

Research Article

Monitoring of the Deposition of PAHs and Metals Produced by a Steel Plant in Taranto (Italy)

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A high time-resolved monitoring campaign of bulk deposition of PAHs and metals was conducted near the industrial area and at an urban background site in province of Taranto (Italy) in order to evaluate the impact of the biggest European steel plant. The deposition fluxes of the sum of detected PAHs at the industrial area ranged from 92 to 2432 ng m⁻² d⁻¹. In particular the deposition fluxes of BaP, BaA, and BkF were, on average, 10, 14, and 8 times higher than those detected at the urban background site, respectively. The same finding was for metals. The deposition fluxes of Ni (19.8 μg m⁻² d⁻¹) and As (2.2 μg m⁻² d⁻¹) at the industrial site were about 5 times higher than those at the urban background site, while the deposition fluxes of Fe (57 mg m⁻² d⁻¹) and Mn (1.02 mg m⁻² d⁻¹) about 31 times higher. Precipitation and wind speed played an important role in PAH deposition fluxes. Fe and Mn fluxes at the industrial site resulted high when wind direction favored the transport of air masses from the steel plant to the receptor site. The impact of the industrial area was also confirmed by IP/(IP + BgP), IP/BgP, and BaP/BgP diagnostic ratios.

1. Introduction

Atmospheric deposition has been identified as an important source of pollutants for terrestrial and aquatic environments, especially near urban and industrial areas, where a great amount of particulate polycyclic aromatic hydrocarbon (PAHs) and metal concentrations are emitted [1–3]. These pollutants can be transported far from their sources and they may reach very remote environments. PAHs are produced as byproducts of the incomplete combustion of fossil fuels or pyrolysis of organic materials, while metals are emitted in gaseous form from combustion processes, adsorbed on fine particles, and retained in heavier ash [4–8]. The growing interest in these pollutants is due to their toxicity for human health [9–14]. Iron and steel industries are known to be hot spots of organic micropollutants, such as PAHs, and heavy metals. Steel is mainly produced in integrated works using a series of closely linked phases: coke ovens, sintering, blast furnace, basic oxygen steelmaking, and finishing procedures. Among these processes, coke ovens and sinter plants have

been identified as potential sources of metals and PAHs. Therefore, air pollution has become a serious problem for highly industrialized areas such as Taranto (Apulia region, Italy). Taranto is one of the areas identified at high risk of environmental crisis in Italy and it has been included in the list of the polluted sites of national interest (SIN) because of a wide industrial area developed close to the urban settlement, having a high population density [15, 16]. Although several studies were carried out in the last decade in order to evaluate pollutant concentrations in atmosphere [17–21], no study was performed to evaluate deposition fluxes of PAHs and metals near the steel plants of Taranto. Therefore, this work aims to present the first and high time-resolved study on atmospheric deposition fluxes and chemical imprints near the biggest steel plant in Europe. To this end, monitoring campaigns of bulk deposition were conducted near the industrial area and at an urban background site in the province of Taranto (South of Italy). In particular, sampling periods of a week at the most critical site and two weeks in the urban background site were performed. PAHs and some metals were analyzed, and

deposition fluxes were quantified. The comparison between the two sampling sites and the effect of meteorological parameters (rainfall and wind speed and direction) on the deposition fluxes of PAHs and metals were investigated.

2. Material and Methods

2.1. Sampling Sites. Bulk deposition samples were collected at an industrial site of Taranto (South of Italy) and at an urban background site of Mottola, a city of Taranto province (see Figure 1). Taranto ($40^{\circ}28'N$ $17^{\circ}14'E$) is the third most populated city of Southern Italy and it is the seat of one of the biggest steel plants in Europe. Moreover, in Taranto, there is an important industrial area in which metallurgical, chemical, petrochemical, and cement-producing plants, military and trade harbor, and naval shipbuilding industry are located. The industrial site (Taranto) was located near the iron and steel pole of Taranto (Figure 1). Mottola ($40^{\circ}38'0''N$, $17^{\circ}02'0''E$) is a small city of about fifteen thousand inhabitants, situated on a hill (370 meters on sea levels) in the subregion of Murgia. The monitoring site (Mottola) was located in a suburban area of the city but close to a busy regional highway, so it can be classified as urban background site (Figure 1).

2.2. Sampling. Bulk deposition samples were collected from October 16, 2007, to February 13, 2008, with sampling periods of 7 and 15 days each month at industrial and urban background sites, respectively. A total of 16 samples at the industrial site and 8 samples at the urban background site were collected over the investigated period. Bulk particle deposition (wet + dry depositions) collections were achieved using two bulk collectors consisting of a funnel-bottle combination openly exposed at all times (LabService Analytica Srl, Italy). Collectors were made in glass for PAHs and high density polyethylene for metals. They have an aperture of 800 cm^2 placed at 1,5 meters above ground in order to avoid the sample contamination due to ground during heavy rains. Prior to the sampling, the inner surface of the funnel was washed according to UNI EN 15980:2011 and UNI EN 15841:2010 [21, 22]. In each site the following meteorological parameters were also monitored: ambient temperature, solar radiation, barometric pressure, rainfall, and wind speed and direction.

2.3. Analysis of Polycyclic Aromatic Hydrocarbons (PAHs). After sampling, the inner surfaces of the funnel were wiped with precleaned cotton and the collected water was filtered through precleaned glass fibre filters ($0.7\ \mu\text{m}$, 47 mm i.d., Whatman). The filtrate was liquid-liquid extracted with DCM in accordance with UNI EN 15980:2011. The filter and the wiping material were extracted with a mixture of acetone/hexane by means of microwave assisted solvent extraction [17, 23]. PAH extraction was realized using Milestone, model Ethos D (Milestone s.r.l., Sorisole (BG), Italy). The extracted samples were individually analysed using an Agilent 6890 PLUS gas chromatograph (Agilent Technologies, Inc., Santa Clara, CA, USA) equipped with

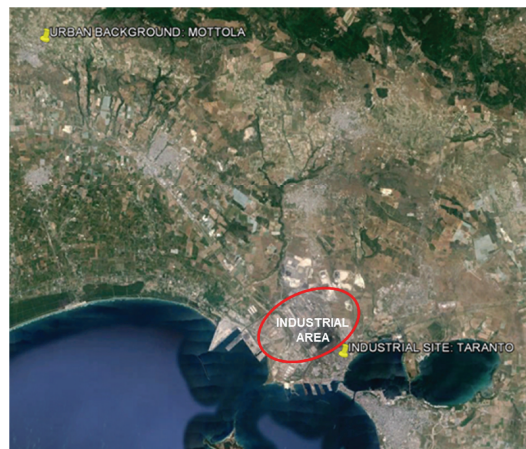


FIGURE 1: Map of the investigated area.

a programmable temperature vaporization injection system (PTV) and interfaced to a mass spectrometer, operating in electron impact ionization (Agilent MS-5973 N) [19]. In this work, benzo[a]anthracene (BaA), benzo[b+j]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (Ip), benzo[ghi]perylene (BgP), and dibenzo[a,h]anthracene (DBA) were analysed as they represent harmful substances for human health [24]. The 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), BgP (276), and DBA (278). Perylene-D12 (PrD, 264) was used as internal standard (I.S.). The analytical performances (extraction recovery, extraction linearity, analytical repeatability, and LOD) were verified in our previous work [23].

2.4. Analysis of Metals. The sample was acidified on arrival at the laboratory by adding 1 mL of concentrated nitric acid per 100 mL sample to dissolve the metals bound to particles or adsorbed to the walls of the container and to prevent growth of microorganisms [22]. The whole acidified sample was vacuum filtered and the filter (cellulose acetate; pore size $0.45\ \mu\text{m}$) was digested in 8 mL of nitric acid and 2 mL of hydrogen peroxide solution by using a microwave system (Milestone model Ethos D) [22]. The extract was analysed by inductively coupled plasma-mass spectrometry (ICP-MS, Perkin Elmer ELAN 9000). Acidified filtrates were individually analysed by ICP-MS [22]. The concentrations of Fe and Mn in bulk deposition were determined as micrograms per square metre day and Cd, As, and Ni as nanograms per square metre day.

2.5. Data Treatment. Pearson correlation analysis was applied to collected data. Pearson's correlation coefficient (Pearson's r) is a measure of the linear correlation between two variables, giving a value between +1 and -1. Total positive or negative correlation occurred between two variables when r is equal to 1 or -1, respectively. There is no correlation between variables when r is equal to 0.

3. Results and Discussion

Bulk deposition fluxes of PAHs and metals obtained during the monitoring campaign at the industrial and urban sites are listed in Tables 1–4. The deposition fluxes of the sum of investigated PAHs (\sum PAHs) at the industrial area ranged from 92 to 2432 $\text{ng m}^{-2}\text{d}^{-1}$ with an average flux of 1012 $\text{ng m}^{-2}\text{d}^{-1}$. Moreover, it was found that the daily mean flux of BaP was 148 $\text{ng m}^{-2}\text{d}^{-1}$ with a range from 11 to 303 $\text{ng m}^{-2}\text{d}^{-1}$. BaP fluxes are comparable to those reported by Esen et al. in an industrial site of Turkey or monitored during the winter in China (220 $\text{ng m}^{-2}\text{d}^{-1}$) [25, 26]. Pearson correlation analysis was also applied to data set showing that individual PAHs were strongly correlated with each other (Pearson's r in the range: 0.75–0.99) with the exception of BaP for which lower correlation was found (Pearson's r in the range: 0.49–0.76). This finding is not in line with the results reported in our previous work which focused on particulate PAH concentrations monitored in the same industrial area [17]. However Li et al. (2009) showed that deposition fluxes of PAHs were not correlated with particulate PAHs in air because they were affected by different factors during the several seasons [27]. This change can be attributed to the different distribution patterns of PAHs among the several particle size fractions, different precipitation scavenging ratios, and deposition velocities of different size particles. Moreover the different reactivity of PAHs in atmospheric processes period should be also considered [27]. Various studies demonstrated that BaP degrades photolytically in the atmosphere at much faster rates than its isomers or other commonly measured parent PAHs [28, 29]. In highly polluted areas, as the industrial area of Taranto, the high concentrations of pollutants such as ozone and/or oxides of nitrogen promote BaP degradation.

Lower PAH deposition fluxes were detected at urban background site of Mottola: average flux over the monitoring period was 211 $\text{ng m}^{-2}\text{d}^{-1}$ which ranged between 87 and 476 $\text{ng m}^{-2}\text{d}^{-1}$. This site was characterized by daily mean BaP flux of 17 $\text{ng m}^{-2}\text{d}^{-1}$ (7–38 $\text{ng m}^{-2}\text{d}^{-1}$) as in Venice Lagoon site (Italy) (33.7 $\text{ng m}^{-2}\text{d}^{-1}$) [30]. As shown in Table 2, the highest deposition fluxes were determined for BgP confirming Mottola site as urban one [31, 32]. Moreover, significant positive correlations were found among investigated PAHs (average Pearson's $r = 0.88$) and also for BaP (Pearson's r in the range 0.76–0.99). Bulk deposition fluxes of the sum of PAHs (\sum PAHs) measured at industrial site were averaged over a period of 15 days in order to compare the two monitored sites (see Figure 2). Deposition fluxes of \sum PAHs near the industrial area of Taranto were on average six times higher than those at the urban background site with peak values 10 times higher during the first four monitored periods. About single PAH, it was found that deposition fluxes of BaP, BaA, and BkF at industrial site were on average substantially 10, 14, and 8 times higher than those detected in urban background site, respectively. Lower enrichments (4–6 times) were determined for other investigated PAHs.

Average deposition fluxes of Fe, Mn, Ni, As, and Cd at the industrial and the urban background sites are shown

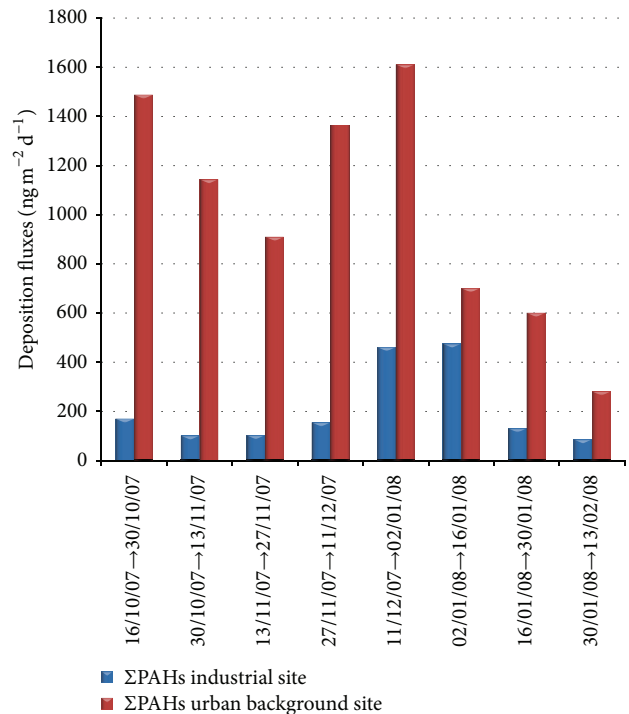


FIGURE 2: Sum of the PAHs detected (\sum PAHs) in $\text{ng m}^{-2}\text{d}^{-1}$ at two monitored sites.

in Tables 3 and 4. The deposition fluxes of metals near the industrial area were higher than those determined at the urban background site for all sampling periods, except for Cd. Several studies on elemental composition of PM demonstrated that Cd can be considered as a traffic marker because it is emitted by the wearing of tyres, brakes, and other parts of vehicles [33–35]. In particular, the deposition fluxes of Ni and As at industrial site were about 5 times higher than those determined at the urban background site, while the deposition fluxes of Fe and Mn were 31 times higher. For example, the comparison between Fe deposition fluxes at two monitored sites is reported in Figure 3. Ni and As deposition fluxes at industrial site (19.8 and 2.2 $\mu\text{g m}^{-2}\text{d}^{-1}$ on average, resp.) were similar to those determined at other coastal sites in Tokyo, France, and China and at industrial site in Spain [36–39]. The mean deposition fluxes for Ni and As at urban background site (3.7 and 0.5 $\mu\text{g m}^{-2}\text{d}^{-1}$, resp.) were similar to those determined in USA by Sweet et al. [40]. Manganese at the industrial site (1.02 $\text{mg m}^{-2}\text{d}^{-1}$ on average) resulted higher than that determined in many polluted countries such as in China [38]. Nowadays no information is available on Fe concentrations in bulk deposition fluxes at the industrial and the urban sites and even less at the industrial area of Taranto that was identified as an area of high environmental risk in Italy. Therefore the high-time resolved information on Fe bulk deposition obtained by this study (57 $\text{mg m}^{-2}\text{d}^{-1}$ on average) is of great interest to the scientific community and stakeholders. In particular it was found that Fe fluxes were two orders of magnitude higher than those determined only in dry deposition in USA and five times higher than those

TABLE 1: Bulk deposition flux $\text{ng m}^{-2} \text{d}^{-1}$ and the measurement uncertainty (SD) of each PAH for the industrial site. The sum of detected PAHs (\sum PAHs) during sampling periods is listed in the last column.

Sampling period	BaA $\text{ng m}^{-2} \text{d}^{-1}$	SD BaA	BbF $\text{ng m}^{-2} \text{d}^{-1}$	SD BbF	BkF $\text{ng m}^{-2} \text{d}^{-1}$	SD BkF	BaP $\text{ng m}^{-2} \text{d}^{-1}$	SD BaP	IP $\text{ng m}^{-2} \text{d}^{-1}$	SD IP	BgP $\text{ng m}^{-2} \text{d}^{-1}$	SD BgP	DBA $\text{ng m}^{-2} \text{d}^{-1}$	SD DBA	\sum PAHs $\text{ng m}^{-2} \text{d}^{-1}$
16/10/07 → 23/10/07	508	31	499	29	386	28	303	26	289	21	367	18	80	14	2432
23/10/07 → 30/10/07	72	4	151	9	81	4	50	4	75	5	89	2	26	3	544
30/10/07 → 06/11/07	88	11	173	27	92	13	93	12	104	17	128	5	45	10	723
06/11/07 → 13/11/07	300	12	298	27	226	14	202	12	194	16	256	5	89	11	1565
13/11/07 → 20/11/07	265	21	408	48	285	23	196	21	251	26	255	9	69	21	1729
20/11/07 → 27/11/07	16	1	22	1	5	0.4	11	3	12	1	23	2	3	1	92
27/11/07 → 04/12/07	122	13	147	32	100	15	88	13	92	19	112	6	48	14	709
04/12/07 → 11/12/07	296	17	450	41	331	20	291	17	255	23	307	8	84	17	2014
11/12/07 → 19/12/07	225	58	523	43	162	27	236	30	293	21	323	23	60	15	1822
19/12/07 → 02/01/08	247	29	352	22	158	22	171	15	210	11	229	12	34	7	1401
02/01/08 → 09/01/08	108	3	176	3	113	7	102	9	97	5	123	7	25	4	744
09/01/08 → 16/01/08	76	2	132	1	73	3	169	6	88	3	105	4	16	2	659
16/01/08 → 23/01/08	78	1	100	1	64	3	192	5	43	2	66	3	8	1	551
23/01/08 → 30/01/08	107	3	125	3	94	7	153	10	65	6	93	8	14	3	651
30/01/08 → 06/02/08	46	3	46	3	59	6	53	8	20	3	39	5	10	2	273
06/02/08 → 13/02/08	42	5	54	3	26	3	51	2	41	2	52	2	23	3	289

TABLE 2: Bulk deposition flux $\text{ng m}^{-2} \text{d}^{-1}$ and the measurement uncertainty (SD) of each PAH for the urban background site. The sum of the PAHs detected (\sum PAHs) during sampling periods is listed in the last column.

Sampling period	BaA $\text{ng m}^{-2} \text{d}^{-1}$	SD BaA	BbF $\text{ng m}^{-2} \text{d}^{-1}$	SD BbF	BkF $\text{ng m}^{-2} \text{d}^{-1}$	SD BkF	BaP $\text{ng m}^{-2} \text{d}^{-1}$	SD BaP	IP $\text{ng m}^{-2} \text{d}^{-1}$	SD IP	BgP $\text{ng m}^{-2} \text{d}^{-1}$	SD BgP	DBA $\text{ng m}^{-2} \text{d}^{-1}$	SD DBA	\sum PAHs $\text{ng m}^{-2} \text{d}^{-1}$
16/10/07 → 30/10/07	13	2	57	5	20	2	16	2	20	3	35	1.0	10	2	171
30/10/07 → 13/11/07	6	3	24	5	8	2	9	2	12	3	35	1.0	8	3	102
13/11/07 → 27/11/07	10	1.0	16	1.0	29	4	9	1.0	13	1.0	24	2	3	1.0	104
27/11/07 → 11/12/07	10	1.0	35	1.0	25	1.0	20	2	23	1.0	38	1.0	4	1.0	155
11/12/07 → 02/01/08	45	1.0	142	1.0	98	3	29	3	66	2	72	3	10	1.0	462
02/01/08 → 16/01/08	39	2	128	2	71	2	38	1.0	80	1.0	87	1.0	33	1.0	476
16/01/08 → 30/01/08	9	2	25	1.0	9	1.0	11	1.0	19	1.0	48	1.0	10	1.0	131
30/01/08 → 13/02/08	6	2	18	1.0	6	1.0	7	1.0	15	1.0	27	1.0	8	1.0	87

TABLE 3: Bulk deposition flux and the measurement uncertainty (SD) of Fe and Mn $\mu\text{g m}^{-2} \text{d}^{-1}$ and of Ni, As, and Cd $\text{ng m}^{-2} \text{d}^{-1}$ for the industrial site.

Sampling period	Fe $\mu\text{g m}^{-2} \text{d}^{-1}$	SD Fe	Mn $\mu\text{g m}^{-2} \text{d}^{-1}$	SD Mn	Ni $\text{ng m}^{-2} \text{d}^{-1}$	SD Ni	As $\text{ng m}^{-2} \text{d}^{-1}$	SD As	Cd $\text{ng m}^{-2} \text{d}^{-1}$	SD Cd
16/10/07 → 23/10/07	94495	818	1966	29	42987	564	2969	31	872	31
23/10/07 → 30/10/07	19398	406	541	6	10114	67	1189	43	391	22
30/10/07 → 06/11/07	83990	409	1464	18	34958	393	1598	48	287	16
06/11/07 → 13/11/07	102358	1630	2239	28	50575	1003	3704	47	618	14
13/11/07 → 20/11/07	66651	816	1155	20	25823	229	2186	50	397	34
20/11/07 → 27/11/07	4450	248	107	4	4111	62	363	18	140	17
27/11/07 → 04/12/07	55716	405	1055	16	26769	476	1862	38	380	46
04/12/07 → 11/12/07	86231	409	2557	32	36221	664	3291	50	608	4
11/12/07 → 19/12/07	90099	1426	1856	66	36382	375	3314	66	619	26
19/12/07 → 02/01/08	46449	613	1152	36	19265	358	2007	71	358	21
02/01/08 → 09/01/08	33832	410	796	15	12793	205	1277	32	258	19
09/01/08 → 16/01/08	36963	815	679	18	12138	183	5083	764	535	44
16/01/08 → 23/01/08	45999	1228	1144	51	14279	283	1432	91	395	15
23/01/08 → 30/01/08	106110	2558	2359	96	35150	508	5900	188	478	24
30/01/08 → 06/02/08	21899	410	487	10	5466	255	1120	24	185	6
06/02/08 → 13/02/08	31665	818	551	9	16238	718	901	24	246	22

TABLE 4: Bulk deposition flux and the measurement uncertainty (SD) of Fe and Mn $\mu\text{g m}^{-2} \text{d}^{-1}$ and of Ni, As, and Cd $\text{ng m}^{-2} \text{d}^{-1}$ with standard deviation for the urban background site.

Sampling period	Fe $\mu\text{g m}^{-2} \text{d}^{-1}$	SD Fe	Mn $\mu\text{g m}^{-2} \text{d}^{-1}$	SD Mn	Ni $\text{ng m}^{-2} \text{d}^{-1}$	SD Ni	As $\text{ng m}^{-2} \text{d}^{-1}$	SD As	Cd $\text{ng m}^{-2} \text{d}^{-1}$	SD Cd
16/10/07 → 30/10/07	3036	143	73	1	4678	30	810	18	251	7
30/10/07 → 13/10/07	2825	143	57	1	4742	191	613	9	292	6
13/11/07 → 27/11/07	1351	145	40	1	2449	43	368	7	977	8
27/11/07 → 11/12/07	1224	143	27	1	2960	33	359	28	142	11
11/12/07 → 02/01/08	1201	104	26	0	3414	10	481	33	293	10
02/01/08 → 16/01/08	1297	163	32	1	1621	31	479	18	203	5
16/01/08 → 30/01/08	3317	164	62	2	6167	157	552	12	450	10
30/01/08 → 13/02/08	1310	143	27	1	4027	73	342	10	158	3

determined at highly industrialized area in Turkey (Izmir) [41, 42].

The high content of Mn and Fe in deposition fluxes at industrial site and the strong correlation between these pollutants (Pearson's correlation coefficient = 0.95) are in line with results obtained by chemical characterization of atmospheric particulate matter in the same area [16, 20, 24]. As reported in previous papers, Mn and Fe atmospheric concentrations measured near Taranto industrial area were the highest in Apulia region. Moreover Mn and Fe were the most significant markers of mineral park emissions within at the steel plant [16, 20, 24]. The impact of the industrial area on two sampling sites can be highlighted by the contributions of each PAH to the total deposition fluxes. At industrial site, each PAH accounted for similar percentage to the total PAH flux (about 15–20%), except for DBA which accounted for about 4% (see Figure 4). On the contrary, the deposition fluxes at the urban background site (Figure 5) were principally due

to benzo[ghi]perylene (25% of the total flux) identified as marker of vehicular traffic emissions [40, 41]. The different percentage compositions obtained in two sites can be due to predominant contribution of the steel plant on the industrial site. This finding was also confirmed by significant correlation among PAHs and metals at the industrial area (Table 5) and no correlation at the urban background site (Table 6). This evidence highlighted that PAHs and metals at the industrial site were emitted from the common source, the steel plant.

The high time-resolved monitoring campaign enabled us to study the impact of meteorological parameters on daily deposition fluxes of PAHs and metals. The PAH fluxes were positively correlated with rainfall during the sampling period, but significant inverse correlation was found with wind speed [27, 43, 44]. In fact the highest PAH fluxes were registered during the periods characterized by wind calm and/or high rain frequency (>10%). As concerns metals, it was found that when wind direction favored the transport of air masses

TABLE 5: Correlation coefficients among PAHs and metals collected at the industrial site.

	BaA	BbF	BkF	BaP	IP	BgP	DBaA	Fe	Mn	Ni	As	Cd
BaA	1.00	0.88	0.95	0.72	0.89	0.94	0.85	0.66	0.67	0.73	0.34	0.83
BbF		1.00	0.88	0.76	0.99	0.98	0.83	0.64	0.66	0.67	0.33	0.75
BkF			1.00	0.75	0.88	0.91	0.88	0.65	0.69	0.69	0.33	0.77
BaP				1.00	0.71	0.76	0.49	0.73	0.79	0.69	0.57	0.88
IP					1.00	0.99	0.86	0.65	0.65	0.69	0.34	0.75
BgP						1.00	0.88	0.70	0.71	0.75	0.37	0.81
DBaA							1.00	0.71	0.70	0.83	0.27	0.70
Fe								1.00	0.95	0.96	0.67	0.73
Mn									1.00	0.90	0.67	0.74
Ni										1.00	0.55	0.75
As											1.00	0.65
Cd												1.00

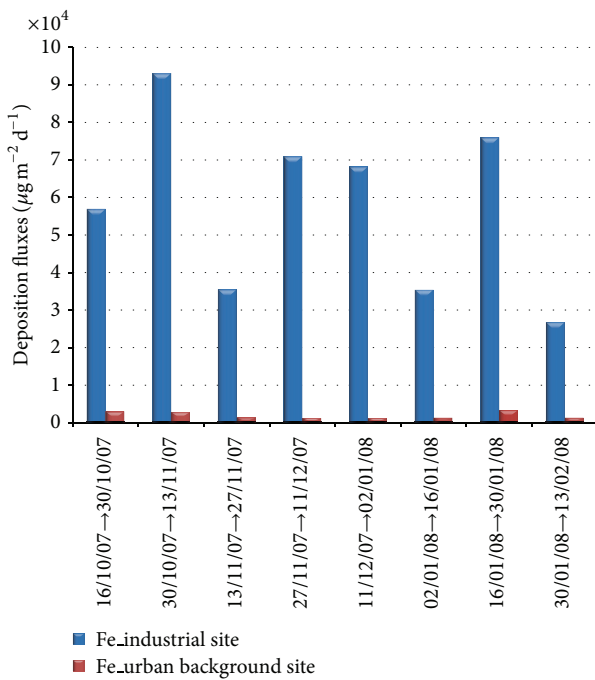


FIGURE 3: Iron (Fe) deposition fluxes ($\mu\text{g m}^{-2} \text{d}^{-1}$) at two monitored sites.

from the steel plant to receptor site, the highest Fe and Mn fluxes were detected (Figure 6). Moreover, high fluxes were registered even during calm period. This evidence can be explained considering the proximity of receptor site to the industrial source.

At the end, several diagnostic ratios ($IP/(IP + BgP)$, IP/BgP , and BaP/BgP) were calculated in order to identify the industrial area as the main emission source. PAH diagnostic ratios have recently come into common use as a tool for identifying and assessing pollution emission sources [17, 28, 45–49]. The use of diagnostic ratios is based on the principle

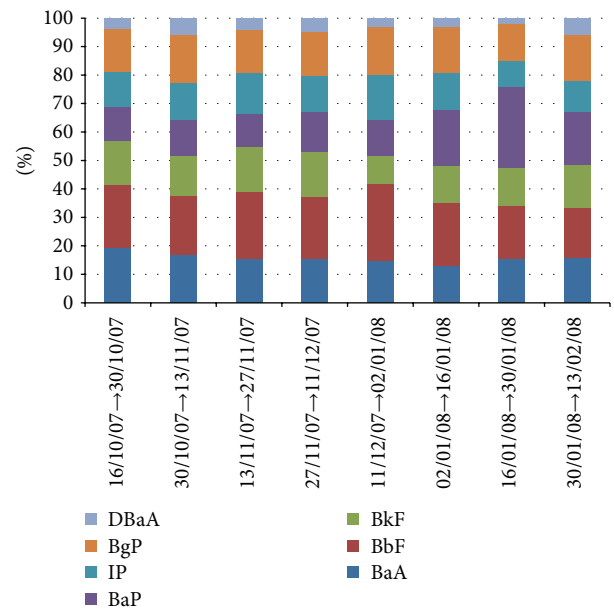


FIGURE 4: Percentage contributions of each PAH to the total deposition fluxes at the industrial site.

that some PAHs are emitted in reasonably regular proportions and the paired compounds are diluted to a similar extent during transport, and thus their subsequent ratios remain constant between the source and receptor. Diagnostic ratios were used to identify pyrogenic or petrogenic sources, diesel or gasoline emission, fuel or biomass combustion, and traffic related sources [17, 28, 45–49]. Values of $IP/(IP + BgP)$, IP/BgP , and BaP/BgP were 0.44, 0.78, and 1.13, respectively, in agreement with those reported in literature for coke combustion emissions [17, 45–50]. Lower diagnostic ratio values were found for urban background site (0.60 for all ratios) confirming the combustion processes of gasoline and diesel as the most important source of PAHs in this site [49, 50].

TABLE 6: Correlation coefficients among PAHs and metals collected at the urban background site.

	BaA	BbF	BkF	BaP	IP	BgP	DBaA	Fe	Mn	Ni	As	Cd
BaA	1.00	0.98	0.98	0.90	0.96	0.90	0.63	-0.43	-0.42	-0.50	-0.01	-0.18
BbF		1.00	0.94	0.92	0.96	0.91	0.66	-0.35	-0.33	-0.45	0.11	-0.31
BkF			1.00	0.85	0.91	0.82	0.48	-0.53	-0.50	-0.57	-0.11	-0.07
BaP				1.00	0.96	0.92	0.76	-0.41	-0.39	-0.59	0.00	-0.36
IP					1.00	0.96	0.79	-0.44	-0.44	-0.55	-0.06	-0.29
BgP						1.00	0.82	-0.23	-0.29	-0.36	0.05	-0.33
DBaA							1.00	-0.11	-0.11	-0.40	0.13	-0.33
Fe								1.00	0.95	0.84	0.79	0.01
Mn									1.00	0.69	0.86	0.15
Ni										1.00	0.51	-0.10
As											1.00	-0.17
Cd												1.00

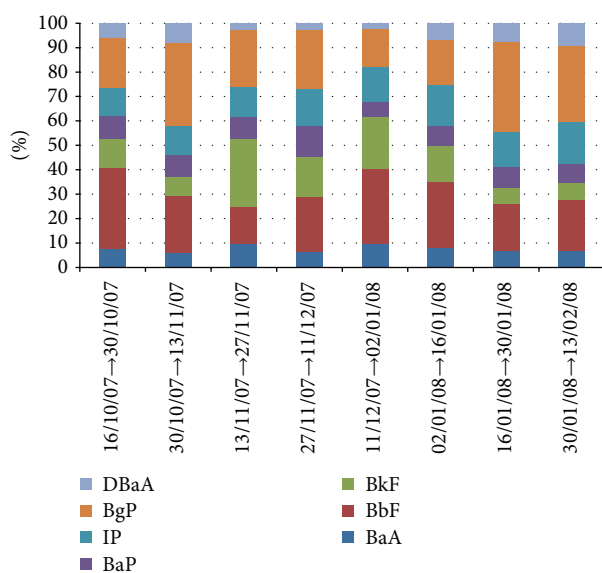
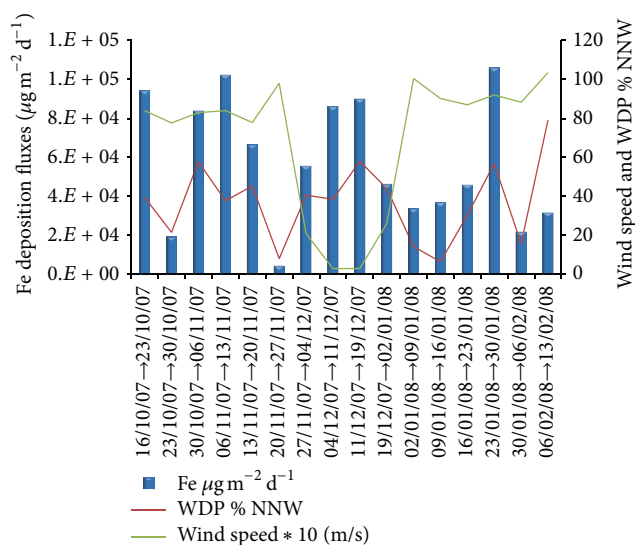


FIGURE 5: Percentage contributions of each PAH to the total deposition fluxes at the urban background site.

4. Conclusions

A high time-resolved monitoring campaign of bulk depositions of PAHs and metals was conducted at an industrial site (sampling period of one week) and at an urban site (sampling period of two weeks) in province of Taranto from October 16, 2007, to February 13, 2008. The analysis of deposition fluxes and the study of the impact of meteorological parameters enabled the evaluation of the impact of the biggest European steel plant on the surrounding area. It was found that average deposition fluxes of BaP ($147.6 \text{ ng m}^{-2} \text{ d}^{-1}$), BaA ($162.3 \text{ ng m}^{-2} \text{ d}^{-1}$), and BkF ($140.9 \text{ ng m}^{-2} \text{ d}^{-1}$) at the industrial site were on average 10, 14, and 8 times higher than those detected in urban sites, respectively. The impact of the industrial was also confirmed by diagnostic ratios as IP/(IP + BgP), IP/BgP, and BaP/BgP. The same findings were obtained for most metals. The deposition fluxes of Ni ($19.8 \mu\text{g m}^{-2} \text{ d}^{-1}$), As ($2.2 \mu\text{g m}^{-2} \text{ d}^{-1}$), Fe ($57 \text{ mg m}^{-2} \text{ d}^{-1}$),

FIGURE 6: Fe deposition fluxes ($\mu\text{g m}^{-2} \text{ d}^{-1}$), wind speed (m/sec), and probability of wind direction (WDP) from North-North-West (NNW) in percentage at the industrial site.

and Mn ($1.02 \text{ mg m}^{-2} \text{ d}^{-1}$) at industrial site were 6, 5, 31, and 31 times higher than those determined at urban site, respectively. Therefore, this work has enabled us to obtain useful information about deposition fluxes of micropollutants near the biggest European steel plant, information not available in the literature up to now.

Conflict of Interests

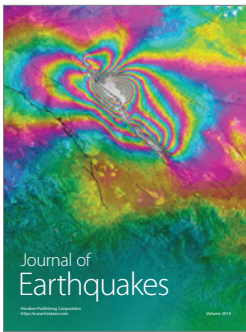
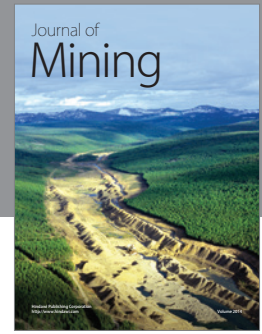
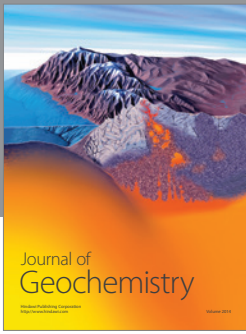
The authors declare that there is no conflict of interests regarding the publication of this paper.

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