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How a Steel Plant Affects Air Quality of a Nearby Urban Area: A Study on Metals and PAH Concentrations

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ABSTRACT

Taranto (in the Apulia Region of southern Italy) has been included in a list of the most polluted sites of national interest because of its large industrial area that is situated near the urban centre. The impact of this on urban air quality has been evaluated by monitoring $PM_{2.5}$ and PM_{10} at the industrial site of 'via Orsini' and the urban station of 'via Dante'. At both sites, the temporal distribution and chemical composition of PM, in terms of PAHs and element concentrations, were used to characterize the air quality in the urban area and to deduce the possible and theoretical carcinogenic indices, and thus the impact on human health. High PM concentrations were found to be caused by wind coming from the north (industrial area), and during days when the wind was from this direction the PAH and elemental concentrations (such as iron, manganese and zinc) were the highest of the sampling period. These data confirm the impact of this industrial area, in particular its steel plant activities, on urban air quality in Taranto. In order to determine the source contributions to PM levels at the two investigated sites, Principal Component Analysis was applied to the collected data. Statistical investigations also included PAH and elemental concentrations determined at two other sites in Apulia Region, characterized by traffic and biomass burning sources. These investigations made it possible to distinguish the samples collected in via Dante and via Orsini from those collected at the two other sites, confirming the effects of industrial activities on urban air quality in Taranto.

Keywords: Industrial source; PAHs; Heavy metals; PCA; Coke oven.

INTRODUCTION

The visible air pollution, such as smoke, dust and smog, has disappeared from many cities thanks to local, national and European regulations. Nevertheless, in many European cities, air quality is still a concern and therefore it is monitored around the clock. In particular, air pollution controlling and curtailment of industrial sources is essential for improving air quality in a selected area. In recent years, the growing interest in Particulate Matter (PM) has been related to its dangerous consequences to human health. As a matter of fact, several epidemiological studies have indicated a strong association between high concentrations of inhalable particles and increased mortality and morbidity (Lin and Lee, 2004; Arditsoglou and Samara, 2005; Namdeo and Bell, 2005; Lammel *et al.*, 2010). The chemical composition of PM and particle size distributions are the most significant factors affecting air quality. In particular, the exposure to finer particles can cause short and long-term effects such as increased respiratory symptoms, decreased lung function, alterations in tissue and structure lung, in respiratory tract and premature death (Prieditis *et al.*, 2002, Damek-Poprawa, 2003, Wahab *et al.*, 2004, Huang and Ghio, 2006, Ahumada *et al.*, 2007, Huang *et al.*, 2007, Magas *et al.*, 2007, Wild *et al.*, 2009, Daresta *et al.*, 2010, Liuzzi *et al.*, 2011). Moreover, near industrial areas, where elements and Polycyclic Aromatic Hydrocarbons (PAHs) are strongly associated with fine particles, increased toxicity and PM carcinogenicity have been determined (Bruno *et al.*, 2002; Caselli *et al.*, 2003; Pozzoli *et al.*, 2004; Vione *et al.*, 2004; Dvorskà *et al.*, 2011; Castro-Jiménez *et al.*, 2012; Tobiszewski and Namiesnik, 2012).

In combustion processes, elements can be emitted in gaseous form, adsorbed on fine particles and retained within heavier ash (Helble *et al.*, 1996). Some elements are essential to maintain metabolism of human body but, at higher concentrations, they can lead to poisoning (Carpi, 1997; Lighty *et al.*, 2000; Linak, 2000; Huggins, 2004). Among these, more attention is required for "Heavy metals", usually referred to any metallic chemical elements having a relatively high density and toxic or poisonous at low concentrations (mercury: Hg, cadmium: Cd, arsenic: As, chromium: Cr, nickel: Ni and lead: Pb).

PAHs include a large group of compounds consisting of

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two or more fused aromatic rings. Among these, a group of 16 PAHs was identified as priority pollutants by the US Environmental Protection Agency (US EPA, 1989). PAHs can be emitted by a wide range of sources associated with human activities, including steel industry. As concerns steel plants, in most European countries production is carried out by using an integrated steel manufacturing process: coke ovens, sintering, blast furnace, basic oxygen steelmaking and finishing processes. Among these processes, coke ovens and sinter plants have been identified as potential sources of organic pollutants (Khalili *et al.*, 1995; Fisher 2001; Yang *et al.*, 2002; Tsai *et al.*, 2007; Amodio *et al.*, 2010b; Tobiszewski and Namiesnik, 2012). These papers have shown the relevance of PM monitoring and associated micropollutants for air quality management studies (Directive 2008/50/EC 2008).

In this study, industrial air pollution implications on human health in Taranto (Apulia Region, South of Italy) were investigated. Taranto is one of the identified areas at high environmental risk in Italy, deeply investigated for the presence of a wide industrial area near the urban centre (Amodio *et al.*, 2009). The industrial complex includes: one of the greatest steel manufacturing plants in Europe, a oil refinery, shipbuilding activities, a navy arsenal, a cement plant and two thermoelectric power plants.

Particulate Matter, PAHs and elements were monitored in order to assess air emissions in the neighbourhood of the industrial area and to evaluate the concentrations of these pollutants at the receptor site in the urban area of Taranto. In particular, concentrations of $PM_{2.5}$ and PM_{10} were evaluated at two sites: a site close to the industrial area (called "via Orsini") and a site in the urban area (called "via Dante"). The temporal distribution of $PM_{2.5}$, PAHs and elemental PM_{10} composition was analysed. Finally, Principal Component Analysis (PCA) was applied to the dataset. This included PAH and elemental concentrations determined at two other sites in Apulia Region, characterized by traffic and biomass burning source. These investigations highlighted a greater similarity among the samples collected at the two sites of Taranto than those collected at the other regional considered stations (Amodio *et al.*, 2011).

This study allowed to deeply characterize the samples collected in the industrial and urban areas of Taranto in order to determine the days affected by the most significant pollution of steel plant emissions on urban air quality and to develop the "right" strategies for reducing emissions from these processes.

EXPERIMENTAL

Study Area

The industrial area investigated in this paper is located in Taranto (Apulia Region, South of Italy) and includes one of the biggest European steel manufacturing plants. It is composed by an iron and steel pole extending on a surface of 15.000.000 m^2 and concerning 200 km of railway tracks, 50 km of roads, 190 km of conveyor belts, 5 blast furnaces and 5 converters. This area, which is about 5 km north of Taranto, also includes a refinery, a cement plant and other small industries. Taranto (198.000 inhabitants) is a coastal city on the Mediterranean Sea. It is the chief town of the homonymous province and the third most densely populated town of Southern Italy. The city, located in the middle of an area of 217 km^2, is also characterized by maritime and military activities in the harbour area and a high density of vehicular traffic. For these reasons, several environmental regulations have been provided in order to assess and restore air quality in the area. Daily samples of PM_{10} and $PM_{2.5}$ were collected at two different sites: the industrial site denominated 'via Orsini' and the urban site in the urban area of Taranto denominated 'via Dante' (Fig. 1).

Sampling Method

Samples of $PM_{2.5}$ and PM_{10} were collected on quartz filters QM-A Whatman (Maidstone, Kent, UK) and on polycarbonate membranes (Millipore, 47 mm diameter, pore size 0.4–0.8 μm), respectively. Sampling was performed by an HYDRA low volume sampler (FAI Instruments S.r.l., Roma, Italy) which, with a volumetric flow of 1 m^3/h and a size selective inlet (SSI), allowed the simultaneous collection of particles with an aerodynamic diameter less than 2.5 μm and 10 μm. A monitoring campaign was performed from the 1st to the 31th October 2005 and from the 31th January to the 28th February 2006. In order to determine the mass of the PM_{10} and $PM_{2.5}$, a total of 120 filters were weighed, before and after sampling, using a Genius Sartorius SE2-F analytical microbalance with a sensitivity of 0.0001 mg (Sartorius AG, Goettingen, Germany) provided with an ionizer for electrostatic charge abatement. In the weighing room, the relative humidity (RH) and temperature were 44 ± 7% and 22 ± 3°C and the samples were kept in these conditions for 48 hours before weighing. Then PM filters were easily cut in two parts by using a stainless steel socket punch and stored in a refrigerator at 4°C before the analysis. A part of $PM_{2.5}$ filter was used for PAH content determination and PM_{10} samples for elemental analysis.

PAH Analysis

Extraction of PAHs collected on $PM_{2.5}$ sample was performed by a microwave assisted solvent extraction (MAE) by means of Milestone model Ethos D (Milestone S.r.l., Sorisole (BG), Italy), which allowed the simultaneous extraction up to 10 samples at the same conditions. This procedure was optimized in order to perform a simple, fast and efficient extraction of PAHs contained in 47 mm sampled filters (Bruno *et al.*, 2007). The samples were extracted by a mixture of acetone/hexane (1:1) and were analyzed by using an Agilent 6890 PLUS gas chromatograph (Agilent Technologies, Wilmington DE) equipped with a programmable temperature vaporization injection system (PTV) and interfaced to a mass selective spectrometer with an inert ion source (Agilent MS-5973 N) (Bruno *et al.*, 2007). Quantitative determination was carried out using the signals corresponding to the molecular ions of PAHs: BaA (228), BbF (252), BkF (252), BaP (252), Ip (276), DbA (278). Perylene-D12 (PrD, 264) was used as internal standard (I.S.). The analytical performances of the whole procedure (extraction recovery, extraction linearity, analytical

Fig. 1. Map of two sampling sites in Taranto: industrial site in Via Orsini and urban site in via Dante.

repeatability, LOD) were verified in previous work (Bruno *et al.*, 2007).

Elemental Analysis

The determination of metals collected on PM_{10} polycarbonate filters was performed by Quant X EDXRF spectrometer (Spectrace Instruments, Sunnyvale, CA). A quarter of filter was enclosed between two films transparent to X-rays. For the excitation step of the procedure, an X-ray tube with a rhodium target was used (maximum voltage: 50 kV and maximum current: 1 mA). The selection of different filters (cellulose, Al, Pd-thin, Pd-med, Pd-thick, Cu-thin, Cu-thick), in combination with the acceleration voltage, was required to optimise the background. The sample was placed at a fixed distance of 80.3 mm from X-ray tube. The characteristic fluorescent X-rays from the sample were collected by a liquid nitrogen cooled lithium drifted silicon (Si(Li)) detector located at a distance of 33 mm from the sample. A linear calibration, without inter-elemental or matrix corrections, was performed by mono-elemental standards. The standards used to obtain calibration curves were homemade by deposing and drying known volumes of mono-elemental ICP standard solutions with concentration of 1000 μg/mL (Baker Instra Analyzed). The elemental composition was determined, in particular the concentrations of Magnesium (Mg), Silicon (Si), Calcium (Ca), Zinc (Zn), Iron (Fe), Manganese (Mn), Arsenic (As), Nickel (Ni), Cadmium (Cd) and Lead (Pb). Accuracy of the analytical methodology was verified analyzing the standard reference material SRM 2783 ($PM_{2.5}$ on Nuclepore polycarbonate membrane, National Institute of Standards and Technology [NIST]). Detection limits ranged from 0.1 to 60 ng/cm^2 (mass of each element on the filter deposit area) and from 0.38 to 18 ng/m^3 assuming a sample air volume of 24 m^3 (Amodio *et al.*, 2011).

Principal Component Analysis

Statistical methods as Principal Component Analysis (PCA) are widely used in air quality studies in order to provide information about PM or gaseous pollutant sources (Querol *et al.*, 2001; Mishra *et al.*, 2004; Bruno *et al.*, 2008; Moreno *et al.*, 2009; Sosa *et al.*, 2009; Amodio *et al.*, 2010a; Andriani *et al.*, 2010, Hellebust *et al.*, 2010; Andriani *et al.*, 2011). PCA aims to reduce data dimensionality by performing a covariance analysis between factors. This purpose is achieved by creating new orthogonal and uncorrelated variables, called Principal Components (PCs), that are linear combinations of the original variables. The coefficients of the Principal Components are calculated so that the first PC contains the maximum variance (which we may tentatively think of as the "maximum information"). The second PC is calculated to have the second most variance, and, importantly, is uncorrelated with the first principal component. The Varimax rotation is an important

step in PCA method as it allows to obtain components more representative of the contribution of each variable to a specific PCs. PCA with Varimax normalized rotation was applied to PM samples collected in via Orsini and via Dante sampling sites and in two other different sites (Galatina - urban and Torchiarolo - regional background) of Apulia Region (Amodio *et al.*, 2011). A matrix of 81 PM samples and 12 variables (Si, Ca, Mn, Fe, Zn, B(a)A, B(b+j)F, B(K)F, B(a)P, Ind, B(g,h,i)P, DiB(ah)A) was analysed.

RESULTS AND DISCUSSION

The daily mean concentrations of $PM_{2.5}$ samples, collected at monitoring sites of Taranto, are shown in Fig. 2. $PM_{2.5}$ concentrations are on average lower than the European target value (25 μg/m^3, Directive 2008/50/EC) for all sites: the mean concentrations in via Orsini (average value of 56 samples) and in via Dante (average value of 40 samples) are equal to 21.85 ± 8.35 μg/m^3 and 18.04 ± 6.30 μg/m^3, respectively. However, concentrations higher than 25 μg/m^3 were determined at Orsini site during some monitoring days and in particular on 4, 6, 16–17, 26–28 October and from 31 January to 6 February. The same findings were observed for PM_{10} concentrations: daily concentrations are usually lower than European daily limit value (50 μg/m^3, Directive 2008/50/EC) and PM_{10} mean concentrations are equal to 49.03 μg/m^3 and to 29.05 μg/m^3 at via Orsini and via Dante sites, respectively. Therefore, PM_{10} daily concentrations higher than 50 μg/m^3 were determined during the $PM_{2.5}$ days of peak previously discussed. Daily concentrations of individual PAH were strongly correlated to each other ($r \geq 0.85$). The highest concentrations of PAHs, ranging from 26 to 54 ng/m^3, were detected in via Orsini especially on 15–18, 27–28 October and 5–6, 26–27 February (see Table 1 and Table 2). Considering main meteorological conditions (wind direction, wind speed and temperature), it was observed these days were characterized by wind coming from the north (industrial area, Fig. 1). During these days, industrial area emissions also contributed to PAH concentrations in the urban area of Taranto. In fact, even if the concentrations in via Dante were about 10 times lower than those of via Orsini, peaks of concentrations occurred at the two considered sampling sites. During the other days, similar PAH concentration levels were found at Orsini and Dante sites. Moreover good positive correlation ($r = 0.79$ for Orsini site and 0.65 for Dante site) was found between the frequency that wind came from the industrial area (from the north) and PAH concentrations. The industrial area impact can also be pointed out by determining the carcinogenic potency of total PAHs, i.e., totalBaPeq, and by considering molecular diagnostic ratios among PAHs (Dickhut *et al.*, 2000; Dvorská *et al.*, 2011; Katsoyiannis *et al.*, 2011; Tobiszewski *et al.*, 2012). The determination of BaPeq concentration for each PAH compound was performed by multiplying its toxic equivalent factor (TEF), which represents the relative carcinogenic potency of the given compound using benzo[a]pyrene as a reference compound, and its concentration (see Table 1 and Table2). Table 3 shows the average values of BaP equivalent calculated for the two sampling sites considering both the whole period and excluding the "days of peak". Data analysis allowed to point out a different potential impact on human health, resulting from exposure to PAHs in the two sampling sites: BaPeq in via Orsini was much higher than in via Dante and it reached 15 ng/m^3 during the days characterized by wind blowing from the industrial area (Fig. 3). As concerns diagnostic ratios, previous studies have shown that Indeno[1,2,3-cd]pyrene/benzo[g,h,i]perylene (IP/BgP) ratio was the most suitable to discriminate among the PAHs sources in Taranto (Amodio *et al.*, 2009). In fact, as shown in Fig. 4, the mean ratio was equal to 0.97 during the days of maxima concentrations, confirming the relevance of the industrial emission as the main source of PAHs (Table 4). During the other days, the IP/BgP ratio showed the typical value for the source vehicular traffic (0.33). Analysis of PM_{10} elements in Taranto showed concentrations of Fe, Mn and Zn significantly higher concentrations than those reported

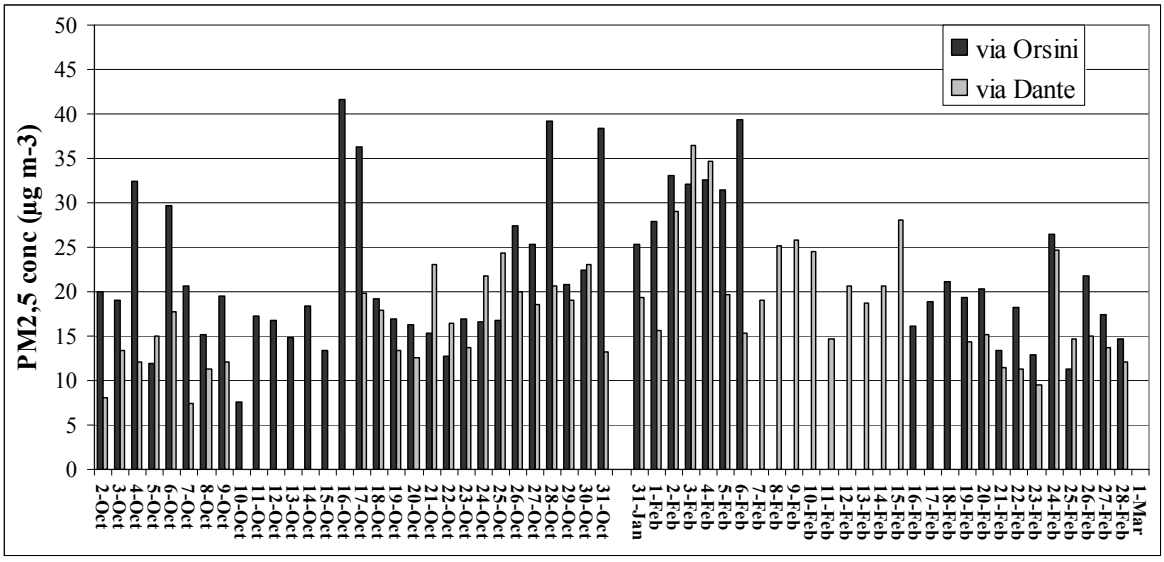


Fig. 2. $PM_{2.5}$ concentration trend in Via Orsini and via Dante during the monitoring campaign.

Table 1. Daily concentrations of individual PAH collected in via Dante site. BaPeq concentration for each PAH was performed by multiplying its toxic equivalent factor (TEF), which represents the relative carcinogenic potency of the given compound using benzo[a]pyrene as a reference compound, and its concentration.

Dante	BaA (ng/m^3)	BbF (ng/m^3)	BkF (ng/m^3)	BaP (ng/m^3)	Ip (ng/m^3)	BgP (ng/m^3)	DbA (ng/m^3)	BaPeq (ng Teq/m^3)
02/10/05	0.06	0.18	0.05	0.06	0.08	0.12	0.01	0.11
03/10/05	0.02	0.05	0.03	0.02	0.03	0.03	0.06	0.09
04/10/05	0.03	0.06	0.01	0.03	0.03	0.06	0.01	0.05
05/10/05	0.17	0.64	0.21	0.20	0.28	0.35	0.05	0.38
06/10/05	0.03	0.10	0.04	0.03	0.05	0.10	0.02	0.07
07/10/05	0.01	0.05	0.04	0.01	0.03	0.07	0.01	0.04
08/10/05	0.02	0.04	0.03	0.01	0.03	0.08	0.01	0.04
09/10/05	0.004	0.01	0.01	0.004	0.01	0.03	0.01	0.02
17/10/05	0.37	1.09	0.34	0.50	0.53	0.64	0.13	0.87
18/10/05	0.54	1.78	0.59	0.68	0.84	0.94	0.21	1.28
19/10/05	0.19	0.62	0.22	0.25	0.28	0.37	0.07	0.46
20/10/05	0.12	0.38	0.15	0.13	0.17	0.21	0.05	0.26
21/10/05	0.03	0.06	0.04	0.02	0.03	0.08	0.01	0.05
22/10/05	0.05	0.08	0.04	0.01	0.01	0.03	0.01	0.04
23/10/05	0.04	0.11	0.05	0.05	0.07	0.10	0.02	0.10
24/10/05	0.08	0.26	0.11	0.12	0.14	0.20	0.04	0.22
25/10/05	0.06	0.22	0.08	0.10	0.12	0.23	0.03	0.18
26/10/05	0.08	0.30	0.10	0.11	0.15	0.22	0.03	0.21
27/10/05	0.56	1.29	0.43	0.62	0.60	0.67	0.16	1.07
28/10/05	0.27	0.72	0.25	0.33	0.37	0.54	0.08	0.58
29/10/05	0.08	0.22	0.08	0.10	0.12	0.18	0.03	0.17
30/10/05	0.03	0.11	0.05	0.04	0.06	0.08	0.02	0.08
31/10/05	0.03	0.15	0.06	0.05	0.08	0.12	0.03	0.10
31/01/06	0.16	0.63	0.22	0.25	0.48	0.88	0.05	0.47
01/02/06	0.57	1.58	0.55	0.77	1.01	1.14	0.21	1.36
02/02/06	0.40	1.52	0.47	0.66	0.91	1.14	0.16	1.16
03/02/06	0.30	1.31	0.43	0.62	0.97	1.37	0.13	1.06
04/02/06	0.34	1.44	0.46	0.57	0.85	1.04	0.15	1.04
05/02/06	0.35	1.15	0.41	0.46	0.61	0.62	0.13	0.85
06/02/06	0.32	0.89	0.31	0.33	0.46	0.48	0.10	0.63
19/02/06	0.07	0.29	0.10	0.09	0.17	0.27	0.03	0.19
20/02/06	0.04	0.13	0.06	0.04	0.09	0.16	0.02	0.10
21/02/06	0.07	0.19	0.08	0.07	0.11	0.24	0.02	0.14
22/02/06	0.08	0.35	0.12	0.12	0.20	0.31	0.04	0.23
23/02/06	0.04	0.24	0.09	0.07	0.17	0.24	0.03	0.16
24/02/06	0.18	0.50	0.18	0.24	0.27	0.44	0.04	0.40
25/02/06	0.13	0.58	0.18	0.20	0.37	0.57	0.07	0.40
26/02/06	0.63	1.82	0.64	0.83	1.07	1.07	0.23	1.49
27/02/06	0.05	0.35	0.12	0.10	0.23	0.34	0.04	0.22
01/02/06	0.55	1.29	0.45	0.60	0.70	0.80	0.16	1.06

in literature (Harrison *et al.*, 2000; Fang *et al.*, 2005). High Fe values and a similar trend for Fe and BaP concentrations were observed during the monitoring campaign at via Dante site (Fig. 5). Moreover good positive correlation (r = 0.63 for Orsini site and 0.58 for Dante site) was found between the frequency that wind came from the industrial area (from the north) and Fe concentrations. Silicon (Si) concentration was usually much lower than Fe value and a very low Si/Fe concentration ratio at urban and suburban sites was determined (0.06) during the "days of peak" (Chow *et al.*, 2002; Alastuey *et al.*, 2004; Rodríguez *et al.*, 2004). The same data were obtained by considering pollutant concentrations at via Orsini site. These results suggested the presence of a common source contributing to the levels of PAHs, Mn, Zn and Fe in the investigated area: the industrial area steel plant. High Fe concentration was also determined on the 24th February, but no corresponding peak in BaP concentration was observed and Si concentration resulted to be higher than

Table 2. Daily concentrations of individual PAH collected in via Orsini site. BaPeq concentration for each PAH was performed by multiplying its toxic equivalent factor (TEF), which represents the relative carcinogenic potency of the given compound using benzo[a]pyrene as a reference compound, and its concentration.

Orsini	BaA (ng/m^3)	BbF (ng/m^3)	BkF (ng/m^3)	BaP (ng/m^3)	Ip (ng/m^3)	BgP (ng/m^3)	DbA (ng/m^3)	BaPeq (ng Teq/m^3)
02/10/05	1.38	5.26	1.72	1.88	2.57	2.39	0.70	3.69
03/10/05	0.15	0.17	0.10	0.11	0.08	0.17	0.08	0.24
04/10/05	0.45	0.73	0.33	0.39	0.35	0.41	0.18	0.76
05/10/05	0.48	1.44	0.52	0.63	0.73	0.84	0.21	1.16
06/10/05	0.26	0.45	0.17	0.26	0.24	0.40	0.11	0.49
07/10/05	0.32	0.82	0.31	0.41	0.41	0.49	0.15	0.75
08/10/05	0.24	0.57	0.19	0.26	0.32	0.42	0.11	0.50
09/10/05	0.24	0.68	0.24	0.27	0.36	0.43	0.12	0.54
17/10/05	3.14	8.89	2.77	3.79	4.28	3.88	1.11	6.85
18/10/05	4.63	15.84	4.89	5.99	7.47	6.50	2.02	11.36
19/10/05	1.03	4.35	1.36	1.47	2.05	2.15	0.51	2.88
20/10/05	0.41	0.91	0.34	0.42	0.42	0.58	0.14	0.77
21/10/05	0.16	0.25	0.11	0.09	0.08	0.18	0.08	0.24
22/10/05	0.12	0.18	0.10	0.08	0.06	0.13	0.07	0.20
23/10/05	0.37	0.11	0.33	0.41	0.42	0.53	0.14	0.68
24/10/05	0.33	0.88	0.28	0.42	0.45	0.63	0.15	0.77
25/10/05	0.32	0.84	0.29	0.38	0.42	0.61	0.13	0.71
26/10/05	0.34	1.02	0.33	0.46	0.48	0.72	0.12	0.80
27/10/05	1.87	4.24	1.45	2.07	2.04	1.91	0.61	3.66
28/10/05	1.26	3.43	1.11	1.49	1.58	1.61	0.44	2.69
29/10/05	0.32	0.68	0.23	0.34	0.36	0.56	0.13	0.64
30/10/05	0.18	0.36	0.15	0.20	0.19	0.37	0.10	0.39
31/10/05	0.25	0.63	0.23	0.33	0.34	0.57	0.12	0.59
31/01/06	0.61	1.31	0.46	0.56	0.79	1.05	0.14	1.02
01/02/06	3.45	8.05	2.74	4.26	5.10	4.66	1.16	7.40
02/02/06	0.70	2.45	0.79	1.15	1.54	1.88	0.28	2.00
03/02/06	0.46	1.27	0.41	0.54	0.73	1.06	0.10	0.94
04/02/06	0.50	1.40	0.45	0.63	0.87	1.23	0.13	1.09
05/02/06	3.22	7.48	2.48	3.90	4.39	3.82	1.02	6.71
06/02/06	9.00	14.75	5.15	7.83	8.71	7.12	2.16	13.82
19/02/06	0.13	0.34	0.15	0.13	0.21	0.41	0.04	0.26
20/02/06	0.09	0.23	0.09	0.09	0.14	0.30	0.03	0.18
21/02/06	0.14	0.45	0.16	0.17	0.27	0.40	0.05	0.33
22/02/06	0.16	0.62	0.21	0.23	0.38	0.58	0.07	0.44
23/02/06	0.07	0.22	0.08	0.08	0.16	0.25	0.03	0.16
24/02/06	0.19	0.40	0.13	0.22	0.23	0.49	0.04	0.36
25/02/06	0.48	0.92	0.35	0.41	0.52	0.68	0.11	0.76
26/02/06	5.79	10.94	3.80	5.73	6.5	5.78	1.53	10.02
27/02/06	0.19	0.44	0.15	0.14	0.28	0.38	0.05	0.30
28/02/06	7.21	15.19	5.25	8.70	10.12	8.94	2.35	14.92

Table 3. Average values of BaP equivalent calculated for the two sampling sites considering both the whole period and excluding the "days of peak". Moreover the maximum and minimum values are listed.

	Total BaPeq via Orsini	Total BaPeq via Dante
Whole period	2.55	0.43
No days of peak	0.80	0.27
Days of peak	6.90	1.02
Maximum	14.92	1.49
Minimum	0.16	0.02

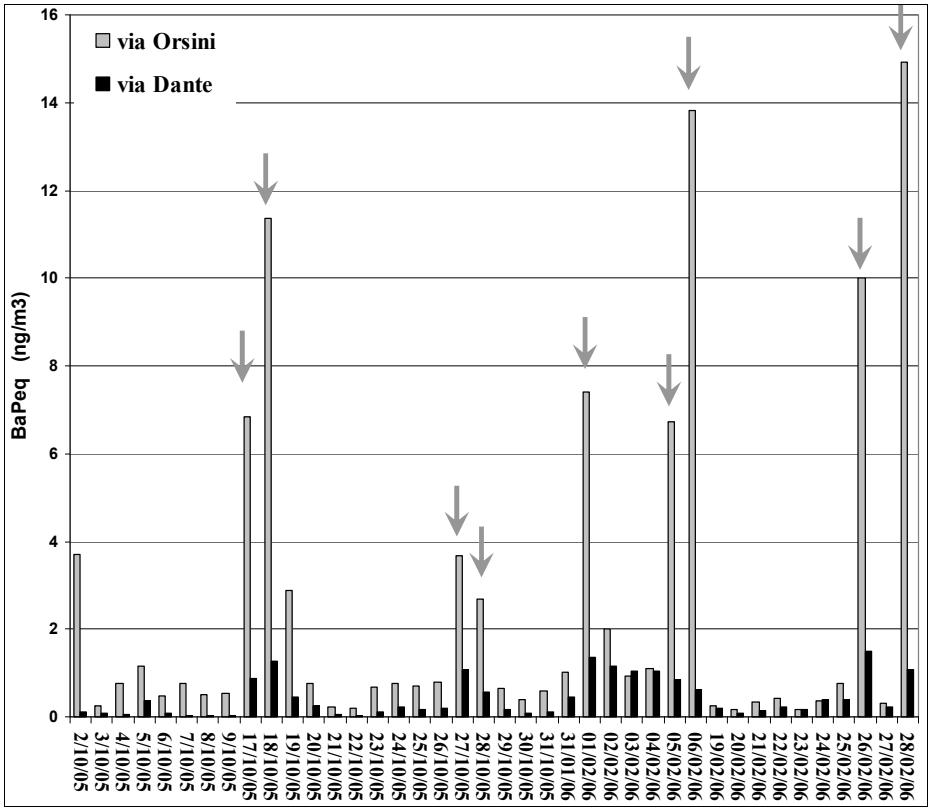
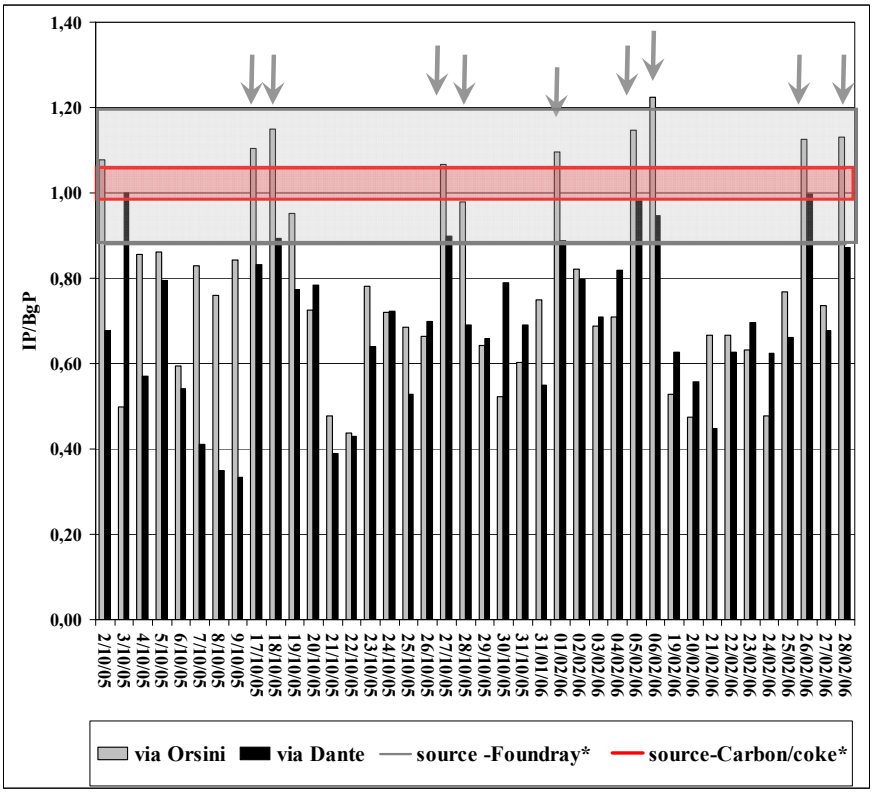


Fig. 3. BaPeq concentration trend in Via Orsini and via Dante during the monitoring campaign. The arrows pointing downwards indicate the days when the wind blew mainly from the north (industrial area).



* Dickhut *et al.*, 2000.

Fig. 4. IP/BgP ratio trend during the monitoring campaign in the two sites. The arrows indicate the days characterized by wind mainly from the North (industrial area).

Table 4. IP/BgP diagnostic ratios for different PAHs sources.

Sources	IP/BgP*
Vehicular traffic	0.33 ± 0.06
Carbon/coke	1.09 ± 0.03
Wood	0.28 ± 0.05
Foundray	1.03 ± 0.15

* Dickhut *et al.*, 2000.

Fe value. During this day satellite data showed an outbreak of Saharan dust occurred in Apulia Region (Amodio *et al.*, 2008). In fact, seven days back trajectories, obtained by CIMEL sun/sky radiometer operating at University of Lecce (40°20'N, 18°6'E) within AERONET network (http://aeronet.gsfc.nasa.gov), and satellite images, obtained by MODIS (http://modis.gsfc.nasa.gov), allowed identifying mineral dust outbreaks from Sahara during this event.

Principal Component Analysis (PCA) with Varimax rotation was applied to the dataset consisting of elemental and PAH concentrations during the PM monitoring campaign discussed in this paper (via Orsini and via Dante sites) and data collected in two other different sites (Galatina - urban; Torchiarolo - regional background) in Apulia Region (Amodio *et al.*, 2011). Principal Component Analysis with Varimax normalized rotation, in particular, was applied on the data matrix of 81 PM samples and 12 variables (Si, Ca, Mn, Fe, Zn, B(a)A, B(b+j)F, B(K)F, B(a)P, Ind, B(g,h,i)P, DiB(ah)A). Since these variables changed by several orders of magnitude, PCA was applied to the normalized data matrix. The main purpose of the procedure was to evaluate the effectiveness of principal components (PCs) in capturing data cluster structure determined by differences existing in sources affecting PM concentrations. Loadings and eigenvalues obtained for each component are summarized in Table 5. Only variables with factor loadings greater than 0.2 are shown. Variables with factor loadings > 0.5 were taken into account in order to characterize PCs. High score values on PC1 and PC2 were obtained for via Orsini data (Orsini) during North wind events (Fig. 6(a)) suggesting the impact of combustion processes (PC1) and mineral dust (PC2) due to steel plant activities. Two different groups of scores can also be observed if Orsini events are not displayed (Fig. 6(b)): even if via Dante (Dante) and Galatina are both considered as urban sites, their score values showed different features characterized by higher values on PC2 than PC1 for samples of Taranto. This result confirmed the impact of air mass transport from the industrial area to receptor sites, also in the urban area of Taranto. Moreover, even if Torchiarolo site was described as regional background site,

Table 5. Loadings, eigenvalues and percentage of variance explained (Variance %) obtained applying PCA to elemental composition and PAHs content of the PM samples collected in via Orsini, via Dante, Galatina and Torchiarolo sites: only component loadings with absolute values greater than 0.2 are listed. Component loadings with absolute values greater than 0.7 are showed in bold, component loadings with absolute values between 0.5 and 0.7 are shown in italics.

	PC1	PC2	PC3
Si			**0.96**
Ca	0.39	**0.70**	*0.52*
Mn	*0.61*	**0.70**	
Fe	*0.65*	*0.63*	0.22
Zn		**0.88**	
B(a)A	**0.94**	0.25	
B(b+j)F	**0.92**	0.32	
B(K)F	**0.97**		
B(a)P	**0.97**	0.22	
Ind	**0.97**	0.23	
B(g,h,i)P	**0.95**	0.28	
diB(ah)A	**0.96**	0.26	
Eigenvalues	8.68	1.52	1.03
Variance %	72	13	9

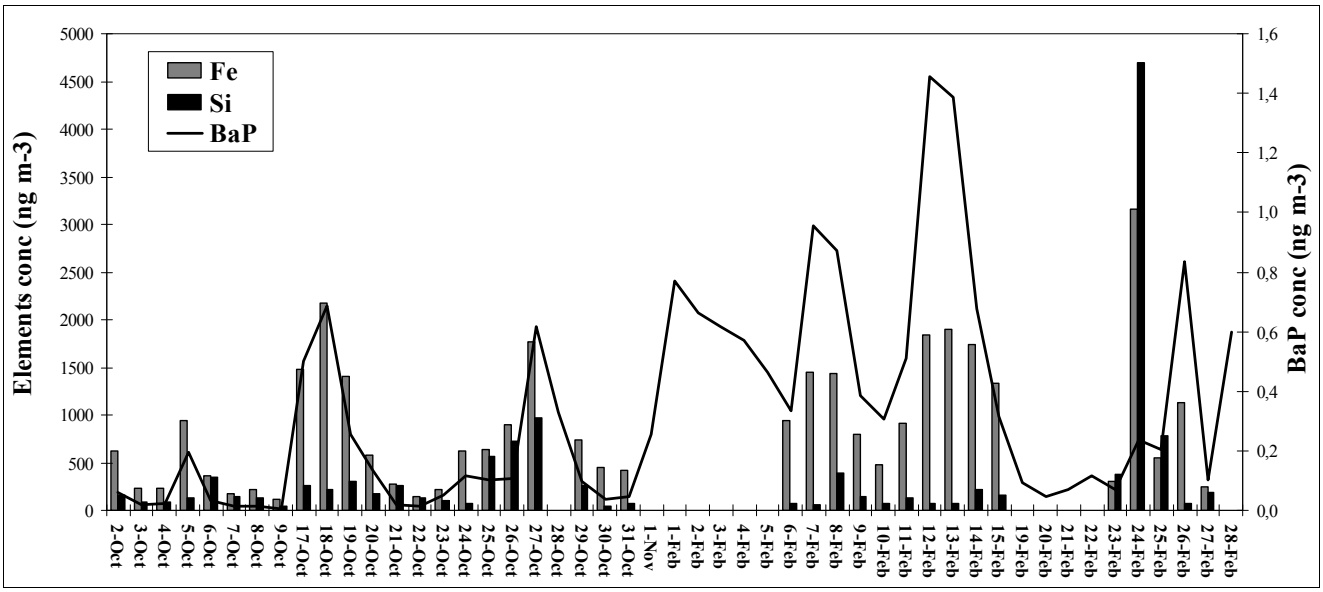


Fig. 5. Fe, Si, and BaP concentrations trend during the monitoring campaign in via Dante site.

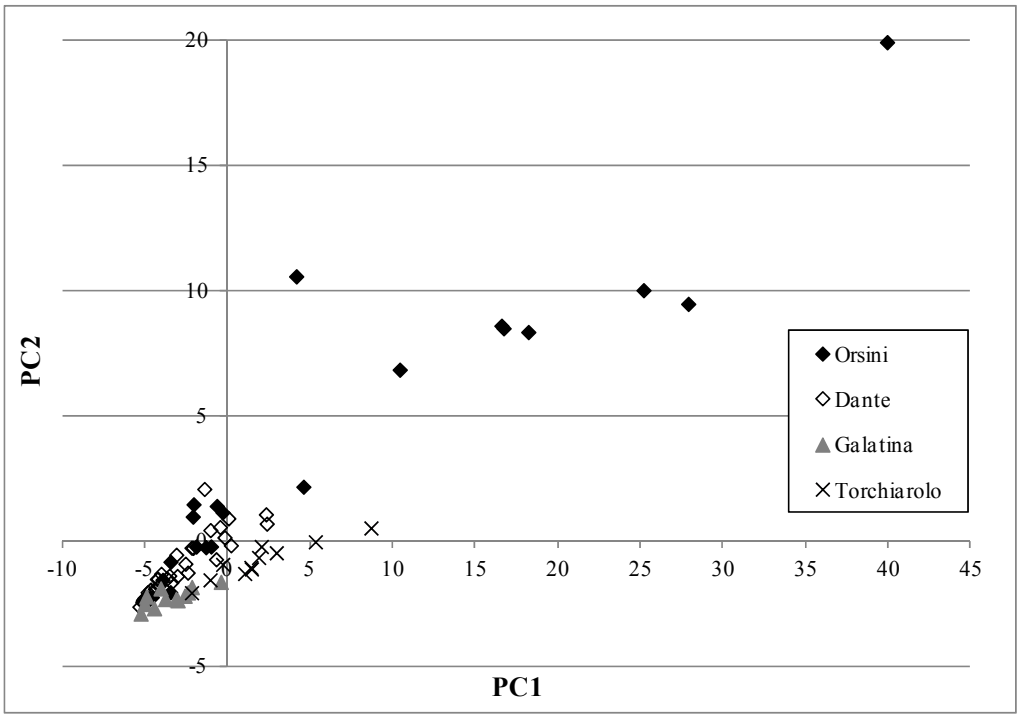


Fig. 6(a). PCA application to data (PAHs, Ca, Fe, Si, Zn, Mn) collected in the following sampling sites: via Orsini, via Dante, Galatina and Torchiarolo (PC1 vs PC2).

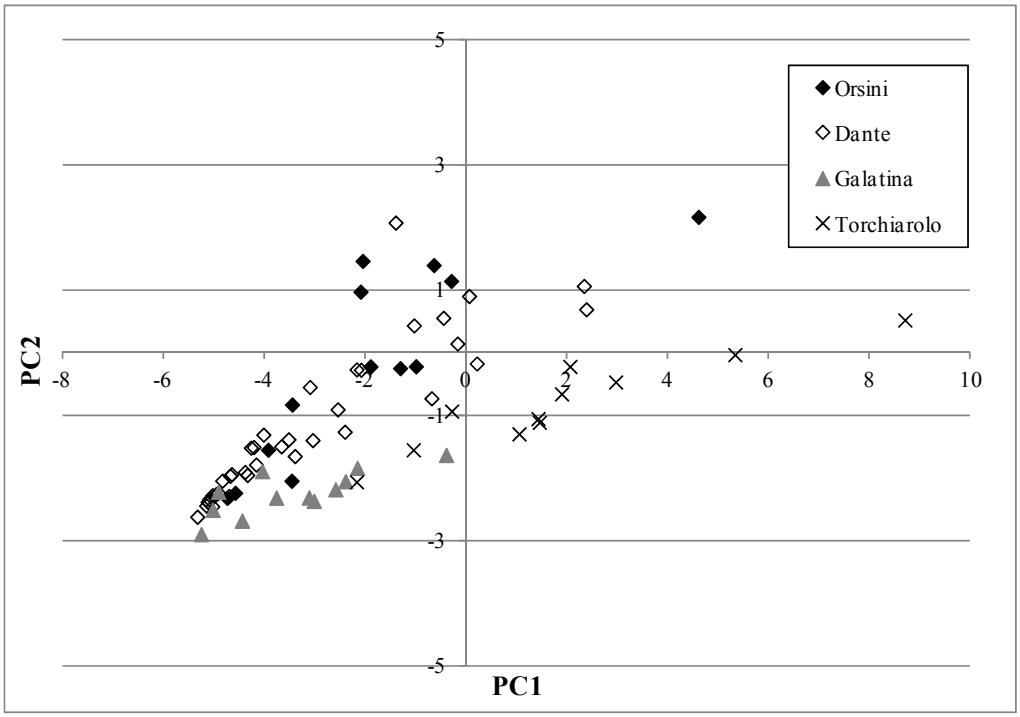


Fig. 6(b). PCA application to data (PAHs, Ca, Fe, Si, Zn, Mn) collected in the following sampling sites: via Orsini, via Dante, Galatina and Torchiarolo: Orsini events are not displayed.

the presence of biomass burning activities in the area should explain the high scores values on PC1 for some samples collected in this sampling site. High score values on PC3 were evaluated for samples collected in Orsini and Dante during Saharan Dust Outbreaks occurred on 24th February: these samples were characterized by high loadings of Si and Ca (PC3) (Fig. 7). North wind events can also be observed in the scoreplot of PC2 vs. PC3, which allowed confirming the mineral dust transport from the industrial area to the Orsini site.

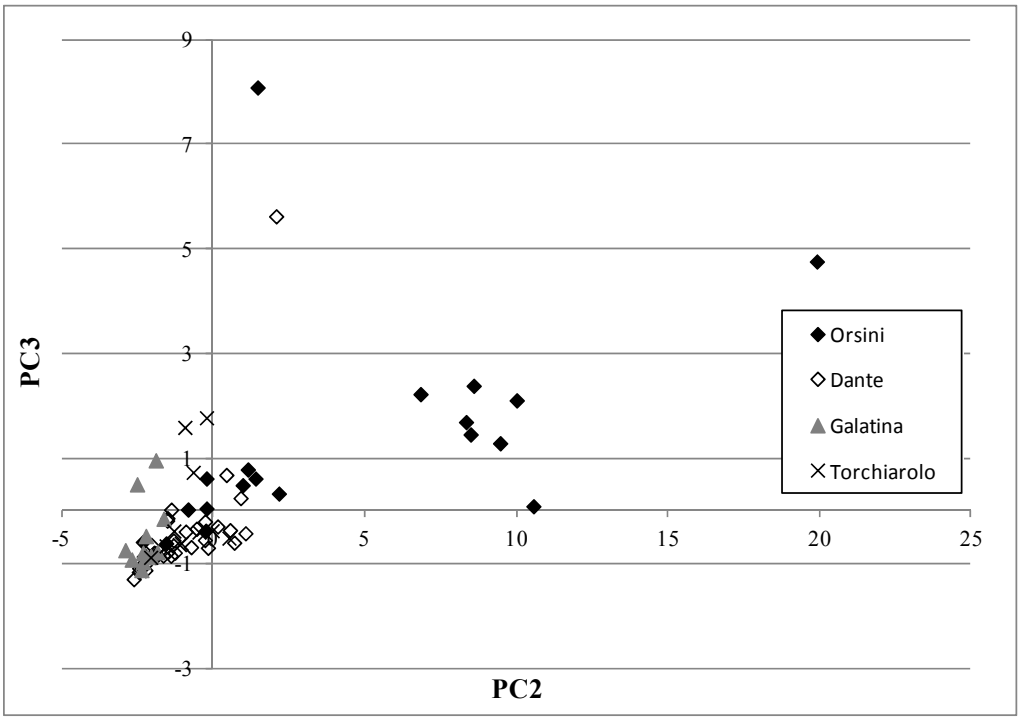


Fig. 7. PCA application to data (PAHs, Ca, Fe, Si, Zn, Mn) collected in the following sampling sites: via Orsini, via Dante, Galatina and Torchiarolo (PC2 vs PC3).

CONCLUSIONS

In order to investigate the industrial area impact on urban air quality, a monitoring campaign of $PM_{2.5}$ and PM_{10} was performed at urban and industrial sites in Taranto (via Dante and via Orsini, respectively). High concentrations of $PM_{2.5}$ and PM_{10} were determined during some monitoring days and, in particular, when meteorological conditions allowed pollutant transport from the industrial area to the urban centre. The same trend was determined for PAH and elemental concentrations, especially for Fe, at the two investigated sites, suggesting the presence of a common source contributing to PAH and element concentrations in the area: the steel plant. Industrial area impact was also pointed out by considering IP/BgP ratio, which was in agreement with the values reported in literature. The ratio was equal to 0.97 during the days of maxima PAH concentrations, confirming the relevance of industrial emissions as the main source of PAHs in the area.

Finally, Principal Component Analysis was applied to dataset including PAH and elemental concentrations determined at two other sites in Apulia Region (Galatina and Torchiarolo characterized by traffic and biomass burning sources, respectively). Two different groups of scores were observed: the samples collected in via Dante and via Orsini can be distinguished from those collected in the two other sites, confirming the contribution of industrial activities to the urban air quality of Taranto.

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