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Total p-PAH Levels Nearby a Complex Industrial Area: A Tailored Monitoring Experiment to Assess the Impact of Emission Sources

Alessia Di Gilio [1,*] , **Jolanda Palmisani** [1,*] , **Livia Trizio** [2], **Gaetano Saracino** [2], **Roberto Giua** [2] **and Gianluigi de Gennaro** [1]

1   Department of Biology, University of Bari Aldo Moro, via Orabona 4, 70126 Bari, Italy; gianluigi.degennaro@uniba.it
2   Regional Agency for Environmental Prevention and Protection (ARPA Puglia), Corso Trieste 27, 70126 Bari, Italy; l.trizio@arpa.puglia.it (L.T.); g.saracino@arpa.puglia.it (G.S.); r.giua@arpa.puglia.it (R.G.)
*   Correspondence: jolanda.palmisani@uniba.it (J.P.); alessia.digilio@uniba.it (A.D.G.); Tel.: +390-80544-3343 (A.D.G.)

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Abstract: In this study, data on the hourly concentrations of the total particle-bound Polycyclic Aromatic Hydrocarbons (p-PAHs) collected between 1 August 2013 and 31 August 2014 by the air quality fence monitoring network of the biggest European steel plant, were analyzed. In contrast with what was predicted, the total p-PAH concentration did not decrease with distance from the steel plant, and higher concentrations were registered at the Orsini site, in the urban settlement, relative to the Parchi site, which is nearest to the coke ovens. Therefore, in order to identify and explain the cause of these high concentrations, a tailored monitoring experiment was carried out on a specific monitoring pathway by using a total p-PAHs monitor placed onto a cart. The real-time monitoring of the total p-PAH concentration on the road revealed to be a useful tool, which identified vehicular traffic as an important source of p-PAHs and highlighted the possible high short-term effect that vehicular traffic sources could have on the health of the exposed human population. Moreover, the study focused attention on the importance of the spatial representativeness of fixed monitoring stations, especially in a highly complex industrial area such as Taranto (Southern Italy).

Keywords: steel plant; vehicular traffic emission; total p-PAHs; high-time resolution monitoring; industrial area

1. Introduction

Polycyclic Aromatic Hydrocarbons (PAHs) are usually emitted from the incomplete combustion or pyrolysis of organic matter, such as petroleum gas, coal, coke, gasoline, diesel and biomass, and thus they are ubiquitous pollutants in both urban and industrial areas. Although atmospheric PAHs can be present in air, both in the particulate or gaseous phase—the most hazardous for human health—they are classified as probable human carcinogens, especially those characterized by a high molecular weight and predominantly in the particulate phase [1–5]. Particle-bound PAHs (p-PAHs) are predominantly associated with the fine particulate matter fraction ($PM_{2.5}$), consisting of particles with an aerodynamic diameter smaller than 2.5 μm, and are able to deeply affect human health due to their intrinsic toxicity along with the high penetration capacity of $PM_{2.5}$ into human airways [6–8]. Moreover, the growing interest of the scientific community and stakeholders on p-PAHs is due to their demonstrated carcinogenicity and mutagenicity, especially regarding Benzo(a)pyrene (BaP) [1]. Therefore, human exposure to p-PAHs is an issue of concern for general public health protection. In the recent years, PAH concentrations have been monitored in several cities and metropolises worldwide,

in order to assess air pollution and identify the main sources of this dangerous pollutant class [9–17]. The main sources of PAHs are vehicular traffic, industrial processes, waste incineration, steel-plant activities and, in particular, the pyrolytic processes occurring inside coke ovens embedded in iron and steel plants, where coal is pyrolyzed to produce coke and pyrolytic gas. Indeed, integrated iron and steel plants release a great amount of PAHs through stacks, fugitive emissions and accidental spillages during operations of various manufacturing units. Even if stack emissions are well quantified by air pollution control, a relevant contribution of fugitive emissions could be underestimated due to difficulty in identification and quantification. Fugitive emission are usually due to leaks from the furnace door, from the lids that cover the charging ports and the off-take system. In addition, they could be associated with mechanical processes, such as coal bulk handling, processing and charging [18,19]. Therefore, as reported in several papers in the literature, their contribution must not be neglected. Especially in highly industrialized areas, fugitive emissions may contribute to pollutant concentrations, such as PAHs, even more than stack emissions [17–20]. On the basis of the experimental evidence progressively obtained over the years, several investigations were carried out in the industrial area of Taranto (Southern Italy), where a complex industrialized area, including the biggest steel plant in Europe and other critical industrial and commercial activities, rises near the urban settlement that is prevalently downwind [21–25]. In all the studies carried out so far, the impact of fugitive emissions from the steel plant on the close urban settlement has been deeply explored. The acquired knowledge on the issue and the collected experimental data allowed the Italian legislators in 2012 to force the steel plant to equip itself with a fence monitoring network, consisting of high time-resolved analyzers capable to monitor total p-PAHs in real time. After the implementation of the fence monitoring network, a preliminary treatment of the experimental data collected over the period 1 August 2013 to 31 August 2014 highlighted that the spatial distribution of the total p-PAH concentrations was worthy to be more deeply investigated. Higher total p-PAH concentrations were registered at a site included in the fence monitoring network and located in the urban area, further away from the coke ovens than the other sites. These concentrations, indeed, were higher than expected on the basis of the distance from the industrial source. Therefore, the aim of the study was to develop a monitoring approach to provide answers and scientific explanations to the question claimed by both the authorities and the exposed population: "Why are the total p-PAH concentrations in the urban area higher than those observed at the other monitoring sites included in the fence monitoring network of the steel plant?". For this purpose, a tailored monitoring experiment was carried out on specific pathway by using a total p-PAHs analyzer placed onto a cart.

2. Materials and Methods

In the recent years, the scientific community paid more and more attention to the use of high-temporal resolution analyzers because they revealed to be useful tools to collect more detailed and time-resolved information about PAH concentrations. Indeed, these devices are able to monitor the daily profile of pollutant concentrations with a high temporal resolution, and are cheaper if compared to the traditional methodological approaches (e.g., filter-based sampling and GC/MS analysis) in terms of analytical costs and personnel working hours [20–25]. Therefore, during the last decade, several studies were carried out in order to compare real-time and conventional measurement of PAH concentrations. In particular, some previous studies revealed good correlation determination coefficients (R^2), ranging from 0.76 to 0.82, for a wide variety of emission sources, including oil burner exhaust, parking garage air, cigarette smoke, burners and urban aerosols [26–30].

2.1. Monitoring Site Description

Monitoring of real-time concentrations of total p-PAHs was performed in a delimited area around the iron and steel plant of Taranto (40°28′ N, 17°14′ E). Taranto is the third most populated city in Southern Italy and its industrial area is characterized by (a) one of the biggest steel plants in Europe; (b) a petrochemical center; (c) a cement plant; (d) a military and trade harbor; and (e) a naval

shipbuilding industry (Figure 1a). Taking into account the complexity of the industrial area and his proximity to urban settlements, Taranto has been identified as an area of high environmental risk in Italy and has been included in the list of polluted sites of national interest. Therefore, in order to evaluate the impact of the steel plant on the health of the exposed population, an air quality fence monitoring network was installed around the steel plant since August 2013. It consists of four stations located along the external plant perimeter (Portineria, Direzione, RIV1 and Parchi), one site located inside the plant near the coke ovens (Cokeria) and one site located in an urban settlement down-wind of the steel plant (Orsini) (Figure 1b). The fence monitoring network coexists in the investigated area with the Regional Air Quality Network, whose monitoring station closer to the steel plant in the urban settlement is named Machiavelli (Figure 1b). In Figure 1b, in addition to the monitoring sites, the main emissions sources inside the steel plant are reported: a mineral park where carbon, iron and manganese minerals are stocked, twelve coke ovens, five blast furnaces and two sinter plants (SP).
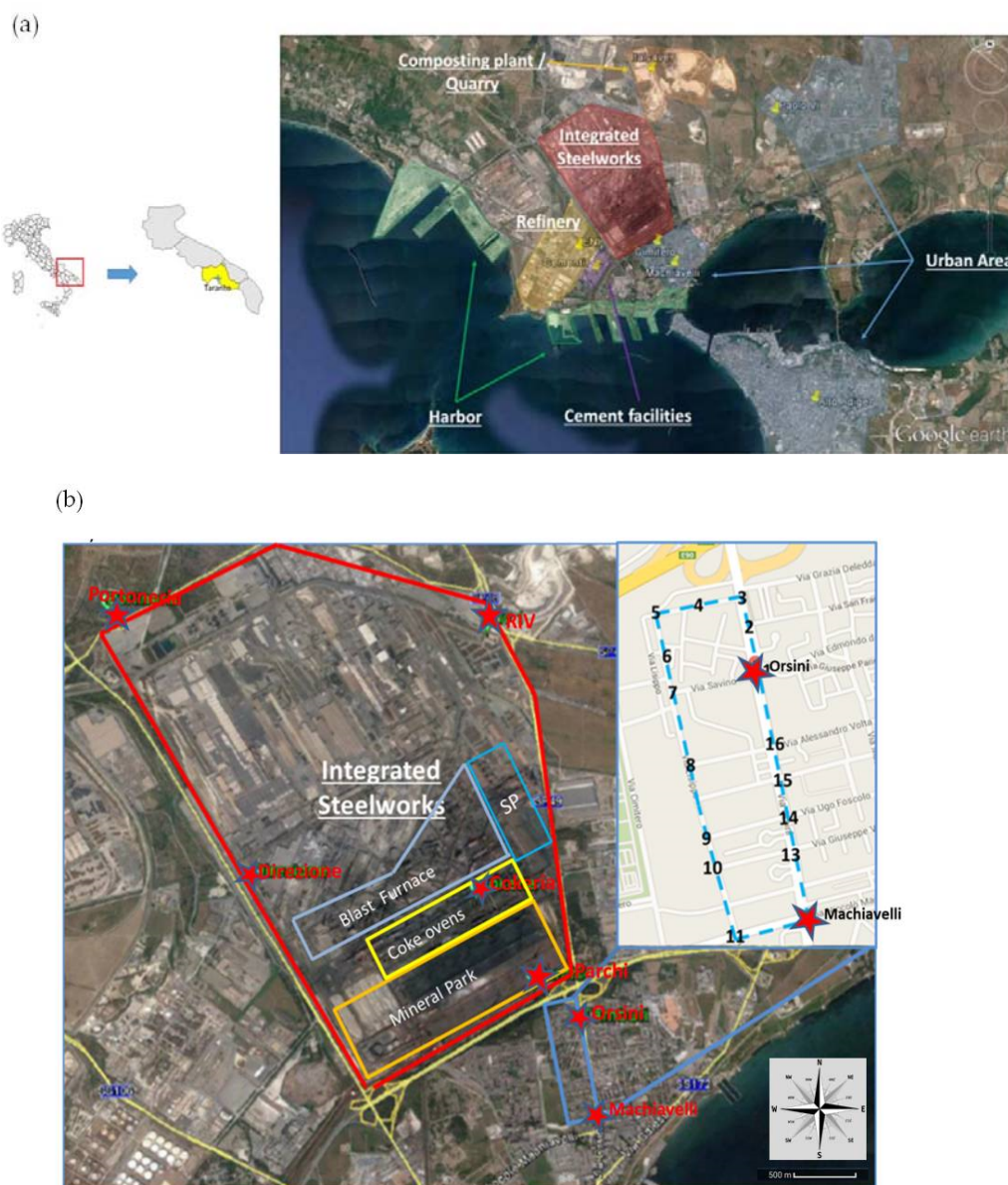

Figure 1. Location of the industrial area of Taranto with respect to Italy and the main industrial activities in this area (**a**); and the monitoring stations inside and surrounding the steel plant and the main emission sources in the steel plant (**b**). Mobile monitoring pathway (insert in (**b**)).

2.2. Monitoring Equipment at the Fixed Stations

The monitoring campaign regarding the total p-PAH concentration at fixed environmental monitoring stations, included in the fence monitoring network and the Regional Air Quality Network, was performed by means of high-temporal resolution analyzers (Ecochem PAS 2000, EcoChem Analytics, League City, Texas, USA). The microscale siting of all the inlet points was according to the Directive 2008/50/CE at about 3 m above the ground. At each site the air flow (2 L/min) was conveyed through a PFA tube (Tygon®) with an inner diameter equal to 4.8 mm, connected to an ambient temperature thermo-regulated manifold before entering the total p-PAHs analyzer. The Ecochem PAS 2000 analyzer does not require a sampling head but allows to measure with high temporal resolution the concentration of total p-PAHs (adsorbed onto the surface of the carbonaceous particles) by benefiting of the photoionization process occurring at a 207 nm wavelength. The operating principle is described as follows: ultraviolet radiation from an excimer lamp determines the ionization of chemicals, adsorbed onto carbonaceous particles, and having a photoionization potential equal to or less than 5.6 eV. The current generated by the photoionization is then measured by an electrometer and it is proportional to the concentration of the p-PAHs. The Ecochem PAS-2000 analyzers used in this study allowed to measure the total p-PAH concentration in the range of 0.01 and 5000 ng/m^3 with a nominal detection limit of 3 ng/m^3. A calibration procedure was performed by the manufacturer before the start of the monitoring campaign and every six months since then. Moreover, quality assurance measures were carried out, including flow and zero bi-weekly checks. All devices were synchronized to a satellite-signaled clock before the start of the monitoring campaign.

2.3. Data Analysis

In this study, the data about the real-time concentrations of total p-PAHs and the meteorological information (i.e., wind speed and direction, atmospheric temperature, pressure and relative humidity) determined for all the monitoring sites included in the fence monitoring network, and for the Machiavelli site included in the Regional Air Quality Network, were downloaded for the period 1 August 2013 to 31 August 2014 by the website of the Regional Agency for Environmental Protection (ARPA Puglia) and statistically treated. In order to localize the pollutant sources, bivariate polar plots of the meteorological data and pollutant concentrations were obtained by using R software, version 3.1.0, portioning wind speed, wind direction and concentration data into wind speed–direction bins and calculating the mean concentration for each bin. Each bin is characterized by wind direction intervals of 10 degrees and wind speed intervals of about 20 m s^{-1}, because several papers have demonstrated that they capture sufficient detail of the concentration distribution [31–33].

2.4. Mobile Monitoring Experiment

On the basis of preliminary results, in the present work a tailored mobile experiment for p-PAH real-time monitoring was also developed to deepen the understanding of the phenomena affecting the high concentrations of total p-PAHs measured at the Orsini site in the urban settlement, denominated the 'Tamburi neighborhood'. In more detail, the total p-PAH real-time concentrations were registered from about 12:00 to 15:00 p.m. on 30 July 2014 along a pathway in the urban settlement, properly chosen for the study purposes. The tailored monitoring experiment was performed (insert in Figure 1) by means of an EcochemPAS 2000 analyzer connected to an Uninterruptible Power Supply (UPS) and manually transported onto a cart. The data were collected along a 1.5 km pathway and at 17 different pit stops, placed at each street corner, for about 5 min. The distance from the steel plant to the farthest pit stop along the pathway was about 1.5 km. In order to avoid that the industrial source contribution was deliberately left out, the mobile monitoring campaign was performed during the hours when the prevailing wind direction at the Orsini site (insert of Figure 1b) was northwest, allowing pollutant transport from the steel plant to the urban settlement. Therefore, during the monitoring hours, the wind direction was NW and the mean wind speed was about 4.1 ms^{-1}.

3. Results and Discussion

Total p-PAH hourly concentrations collected from 1 August 2013 to 31 August 2014 for all the investigated monitoring sites ranged from below the Detection Limit (DL) of 3 ng/m^3 to 508 ng/m^3 and the yearly trend of these concentrations for each monitoring site did not show a significant seasonal difference. In previous studies of the Taranto industrial area, it was widely demonstrated that the impact of the steel plant on the surrounding urban area was so significant that no remarkable variation could be observed, neither across the seasons nor within a single day [21,22]. Moreover, the p-PAHs reactivity (e.g., nitration and oxidation) was deeply investigated, highlighting that the contribution of reactivity in the atmosphere on the p-PAH concentrations at the receptor sites nearby the steel plant was negligible due to the high proximity to the emission source [22]. Anyway, a strong correlation between total p-PAH concentrations and wind direction was found and in particular between pollutant concentrations and wind blowing from the coke ovens to the single monitoring site. As shown in Figure 2, the bivariate polar plot related to the total p-PAH hourly concentrations collected from 1 August 2013 to 31 August 2014 for all the investigated monitoring sites, highlighted that high total p-PAH values occurred at sites downwind from the coke ovens, and at those closer to them. Indeed, the polar plots showed higher values (red-yellow area) in correspondence with the wind blowing from the steel plant to the receptor sites. The only exception was registered at the RIV1 site, where the relatively lower correlation between total p-PAH concentrations and wind direction from the coke ovens could be explained considering that a heavy traffic road runs along this site. Moreover, the highest hourly values were registered at the Cokeria site (maximum value equal to 508 ng/m^3) due to its proximity to facilities where the combustion processes occurred. However, despite the expected decreasing trend of total p-PAH concentrations with the distance from the coke ovens, anomalous higher hourly concentrations were registered at the Orsini site (maximum value equal to 358 ng/m^3), a site included in the fence monitoring network even if located inside the urban settlement. More specifically, the Orsini site showed a total p-PAH concentrations higher than those registered at the Parchi site, the latter being closer to the coke ovens and under low wind speed conditions (<1 m s^{-1}). These findings suggested that vehicular traffic at the Orsini site was probably the most predominant source of p-PAHs, playing an important role in the dispersion of pollutants [10–16].

The mean values and standard deviations of the total p-PAH hourly concentrations, measured on an annual basis at both industrial and urban sites, are reported in Figure 3. In addition, in Table 1, the two-tailed *p*-values obtained by applying Welch's *t*-test to the data set related to the total p-PAH hourly concentrations measured at the Orsini, Machiavelli, Parchi and Cokeria sites are reported. The obtained two-tailed *p*-values were generally lower than 0.05, and the absolute values of the test statistic were higher than the t critical values, confirming that the four population means were statistically different. More specifically, the mean value of total p-PAH hourly concentrations at the Orsini site was significantly higher than that at the Cokeria site, the closest monitoring station to the coke ovens, and more than three times higher than the mean value at Machiavelli site, an urban monitoring site very close to the Orsini site (Figure 3). Findings published in previous papers showed the absence of seasonal variation for PAH atmospheric concentrations at all sites in the surroundings of the steel plant [20,21,25], and highlighted the strong correlation between wind direction and the highest PAH concentrations, regardless of the season. On the contrary, in the present study a seasonal variation of p-PAH concentration was observed for the Orsini site: 16.15 ± 11.76 ng/m^3 for summertime and 40.03 ± 45.02 ng/m^3 for wintertime.
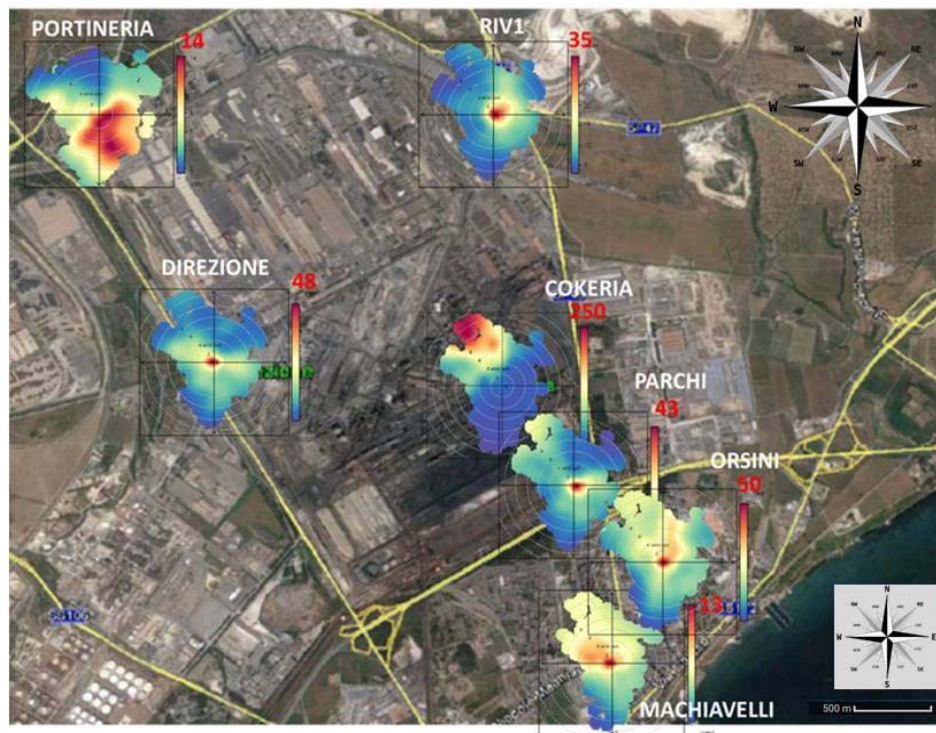
Figure 2. Polar plot of hourly total p-PAH concentrations (ng/m^3) monitored at seven sites included in the fence monitoring network of the steel plant from 1 August 2013 to 30 August 2014.
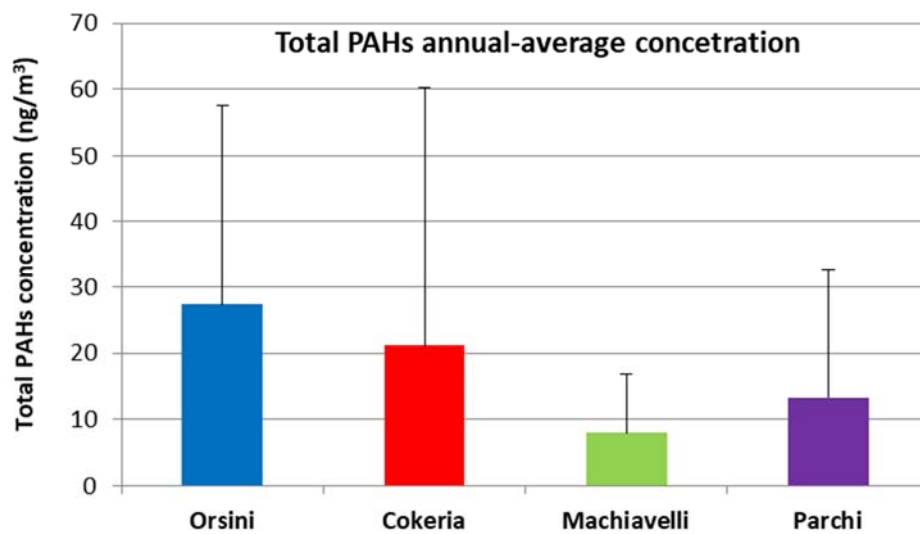

Figure 3. Annual average concentration and standard deviation of total p-PAH concentrations at the Orsini, Cokeria, Machiavelli and Parchi sites from August 2013 to August 2014.

Table 1. Welch's *t*-test results.

Welch's *t*-test	Two-tailed *p*-Value	*t*-Stat	*t*-Critical
ORSINI vs. COKERIA	1.26×10^{-32}	11.92	1.96
ORSINI vs. MACHIAVELLI	2.93×10^{-4}	3.62	1.96
ORSINI vs. PARCHI	6.54×10^{-13}	7.19	1.96
COKERIA vs. PARCHI	1.33×10^{-4}	57.02	1.96
COKERIA vs. MACHIAVELLI	4.17×10^{-201}	30.93	1.96
MACHIAVELLI vs. PARCHI	6.75×10^{-215}	32.97	1.96
ORSINI: Weekdays vs. Sundays	1.1×10^{-20}	9.6	1.96

Moreover, the daily profile of total p-PAH hourly concentrations at the Orsini site showed high values from 6 to 10 a.m. (maximum equal to 57.2 ng/m^3) and from 6 to 9 p.m. (maximum equal to 38.9 ng/m^3); thus, due to the traffic flow in the morning rush hours [15]. The same trend was obtained for the Machiavelli site in the urban settlement while a constant trend was registered for the industrial Cokeria site (Figure 4).
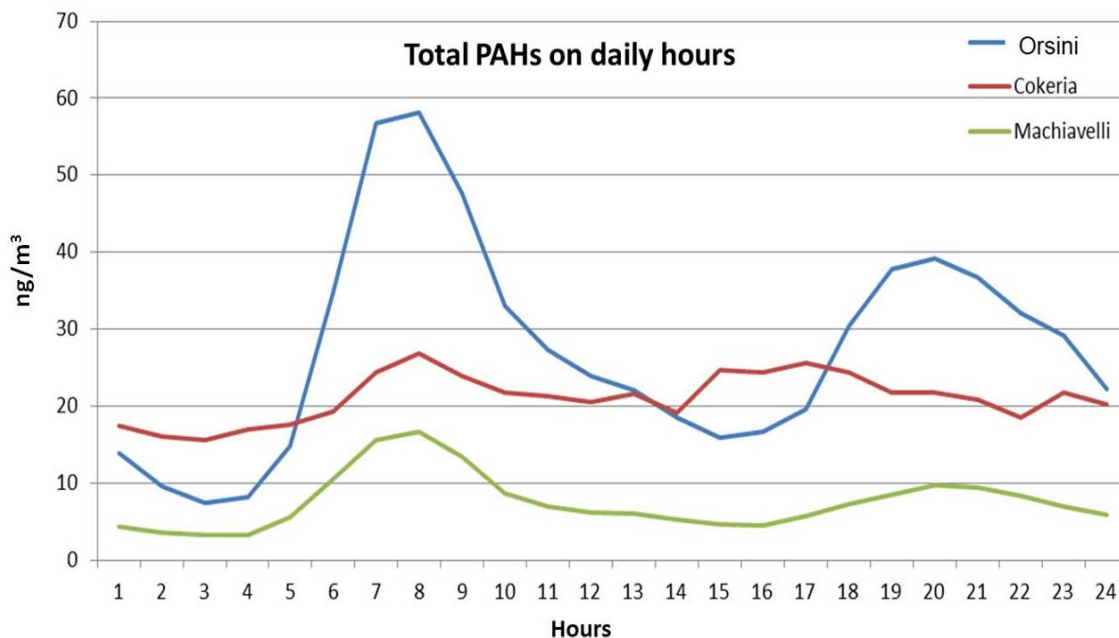

Figure 4. Average concentration of total p-PAHs for each hour of the day at the Orsini, Cokeria and Machiavelli sites. Data collected from 1 August 2013 to 31 July 2014.

These results suggested that the traffic contribution to total p-PAH concentrations at the Orsini site in the Tamburi urban settlement was not negligible with respect to the industrial one, as expected. This finding was also confirmed by the comparison between the mean concentration of total p-PAHs determined at the Orsini site during weekdays (Monday–Saturday) and during Sundays, equal to 28.4 ± 33.1 ng/m^3 and 21.5 ± 37.1 ng/m^3, respectively. Welch's *t*-test showed a two-tailed *p*-value equal to 1.1×10^{-20}, as well as an absolute value of the test statistic equal to 9.6. which is higher than the critical t value (1.96), confirming a significant difference between the means of the total p-PAH concentration measurements during weekdays and Sundays (as shown in Table 1) Moreover, unlike the Cokeria site, the daily profile of mean total p-PAH concentration during weekdays at the Orsini site showed a typical traffic profile, with higher values than those registered on Sundays (Figure 5).

Therefore, in order to explain the observed unexpected values and confirm the preliminary hypothesis of the existence of the additional traffic source at the Orsini site, a mobile monitoring experiment was ad-hoc designed and performed on-field by using a total p-PAHs analyzer placed onto a cart. The mean value of all the experimental data collected at the 17 pit stops (one at each street corner along the pathway) are reported in Table 2 and visualized on the map in Figure 6.
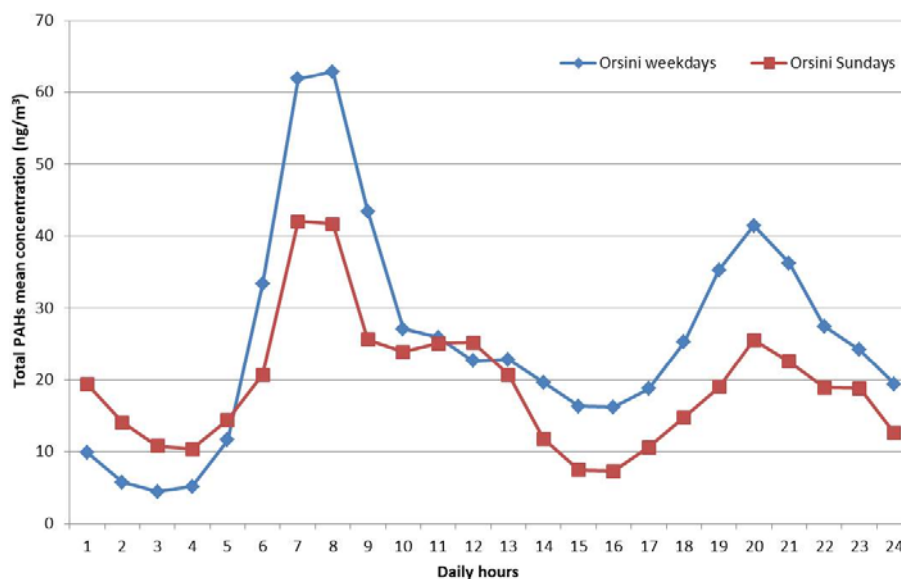
Figure 5. Total p-PAH mean concentrations during weekdays and Sundays at the Orsini site. Data collected from 1 August 2013 to 31 July 2014.

Table 2. Average values of the total p-PAH concentrations at the 17 monitoring points (pit stops).

Monitoring Points (MPs)	Total p-PAH Mean Concentration (ng/m^3)
MP 1	53
MP 2	38
MP 3	23
MP 4	44
MP 5	25
MP 6	12
MP 7	3
MP 8	8
MP 9	9
MP 10	19
MP 11	21
MP 12	27
MP 13	28
MP 14	119
MP 15	91
MP 16	65
MP 17	70

As shown in Figure 6, the two parallel streets of the monitoring pathway, although both downwind to the steel plant, did not show similar concentrations of total p-PAHs, decreasing with the distance from the industrial source and especially from the coke ovens. Taking into account the short duration of the monitoring experiment and the comparable traffic flow along both the parallel streets, it is possible to observe that the main street called Via Orsini showed higher values than via Lisippo, suggesting that this difference was due to the vehicular traffic source in addition to pollutant transport from the industrial source. The vehicular traffic source contribution was also confirmed by hourly concentrations of total p-PAHs, reported in Figure 7. The highest concentrations, indeed, were associated with the movement of both buses for public transportation and trucks that, through the urban streets, have direct access to the industrial area. Moreover, it is important to underline that the fixed environmental monitoring station Orsini is close to the bus station where vehicles stop for a while before leaving again. Therefore, the mobile monitoring experiment of total p-PAH concentrations revealed to be a useful tool to identify the vehicular traffic as an additional and not negligible source of p-PAHs and to

highlight the potential high short-term effect that vehicular traffic sources could have on the health of the exposed general population and, specifically, on those professionals, such as traffic policemen, spending a long time at the road crossings. Indeed, as shown in Figure 7, real-time total p-PAH concentrations (mean value equal to 33.4 ng/m^3) at the road crossings on the monitoring pathway can reach values higher than 1 µg/m^3, confirming the findings of previous studies performed in European, South American and Asian countries, such as Mexico City [13], Zurich [14], Beijing [14], Paris [34] and Tokyo [34] (Table 3). More specifically, in this study, higher concentrations were registered in correspondence with the bus stops along the monitoring pathway and were generally related to both bus and truck movement in the investigated area, suggesting that their contribution to the p-PAH concentrations is greater than that solely related to the passenger vehicles [35], and is similar to the biomass burning contribution [36]. Moreover, these peak concentrations were higher than those registered in other cities worldwide, such as Bangkok [10], Basel [16], Tokyo [10,27], Hong Kong [30], Aosta (Italy) [37], Quito (Ecuador) [38], Los Angeles [39] and Roxbury (Massachusetts) [40], where the highest hourly concentrations of total p-PAHs ranged from 186 ng/m^3 (Tokyo) to 475 ng/m^3 (Aosta) (Table 3).

Figure 6. Visualization of the mean values of the total p-PAH concentrations at the 17 monitoring points along the pathway.
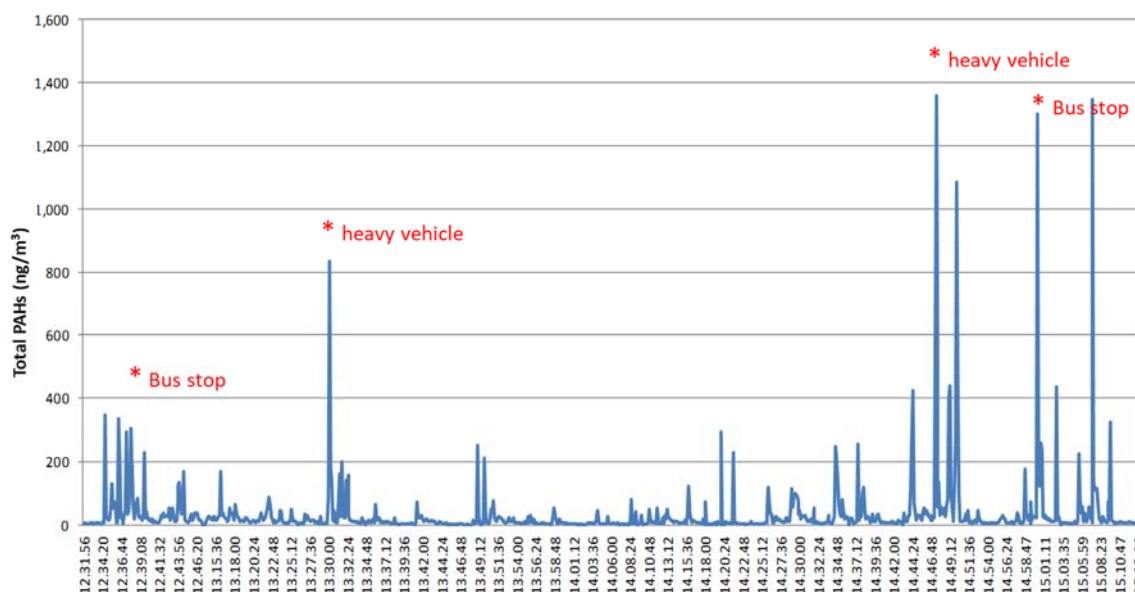
Figure 7. Real-time total p-PAH concentrations on the monitoring pathway. *: traffic source description.

Table 3. Average total p-PAH concentrations and the min–max range (ng/m^3) registered at urban sites in several cities worldwide.

City	Mean Total PAH Concentration (min–max Range), ng/m^3	Reference
Bangkok	(1–195)	[10]
Tokyo	(1–186)	[10]
	926 (3.4–1769)	[14]
Mexico city	(60–950)	[13]
Beijing	208 (1.8–5000)	[14]
Zurich	255 (10–900); 1950 (tunnel)	[14]
Basel	252	[16]
Hong Kong	260 (40–450)	[30]
Paris	659 (110–1400)	[34]
Aosta, Italy	475	[37]
Los Angeles	(10–430)	[39]
Roxbury (Massachussetts)	(0.3–340)	[40]
Taranto, Italy	33.4 (<DL-1358)	[41]

Although the reported comparison is among outdoor urban environments with different climate conditions and sampling site typology characteristics, it is considered useful in the discussion in order to highlight the potentialities of the high temporal resolution methodological approach in detecting short-term peak concentrations, otherwise not detectable with an experimental approach averaged over the time. It is, therefore, possible to point out that, although limited in time and in space, strong emissions of total p-PAHs at the Orsini site are strictly linked to buses and heavy vehicle/truck movement in addition to the industrial source contribution. The Orsini site, in substance, could be not fully considered as a representative site to monitor and assess the potential impact of the steel plant on the urban settlement of Taranto city.

4. Conclusions

Analysis of the data collected by the fence monitoring network of the steel plant in the industrial area of Taranto showed anomalous results. A monitoring site included in the fence monitoring network of the steel plant and which is closer to the urban settlement, the Orsini site, showed total p-PAH concentrations higher than those determined at other sites closer to the coke ovens. In order to identify

and better explain the cause of these high concentrations, a tailored mobile monitoring experiment was carried out by using a total p-PAHs analyzer placed onto a cart. The hourly monitoring of the total p-PAH concentrations on the road revealed to be a useful tool to a) identify the vehicular traffic as an important source of p-PAH concentrations at the Orsini site; and thus b) to confirm that the Orsini site was not a representative site to evaluate the industrial impact of the steel plant on the urban area because it is placed along a main downtown street close to a bus station. The present study, therefore, highlights the need to accurately evaluate the spatial representativeness of the fixed environmental monitoring stations for air quality control. Moreover, the obtained results showed that the contribution of a vehicular traffic source cannot be neglected in the evaluation of the impact of total p-PAH concentrations on the exposed population living in urban settlements. Finally, it is necessary to take into account the potential high short-term effect that a vehicular traffic source could have on the health of professional people that spend a lot of time at road crossings.

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