An integrated approach using high time-resolved tools to study the origin of aerosols

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HIGHLIGHTS

- An integrated approach was developed to characterize local and LRT contributions to PM.
- The use of high time-resolved tools allowed one to identify also time-limited events.
- Hourly ion concentrations enabled an accurate characterization of high-PM events.
- Hourly BT cluster analysis enabled the identification of the LRT pathways.
- This approach is useful to understand air pollution phenomena and support decision making.

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ABSTRACT

Long-range transport of natural and/or anthropogenic particles can contribute significantly to PM10 and PM2.5 concentrations and some European cities often fail to comply with PM daily limit values due to the additional impact of particles from remote sources. For this reason, reliable methodologies to identify long-range transport (LRT) events would be useful to better understand air pollution phenomena and support proper decision-making.

This study explores the potential of an integrated and high time-resolved monitoring approach for the identification and characterization of local, regional and long-range transport events of high PM. In particular, the goal of this work was also the identification of time-limited event. For this purpose, a high time-resolved monitoring campaign was carried out at an urban background site in Bari (southern Italy) for about 20 days (1st–20th October 2011). The integration of collected data as the hourly measurements of inorganic ions in PM$_{2.5}$ and their gas precursors and of the natural radioactivity, in addition to the analyses of aerosol maps and hourly back trajectories (BT), provided useful information for the identification and chemical characterization of local sources and trans-boundary intrusions. Non-sea salt (nss) sulfate levels were found to increase when air masses came from northeastern Europe and higher dispersive conditions of the atmosphere were detected. Instead, higher nitrate and lower nss-sulfate concentrations were registered in correspondence with air mass stagnation and attributed to local traffic source. In some cases, combinations of local and trans-boundary sources were observed. Finally, statistical investigations such as the principal component analysis (PCA) applied on hourly ion concentrations and the cluster analyses, the Potential Source Contribution Function (PSCF) and the Concentration Weighted Trajectory (CWT) models computed on hourly back-trajectories enabled to complete a cognitive framework and confirm the influence of aerosol transported from heavily polluted areas on the receptor site.

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1. Introduction

Developing appropriate control strategies for air quality involves an understanding of the physical and chemical processes that affect the formation and chemical composition of PM as well as the evaluation of PM transport and mixing processes. Locally emitted pollutants are not only diluted with ambient air but also undergo various types of transformations in the atmosphere. Moreover, natural and anthropogenic aerosol components released at one location can travel long distances in the atmosphere depending on the prevailing weather conditions, which change daily. Thus, PM can affect both local and distant air quality. Evidence suggests that long-range transport (LRT) of PM over distances exceeding natural borders may affect air quality in urban and rural areas throughout

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Europe (Abdalmogith and Harrison, 2005; Niemi et al., 2009; Baker, 2010; M.J. Kim et al., 2012; Gao et al., 2012; Moroni et al., 2012).

The most important meteorological factors influencing air pollution concentrations are atmospheric stratification, dispersive capacity of the atmosphere, high convective dynamics, wind speeds, meteorological conditions, topography and solar radiation (Valkama and Kukkonen, 2004). In different Megacities all over northern Europe as well as in northern Italy, air quality is greatly affected by anthropogenic emissions. Evidence suggests that air pollution problems are principally due to unfavorable weather conditions and orographic features which reduce air mass circulation and favor pollutant accumulation (Lenschow et al., 2001; Putaud et al., 2004; Viana et al., 2006; Carbone et al., 2010; Squizzato et al., 2012). In fact, PM concentrations are highly seasonal and reach their maximum levels in winter, when a lower disperdent capacity of the atmosphere is registered. On the contrary, countries bordering the Mediterranean basin are characterized by a higher planetary boundary layer, especially in summer. This situation sometimes causes an inverse seasonality of PM concentrations due to LRT contributions to local PM levels (Katragkou et al., 2009). These LRT contributions may significantly enhance PM10 levels producing mass loads greater than the European Commission (EC) limit value of $50\ \mu g\ m^{-3}$, especially during the summer season (Bonasoni et al., 2004; Querol et al., 2004; Cristofanelli and Bonasoni, 2009; Escudero et al., 2007; Meloni et al., 2008; Perrino et al., 2009; Riccio et al., 2009; Remoundaki et al., 2011; Nava et al., 2012). Because countries bordering the Mediterranean basin are often downwind from African mineral dust plumes, the most commonly discussed LRT contribution is the Saharan dust transport. In fact, in the guidelines provided by the European Commission (671/11, 2011), Member States are instructed to subtract the contribution of natural sources before comparing PM10 concentrations to the established limits.

However, recent studies have noted an influence from the European continent and suggest that there is also an anthropogenic LRT contribution which can produce an increase in finer particle concentrations for compounds such as sulfate and organic carbon (Glavas et al., 2008; Marenco et al., 2006; Riccio et al., 2007; C.H. Kim et al., 2012; Tositti et al., 2013).

The few work conducted on this issue in the Apulia region of southern Italy, report a non-seasonality for PM concentrations with high values in more dispersive conditions of atmosphere and the ammonium sulfate concentrations homogenously distributed in time and space (Amodio et al., 2010, 2011, 2012). Even if these evidences could exclude the local character of ammonium sulfate, more relevant and time-resolved information could be needed for the identification of anthropogenic LRT events.

Therefore in this study an integrated and high time-resolved monitoring approach was carried out in order to enable the discrimination and the chemical characterization of different sources of PM as well as the identification of LRT events, also time limited. Simultaneously the PM10 and PM2.5 sampling, a high time-resolved monitoring campaign was conducted at an urban background site in Bari (southern Italy) for about 20 days (1st–20th October 2011). This campaign enabled to collect hourly information about the dispersion properties in the lower layers of the atmosphere and about the concentrations of ions in PM2.5 and of their gas precursors in ambient air. Finally, statistical investigations such as the principal component analysis (PCA) applied on these hourly data and the cluster analyses, the Potential Source Contribution Function (PSCF) and the Concentration Weighted Trajectory (CWT) models computed on hourly back-trajectories enabled to complete a cognitive framework necessary for the identification and characterization of LRT events, also short-term.

Identifying the origin of the pollutants and distinguishing between long-range and local contribution could give stakeholders crucial information for the development of cost-effective control strategies and effective abatement measures. In fact, it would help avoid unnecessary air quality control measures such as blocking traffic when atmospheric stability is not determined.

2. Materials and methods

2.1. Integrated monitoring approach

An integrated and high time-resolved monitoring approach was carried out during the campaign performed October 1 to 20, 2011 at an urban background site, located at the Campus of the University of Bari (Lat: 47,1252; Long: 16,6667). This approach integrated PM mass measurements with the hourly information about the dispersion properties in the lower layers of the atmosphere and the hourly concentrations of ions and their gas precursors. In addition, the information obtained by principal component analysis (PCA) applied on hourly data collected and by the statistical models applied to hourly backward trajectories (such as Cluster Analyses, Potential Source Contribution Function (PSCF) and Concentration Weighted Trajectory (CWT)) completed the cognitive framework necessary for the identification and chemical characterization of different contributions to PM, as well as LRT events, also short-term.

2.1.1. PM sampling

The daily PM2.5 and PM10 samples were collected on quartz fiber filters (Whatman, 47 mm diameter) using a dichotomous low volume sampler SWAM Dual Sampler (FAI Instruments S.r.l., Roma, Italy) and FAI EN 1234.1 sampling heads operating at a flow rate of $2.3\ m^3\ h^{-1}$. A total amount of 40 PM2.5 and PM10 samples were collected and stored in a freezer at $-4\ °C$.

2.1.2. Time-resolved characterization of the ionic component of PM2.5 and ionic gaseous precursors

An Ambient Ion Monitor (AIM, URG-9000D, URG Corporation) provided time-resolved direct measurement of cations and anions found in PM2.5 both in particulate (NO_3^-, SO_4^{2-}, Cl^-, NH_4^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, found in PM2.5) and gaseous phases (such as HCl, HNO_3, HNO_2, SO_2 and NH_3). The AIM separated and analyzed each ion individually by incorporating the proven analysis method of ion chromatography. In detail, the instrument consisted of a particle collection unit and two ion chromatograph analyzers for cation and anion analyses. Atmospheric aerosol was sampled at a flow rate of $3\ L\ min^{-1}$ through a PM2.5 sharp cut cyclone. The air sample was drawn through a liquid diffusion parallel-plate denuder that consisted of two cellulose membranes (one for plate) constantly supplied with a 5 mM $H_2O_2(aq)$ solution, and separated the gas from the aerosol phase. The soluble f were separated from particles by diffusion and dissolution into the denuder solution. At this point, the air flow, free of soluble gases, passed through the denuder and continued into the particle supersaturation chamber. Here the particle hygroscopic growth into droplets was favored in order to achieve high collection efficiencies.

Then the water-soluble components both in their particle and gaseous phase were collected by four 5 ml-syringes (particle and gaseous phases, cation and anion analyses) loaded into pre-concentrators and then injected automatically by a collector into the two ICs once per hour. Each analyzer (ICS-1100, Dionex Corporation, Sunnyvale, CA) was equipped with a guard column (IonPac CG12A, 5 μm, 2 × 50 mm for cations and IonPac AG14A, 4 × 50 mm for anions), an analytical column (IonPac CS12A, 5 μm, 2 × 250 mm for cations and IonPac AS14A, 4 × 250 mm for anions), and a self-regenerating suppressor (CSRS 300, 2 mm for cations and ASRS 300, 4 mm for anions). The cation analyzer operated in 15 min isocratic elution with 20 mM methanesulphonic at a flow rate of 0.25 mL/min, whereas the anion analysis was performed in a 27 min isocratic elution with 8 mM sodium carbonate/1 mM sodium bicarbonate at a flow rate of 0.6 mL/min. Multi-point calibrations were performed bi-weekly for both ICs by using calibration