the mineralised residual fraction of a group of elements (Mn, Cu, Fe, Ni, Pb) may have different emission sources and that in urban areas the insoluble fractions of these metals have a common source. These last findings point to interesting perspectives in the identification of non-emission traffic contribution (re-suspension, brake and tyre abrasion) to PM levels (Weckwerth, 2001; Sternbeck et al., 2002; Gomez et al., 2005; Almeida et al., 2006).

The coupling of size-segregated sampling techniques and chemical speciation analysis constitutes a step forward in the direction of a sound identification of PM sources in urban areas (Dodd et al., 1991). The purpose of work reported in this paper is the study of the size distribution, spatial variability and temporal variability of two chemical fractions of particulate matter having different elemental solubility. The data were collected during a field study carried out at three urban locations in the city of Rome by using a 13-stage low-pressure impactor and PM_{10} and $PM_{2.5}$ samplers. The analyses were carried out by ICP-OES and ICP-MS. The interpretation of the data was carried out in the light of their space and time variability and of the meteorological conditions during the study.

2. Experimental and method

2.1. Sampling sites and sampling equipment

Sampling was conducted in 2006, from April 12th to 26th, at three locations in the urban area of Rome: Montezemolo (MZ), a traffic site, Villa Ada (VA), an urban background location sited inside the main green park in Rome about 200 m from two highly travelled roads, Chemistry Department (CD), an urban site located inside the area of the University of Rome “La Sapienza”, about 50 m from the nearest urban road but affected by local traffic (parking sites).

The first two stations belongs to the air quality network of the local environmental protection agency (ARPALazio); here daily PM_{10} and $PM_{2.5}$ samples were collected on Teflon filters by means of four automatic sequential samplers operating at the flow rate of $2.3\ m^3\ h^{-1}$ (SWAM 5a, FAI Instruments, Fontenuova, RM, Italy); the mass concentration was determined by the beta accumulation method. The sampled filters were kindly supplied for this study by ARPALazio.

At the Chemistry Department, daily PM_{10} and $PM_{2.5}$ samples were collected on 47 mm diameter PTFE membranes, 1 μm pore size (PALL Corporation, U.S.A.) by means of a dual channel sampling unit (HYDRA Dual Sampler, FAI Instruments, Fontenuova, RM, Italy) equipped with one PM_{10} and one $PM_{2.5}$ sampling head, both operating at the flow rate of $2.3\ m^3\ h^{-1}$. At the same site, a 13-stage low-pressure impactor (DLPI, DEKATI Ltd., Tampere, Finland) was run during the whole period (15 days). The instrument operates at the flow rate of $10\ l\ min^{-1}$ and at the pressure of 100 mbar under the last impactor stage. The