

Hourly elemental composition and source identification of fine and coarse PM₁₀ in an Italian urban area stressed by many industrial activities

M. Chiari^a, P. Del Carmine^a, I. Garcia Orellana^{b,c}, F. Lucarelli^a, S. Nava^{a,*}, L. Paperetti^a

^a Department of Physics, University of Florence and INFN, Florence, via Sansone 1, I-50019 Sesto Fiorentino (Firenze), Italy

^b University of Seville, Spain

^c INFN, Florence, Italy

Available online 26 May 2006

Abstract

A project is in progress to study the environmental problems of Taranto, an industrial town in the South of Italy. Within this framework we studied the atmospheric aerosol composition by means of continuous sampling and PIXE measurements. Particulate matter (PM) was collected simultaneously in two sampling sites during winter and summer 2004 by two streaker samplers, which separate the fine and coarse aerosol modes. Hourly concentrations of elements from Na to Pb were measured at the new 3 MV Tandetron accelerator of the LABEC laboratory of INFN in Florence.

© 2006 Elsevier B.V. All rights reserved.

PACS: 89.60.-k; 02.50.Sk; 82.70.Rr; 82.80.Ej

Keywords: Aerosol; PIXE; Hourly composition; Steel plant

1. Introduction

Taranto, an ancient Italian town lying on the Ionic Sea coast (Fig. 1), is nowadays one of the most industrialized towns in the South of Italy. An industrial area, that includes the biggest steel plant of Europe, one of the biggest Italian refinery, a power plant and a big cement industry, is located in the northern suburbs of the town. During 2004, an extensive investigation, promoted by the Italian Health Ministry, the ISPESL (Istituto Superiore per la Prevenzione e la Sicurezza del Lavoro) and the CNR (Consiglio Nazionale della Ricerca), was carried out, with the aim to quantify the level of pollution in the area and to identify its main sources. Concerning air quality, the project included two sampling campaigns (February–March

and June 2004) in two different sites (Fig. 1): Tamburi (site A in the following), an urban district in Taranto adjacent to the industrial area, and Statte (site B), a small town located ~7 km N of Taranto. Site A is a dense populated quarter subject to a heavy pollution flux; site B is located along the direction of prevalent winds from the industrial area. In both sites, instrumentation by ISPESL and CNR was installed to analyze normal-alkanes, PAHs (polycyclic aromatic hydrocarbons), nitro-PAHs, organic acids, VOCs (volatile organic compounds), dioxins and PCBs (polychlorinated biphenyls).

Within this framework, we were asked to study the aerosol composition with high time resolution (1 h). While aerosol data are usually collected, according to regulatory laws, on a 24 h basis, a better time resolution is necessary to catch the fast events typical of urban and industrialized environments, and to distinguish different aerosol sources. We obtained the hourly concentration of elements with atomic number $Z > 10$ by means of continuous sampling

* Corresponding author. Tel.: +39 055 4572727; fax: +39 055 4572641.
E-mail address: nava@fi.infn.it (S. Nava).



Fig. 1. Taranto map, showing the location of the industrial area and of the sampling sites.

tion of pollution dispersion models could assess the relationships between the emissions and the impact of pollution. Here we will discuss preliminary results concerning the aerosol samples we analysed by PIXE.

2. Experimental

The aerosol has been collected during winter (February 17–March 16) and summer (June 16–30) of 2004, simultaneously in site A and B, by two “streaker” samplers, installed about 4 m above the ground. The sampling devices (PIXE International Corporation [1]) are designed to separate the fine (<2.5 μm aerodynamic diameter) and the coarse (2.5–10 μm) modes of an aerosol. A paraffin-coated Kapton foil is used as an impaction surface for coarse particles and a Nuclepore filter as a fine particle collector. The rotation speed of the two collecting plates during sampling, the pumping orifice width and the beam size we use for the subsequent analysis are such that an overall resolution of about 1 h is obtained on the elemental composition of air particulate.

and PIXE analysis. As a matter of fact, IBA analysis is quite an unique tool to obtain such time resolved concentrations. Data analysis is still in progress. The results of chemical and physical analyses together with the elabora-

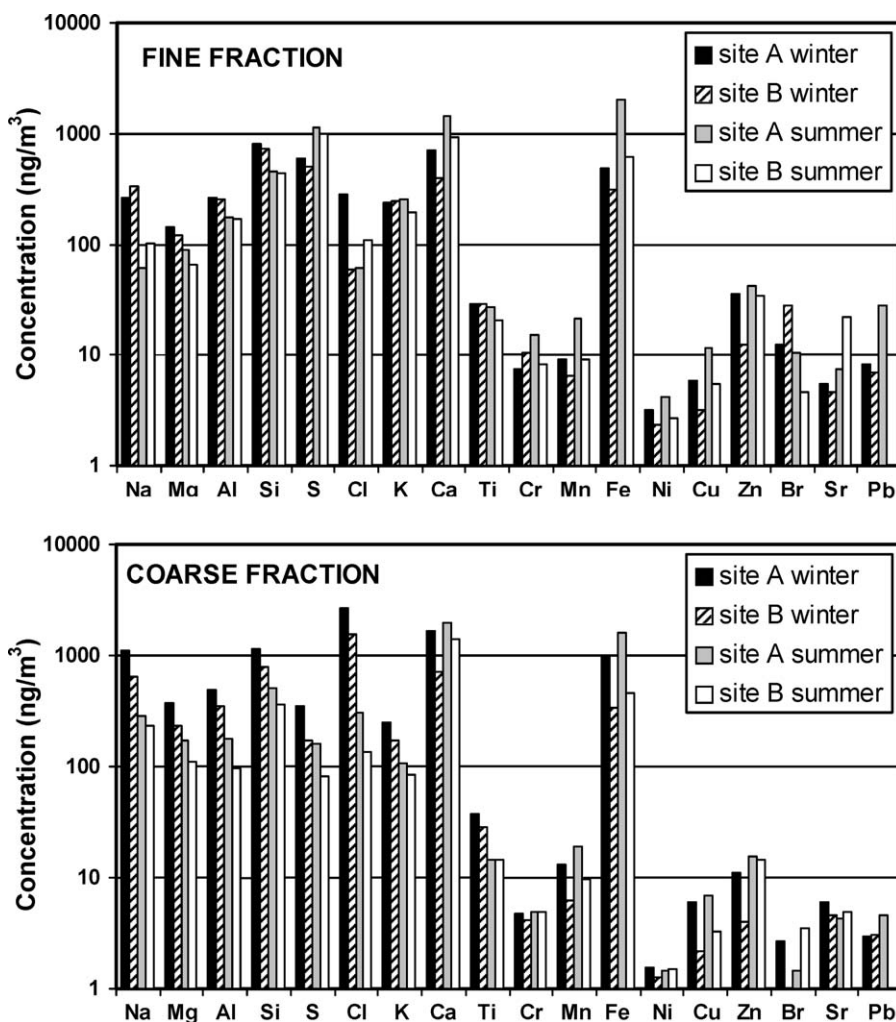


Fig. 2. Average elemental concentrations, measured in the two sites during the winter (23/02–1/03) and the summer (23–30/06) sampling weeks, in the fine and coarse fractions.

Two weeks, one during winter and one in summer, were selected for PIXE analysis: 23/02–1/03 and 23–30/06. Since extremely high PAHs concentrations were found in site A during 2–3/03, we also analysed the Nuclepore filters corresponding to this period. PIXE analyses have been performed with 3 MeV protons from the 3 MV Tandemron accelerator of the LABEC laboratory of INFN in Florence, with the external beam set-up extensively described elsewhere [2]. The beam (20–30 nA) scanned the streak in steps corresponding to 1 h of aerosol sampling; each spot was irradiated for about 200 s. PIXE spectra were fitted using the GUPIX software package [3] and elemental concentrations were obtained via a calibration curve from a set of thin standards of known areal density. Concentration uncertainties were usually around 5% mainly coming from the uncertainties on thickness of standard foils. The uncer-

tainties are obviously higher when concentrations approach minimum detectable limits. Detection limits were about 10 ng/m^3 for low- Z elements and 1 ng/m^3 (or below) for medium–high Z elements. The following elements were detected: Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Br, Sr and Pb.

3. Results

The average concentrations of the various elements (Fig. 2) range from values in the order of hundreds of ng/m^3 (Al, Si, S, K, Ca, Fe in the fine fraction, Na, Mg, Al, Si, Cl, Ca and Fe in the coarse one) to tens of ng/m^3 and below. As could be expected from the characteristics of the sampling sites, most of the elements show higher concentrations in site A, which is closer to the industrial

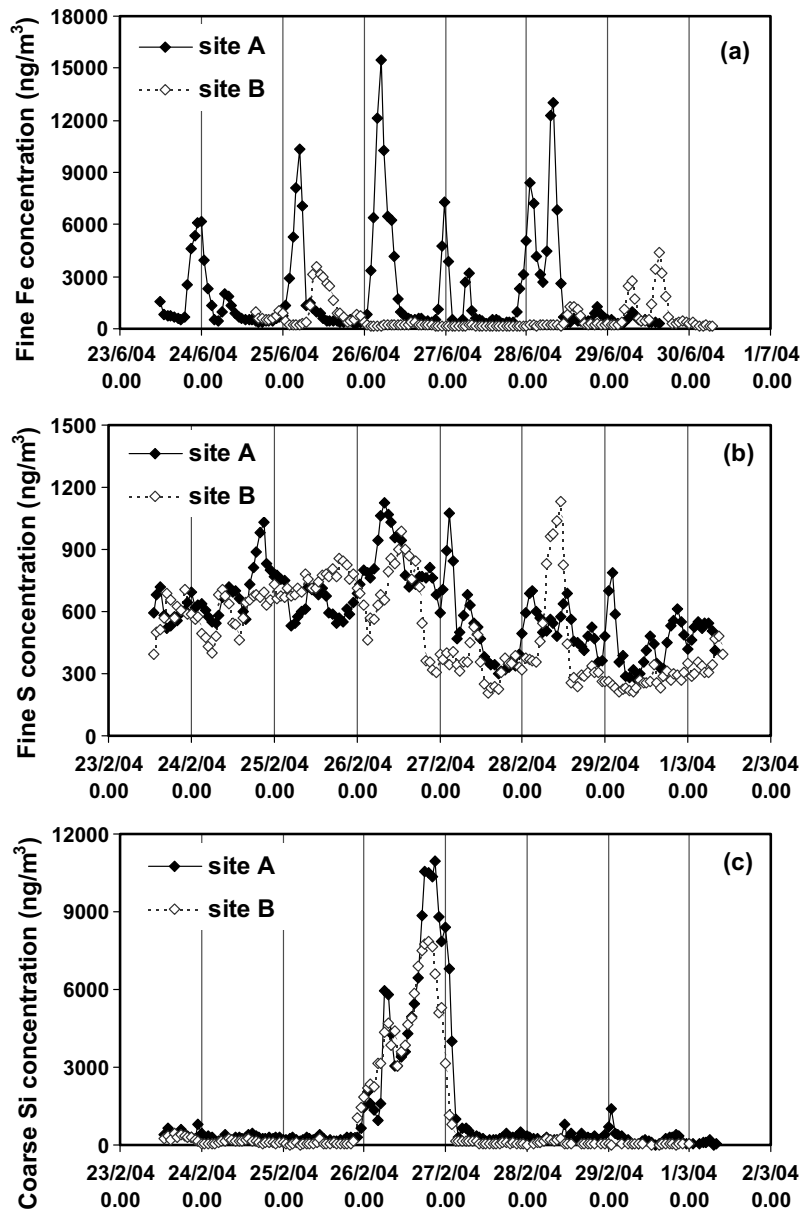


Fig. 3. Hourly time trends of fine Fe during summer (a), fine S (b) and coarse Si (c) during winter.

area. Some elements (S, K, Cr, Ni, Cu, Zn, Br and Pb) are present mainly in the fine fraction, while others (Na, Mg, Cl and Ca) are more abundant in the coarse one; Al, Si, Mn and Fe are quite balanced in the two modes.

Although average values are similar to those measured in other Italian urban environments [4], hourly concentrations of Fe and Mn, which are typical tracers of steel smelter emissions, reached quite high values. These elements show very high correlation coefficients in both sampling sites and during all the weeks: 0.93–0.95 in the coarse fraction and 0.72–0.95 in the fine one (both Fe and Mn show very similar trends in the two fractions). Fine Fe time trends in the two sampling sites are shown in Fig. 3(a). Sharp peaks typical of industrial emission could be clearly seen. Hourly concentrations reached values up to $15 \mu\text{g}/\text{m}^3$ (if fine and coarse fractions are added, these values are about two times greater), similar to those recently found near a steel plant in Genoa [5]. It is worth noting that all the peaks in sites A and B are not coincident, as it could be expected due to the location of the industrial area with respect to the sampling sites (Fig. 1). The analysis of wind directions (measured 10 m above the ground by a SODAR located in the harbour) showed indeed that peaks in site A and site B occur when the wind blows from NW and S–SE, respectively.

As mentioned in Section 1, from the first chemical analysis of samples collected from the 26th of February to the 3rd of March, PAHs concentrations in site A during the 2nd and the 3rd of March resulted one order of magnitude greater than those relative to the other days and to the other site. Similar results have been obtained for fine Fe, whose averages during the 26/02–1/03 and 2–3/03 periods were $530 \text{ ng}/\text{m}^3$ and $1800 \text{ ng}/\text{m}^3$, respectively.

Fine S time patterns (Fig. 3(b)) are characterised by a time component varying on a few hours scale, superimposed to a high slowly varying background, which is similar in the two sampling sites and typical of secondary aerosols of regional origin. This element is indeed present in the fine particulate mainly as sulphate particles, which can be emitted directly from fossil fuel combustion process, but are mainly produced by oxidation (in the atmosphere) of SO_2 .

The analysis of the elemental time series also allowed the identification of long-range natural aerosol transport episodes, the most noticeable being the one showed in Fig. 3(c). During the 26th of February the concentration of all soil related elements (mainly Al, Si, Ca, Ti, but also

K, Mn and Fe) and marine aerosol elements (Na, Mg and Cl) showed a huge increase both in sites A and B. During this episode the elemental ratios changed significantly; for example, considering the sum of the fine and coarse stages (in site A), average values of Ti/Fe–Si/Fe–Al/Fe ratios during the episode and during all the other days were 0.09–3.1–1.3 and 0.03–0.9–0.3, respectively. All these data suggest this peak to be due to a Saharan dust intrusion; backward trajectory calculations (HYSPLIT transport model, NOAA Air Resource Laboratory) confirmed this hypothesis.

To identify the sources of particulate matter, an Absolute principal component analysis (APCA) was performed, separately for the two fractions and for the two sampling periods. In the coarse fraction, the main sources identified in both the seasons and in both the sites are the following: a ‘soil’ source, characterised by high loadings for Al, Si, Ca and Ti, a ‘marine aerosol’ source, marked by Na and Cl, and ‘anthropogenic’ sources, correlated with Mn, Fe and other metals (Cu, Zn and Pb). In the fine fraction the situation is more complex: more factors, characterised by different metals, have been found. They are probably connected with industrial emissions and traffic, however their nature should be further investigated and could be better understood when all the chemical data (PAHs, nitro-PAHs, etc.) would be available.

Acknowledgements

We gratefully acknowledge the Italian Health Ministry and ISPESL for supporting this work. We are deeply indebted to Patrizia Di Filippo (ISPESL) for her kind collaboration.

References

- [1] PIXE International Corp., P.O. Box 7744, Tallahassee, FL 32316, USA.
- [2] M. Chiari, F. Lucarelli, F. Mazzei, S. Nava, L. Paperetti, P. Prati, G. Valli, R. Vecchi, X-ray Spectrometry 34 (2005) 323.
- [3] J.A. Maxwell, W.J. Teesdale, J.L. Campbell, Nucl. Instr. and Meth. B 95 (1995) 407.
- [4] A. D’Alessandro, F. Lucarelli, P.A. Mandò, G. Marazzan, S. Nava, P. Prati, G. Valli, R. Vecchi, A. Zucchiatti, J. Aerosol Sci. 34 (2003) 243.
- [5] F. Mazzei, A. D’Alessandro, F. Lucarelli, F. Marengo, S. Nava, P. Prati, G. Valli, R. Vecchi, Nucl. Instr. and Meth. B, these Proceedings, doi:10.1016/j.nimb.2006.03.050.