An improved method to determine PM-bound nitro-PAHs in ambient air

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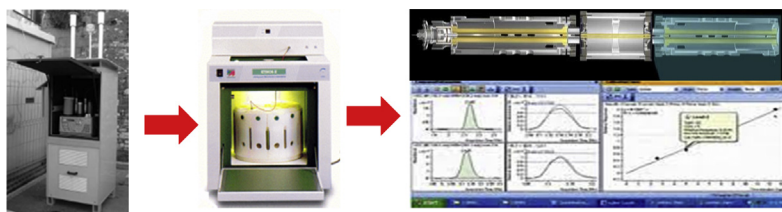
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HIGHLIGHTS

- Analytical method for analysis of fourteen particle-bound NPAHs was developed.
- PM10 microwave-assisted extraction and GC-QQQ-MS analysis were performed.
- High repeatability (RSD% < 10%) and sensitivity for NPAHs determination were obtained.
- NPAHs levels around the biggest European steel plant were determined.
- Primary and secondary NPAHs affect the area around the biggest steel plant in Europe.

GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

Nowadays, no a standard method for the determination of particulate bound nitro-PAHs (NPAHs) has been developed. Existing methods include complex sampling and extraction procedures. Moreover, their sensitivity does not allow to analyze daily PM10 samples, affecting the temporal resolution of NPAH concentrations. In this study an analytical method for the quantification of NPAHs on half 47 mm-filter samples of daily PM10 was developed and validated. NPAHs were recovered by microwave-assisted extraction, and analyzed by using a gas chromatography-triple quadrupole mass spectrometry in MRM mode. The analytical performance for 14 NPAHs (2-nitrofluorene, 9-nitroanthracene, 9-nitrophenantrene, 3-nitrophenantrene, 2-nitroanthracene, 3-nitrofluoranthene, 1-nitropyrene, 2,7-dinitrofluorene, 7-nitrobenzo[a]anthracene, 6-nitrochrysene, 1,3-dinitropyrene, 1,8-dinitropyrene, 1,6-dinitropyrene, 6-nitrobenza[a]pyrene) was investigated. Recovery extraction percentage exceeded 95% for all target compounds in the range between 0.25 and 10 ng/mL. The repeatability, expressed as Relative Standard Deviation percentage (RSD%) of five determinations, was less than 10% for target compounds except for 2,7-dinitrofluorene, 1,3- and 1,8-dinitropyrene (RSD% < 15%). The limit of detection (LOD) ranged from 12 to 84 pg/mL for most of NPAHs, except for dinitro-pyrenes and nitro-benzo(a) anthracene for which the LOD reached 1.8 ng/mL.

The method developed was applied to real samples in order to evaluate the levels of NPAHs in the urban and industrial area of Taranto (South of Italy). The analysis of PM10 samples collected at four industrial and one urban sites, highlighted that in proximity of critical emission source as the biggest

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European steel plant and under certain weather conditions, combustion processes were the main source of NPAHs in atmosphere.

1. Introduction

Particulate matter (PM) is a complex mixture of inorganic and organic species, which could adversely affect human health. In recent years, much attention has been paid to Polycyclic Aromatic Hydrocarbons (PAHs) and Nitro-Polycyclic Aromatic Hydrocarbons (NPAHs) because they include different potent carcinogens (IARC, 2010). NPAHs show toxic, carcinogenic, mutagenic and estrogenic properties higher than those of their parent-PAHs (Bamford et al., 2003; Wang et al., 1980). In fact, they are direct acting mutagens and produce reactive oxygen species, responsible for toxicity (Benbrahim-Tallaa et al., 2012). Incomplete combustion processes, such as emissions from coal and oil combustion, biomass burning, coke and aluminum production, vehicular transport, and waste incineration are the main sources of PAHs and NPAHs in atmosphere (Amodio et al., 2009; Benjamin et al., 2014; Karine et al., 2014; Marino et al., 2000; Okuda et al., 2010; Ringuet et al., 2012a; Zhang and Tao, 2008). Moreover, NPAHs can be formed directly in atmosphere due to photochemical reactions occurring among emitted parent-PAHs in gas phase and atmospheric oxidants and possibly microorganisms (Ringuet et al., 2012a; Vione et al., 2004; WHO, 2003). In details, these reactions are initiated by hydroxyl radicals (OH) in the presence of NO_x during the day and by nitrate radical (NO_3) overnight (Wu et al., 2012). Additionally, NPAHs can be produced by the reaction of particulate PAHs with N_2O_5 or HNO_3 (Karine et al., 2014). Although NPAHs are produced in the gas phase, they are quickly adsorbed on the airborne particles. 2-nitrofluoranthene and 2-nitropyrene are ubiquitous components of particulate matter, although they are not directly emitted from most combustion sources (WHO, 2003). 1-Nitropyrene, 2-nitrofluorene and 3-nitrofluoranthene are the most abundant nitro isomers of pyrene, fluorene and fluoranthene in diesel exhaust. 2-Nitropyrene, 3-nitrofluorene and 2-nitrofluoranthene are the isomers formed during the hydroxyl radical reactions. WHO (2003) showed that the concentration of 1-nitropyrene was lower in gasoline exhaust than in diesel dust particles, while the concentrations of 1,3-, 1,6- and 1,8-dinitropyrenes were the same in both exhaust particles. The main particulate NPAHs in ambient air are 2-nitrofluorene, 9-nitroanthracene, 9-nitrophenanthrene, 2-, 3- and 8-nitrofluoranthene, 1- and 2-nitropyrene, 1,3-, 1,6- and 1,8-dinitropyrene and 6-nitrochrysene. They are usually present in smaller quantities than their parent-PAHs and, at remote sites, NPAHs could be not detected or not exceeded few pictogram per cubic meter. NPAH concentrations in the atmosphere depend on the season, the type and number of sources (heating used, traffic vehicles and industrial plants). Previous studies reported NPAH levels in air lower than 1 ng/m^3 (Karine et al., 2014; WHO, 2003). Therefore, the complexity of atmospheric samples and the expected low concentration range of NPAHs require highly sensitive and selective analytical methods to be optimized. Existing methods include complex sampling and extraction procedures. Ultrasound and soxhlet extraction with HPLC/FL are widely used (Albinet et al., 2008; Barrado et al., 2013). In this case, derivatization of the nitro-compounds is usually required, lengthening the analysis time (Albinet et al., 2008; Delhomme et al., 2007; Kakimoto et al., 2001; Ohno et al., 2009; Portet-Koltalo et al., 2008; Reisen and Arey, 2005; Tang et al., 2005). Other methods are based on gas chromatographic separation followed by electron capture detection (GC-ECD, Campbell and Lee, 1984), negative and positive ion chemical ionization mass spectrometry (GC-NCI-MS, Robbat et al., 1986; Bezabeh et al., 2003), or flame ionization detection (GC-FID, Paschke et al., 1992). These techniques require the separation and preconcentration of the extracts through laborious clean-up procedures using silica gel columns (Chiang et al., 2012; Ding et al., 2012). Therefore, little or no information are still available on ambient NPAH concentrations in Italian urban and industrial areas. In particular, there is no information on NPAH levels at the industrial area of Taranto, identified as an area of high environmental risk in Italy due to the proximity of the biggest steel plant in Europe to urban area. Although several studies were carried out in the last decade to assess the air quality in Taranto, no monitoring campaign was performed to quantify NPAHs near the steel plants and in the city of Taranto (Amodio et al., 2014, 2013a, 2013b, 2011, 2009; Bruno et al., 2006). This work aimed at developing and validating a highly sensitive analytical method for the quantification of particulate NPAHs starting from the procedure used for PAHs determination (Bruno et al., 2007). Briefly, GC analysis was carried out using an injection system characterized by a programmable temperature vaporization (PTV) and applying MS detection with an inert mass ion source and a triple quadrupole mass spectrometer (QQQ). The performance of the method for the determination of 14 NPAHs (2-nitrofluorene, 9-nitroanthracene, 9-nitrophenantrene, 3-nitrophenantrene, 2-nitroanthracene, 3-nitrofluoranthene, 1-nitropyrene, 2, 7-dinitrofluorene, 7-nitrobenzo[a]anthracene, 6-nitrochrysene, 1, 3-dinitropyrene, 1, 8-dinitropyrene, 1, 6-dinitropyrene, 6-nitrobenza[a]pyrene) were investigated. The accuracy of this method was evaluated by analyzing the method detection limit, average recovery percentage, the linear correlation coefficients, and the analytical repeatability. Then, the optimized procedure was applied on real samples collected near the industrial area and in downtown Taranto (Italy).

2. Material and methods

2.1. Real sample

PM10 samples were collected at five sampling sites located around the industrial area of Taranto at different distances from it. Taranto (40°28′N 17°14′E) is the third most populated city of the Southern Italy and hosts the biggest steel plant running in Europe. In addition, metallurgical, chemical, petrochemical and cement-producing plants, military and trade harbor and naval ship-building industry are all located in close proximity to city. Daily PM10 samples were collected from 25th to 31st May 2011 at four sites next to the industrial area (Cimitero and Machiavelli) and at one site in the city center (Alto Adige) (Fig. 1). In details, Cimitero (40°29′N, 17°13′E) Machiavelli (40°29′N, 17°13′E) and Alto Adige (40°27′N, 17°15′E) sites were located South- South- Est of the steel plant and, Eni (40°29′N, 17°11′E) and Cementir (40°29′N, 17°11′E) sites were to its South-South West. The PM samples were collected on 47-mm-diameter quartz fiber filters by a low volume samplers (HYDRA-FAI Instruments s.r.l., Roma, Italy) using sampling heads of FAI EN 1234.1 which operated at a flow rate of 2.3 m^3 h^{-1}. The collected filters were conditioned before and after sampling (25 °C

during 48 h and 50% humidity) and the PM10 concentrations were determined by the gravimetric method. Finally, the filters were stored in a refrigerator at 4 °C before NPAH and PAH analyses (UNI EN 15549, 2008).

2.2. Preparation of standards

The standard solutions of native NPAHs (AccuStandard Inc., USA) and deuterated PAHs (Sigma Aldrich Co., USA) were prepared in hexane–acetone (1:1) mixture. The calibration curves were obtained by dilutions of both standard solutions at six levels of concentrations (0.25, 0.5, 1.0, 2.5, 5.0, 10 ng/mL). Two deuterated PAHs (PAHs-d: benzo[a]pyrene-d12, Perylene-d12) were added to the NPAH solution under investigation as internal standards.

2.3. Extraction

NAPHs and PAHs adsorbed on half of PM filter were simultaneously recovered in 10 mL acetone/hexane mixture (1:1) by microwave-assisted extraction (MAE, model Ethos D, Milestone s.r.l, Italy). This technique combines microwave heating with magnetic stirring of extraction solvent inside closed sample vessels. Agitation ensures homogeneous mixing and uniform temperature distribution throughout extraction mixtures. The procedure was optimized in order to perform a simple, fast and efficient extraction of NPAHs collected on 47 mm sampled filters. In details, amount of solvents, microwave power and extraction time were studied. The best extraction conditions are listed in Table 1. The same procedure

was applied to standard solutions.

2.4. Analytical determination

The extracts were analyzed using an Agilent 7000A GC/MS Triple Quadrupole System (Agilent Technologies Inc, USA) consisting of a High-Performance 7890A gas chromatograph (Agilent Technologies Inc, USA), a programmable temperature vaporization injection system (PTV) and a triple quadrupole mass spectrometer (QQQ) equipped with an inert ion source (7000 series MS, Agilent Technologies Inc, USA). The analytical parameters were optimized and the best obtained ones are listed in Table 2. NPAH quantitative determinations were performed in Multiple Reaction Monitoring (MRM) mode. The retention time (RT), the internal standard used (IS), precursor and product ions monitored for each NPAHs and PAH-d are listed in Table 3.

Table 1
Operating conditions for the optimized extraction procedure.

Extraction parameters	
Solvent	Acetone (5 mL) - Hexane (5 mL)
Volume	10 mL
Time	25 min
Temperature	110 °C
Power	200 W
Vent	5 min

Fig. 1. Map of sampling sites in Taranto.

Table 2
Operating conditions for GC–MS analysis.

GC-QQQ parameters	
PTV temperature	50 °C for 1.2 min, ramp to 300 °C at a rate of 720 °C/min
Vent end time	1.0 min
Vent flow	50 mL/min
Purge time	2 min
Injection volume	10 μL (solvent vent mode)
Analytical column (Rxi R-17Sil MS)	30 m × 0.25 mm ID, 0.25 μm (Crossbond R silarylene phase)
Mobile phase	He
Internal standard	Perylene-d_{12}; Benzo[a]pyrene-d_{12}
Column flow	1.3 mL/min (constant flow mode)
Oven temperature	47 °C (hold time 2.5 min), ramp to 210 °C at a rate of 30 °C/min, ramp to 300 °C At a rate of 5 °C/min (hold time 15 min)
EI Ion source temperature	290 °C
Acquisition mode	Multiple Reaction Monitoring (MRM)

3. Results and discussion

The analytical method proposed in this study, was validated through the determination of fourteen NPAHs: 2-nitrofluorene, 9-nitroanthracene, 9-, 3-nitrophenanthrene, 2-nitroanthracene, 3-nitrofluoranthene, 1- nitropyrene, 2, 7-dinitrofluorene, 7-nitrobenzo[a]anthracene, 6-nitrochrysene, 1, 3–1, 6- and 1, 8-dinitropyrene and 6-nitrobenzo[a]pyrene.

In order to test the recovery of the extraction method, a half of

Table 3
Retention time (RT), precursor and product ions monitored for each NPAHs and for deuterated PAHs used as Internal standard (IS).

Composti	Retention time	Precursor ion	Product ion
2 - Nitrofluorene	15.23	165	139
9 - Nitroanthracene	15.67	176	165
9 - Nitrophenanthrene	16.74	165	165
3 - Nitrophenanthrene	17.39	223	176
2 - Nnitroanthracene	18.19	223	176
Benzo(a)anthracene-D12 (IS)	19.60	240	236
3 - Nitrofluoranthene	22.02	200	174
1 - Nitropyrene	23.15	201	176
2,7 - Dinitrofluorene	24.58	163	163
7 - Nitrobenz[a]anthracene	26.89	226	200
6 - Nitrochrysene	25.48	226	200
Perylene - D12 (IS)	26.85	264	260
1,3 - Dinitropyrene	31.46	200	174
1,8 - Dinitropyrene	28.68	200	174
1,6 - Dinitropyrene	31.11	200	174
6 - Nitrobenz[a]pyrene	34.70	267	239

47 mm diameter quartz blank filter were spiked with known amounts of NPAHs standard solution and of internal standard in accordance with UNI EN 15549:2008. Six level of concentrations were tested in triplicate. The percentage of recovery extraction exceeded 95% for all target compounds (Table 4). The repeatability, expressed as relative standard deviation percentage (RSD%) calculated on five determinations of a spiked sample (five extractions for each amount), was showed in Table 4. RSD% values were less than 10% for most target compounds, except for 2,7-dinitrofluorene, 1, 3- and 1, 8-dinitropyrene (RSD% below 15%). The repeatability of the method and recoveries percentage were independent of the amount of NPAHs spiked onto the filter in the range between 0.25 and 10 ng/mL (Fig. 2). The limits of detection (LOD) and quantification (LOQ) were calculated as 3 and 10 times the average of the height of the noise at the retention time of each detected ±10 times the peak width at half-height determined for the lowest calibration level, respectively (UNI EN 15549, 2008). LOD and LOQ values in atmosphere, expressed in ng/m^3, were calculated considering the nominal daily sampling volume (sampling period of 24 h with a volumetric flow of 2.3 m^3/h) and listed in Table 4.

The linearity of response was evaluated over the range between 0.25 ng/mL and 10 ng/mL by using six concentration levels and five replicates for each level. The curves of calibration for each NPAHs were obtained by considering the response factors, multiplying the ratio between the peak area of analyte and of internal standard by the ratio between their mass. Data analysis by least-squares estimation method showed good linearity of response for all investigated compounds ($R^2 > 0.993$). Taking into account the homogeneity of filter tested in previous work (Bruno et al., 2007),

Table 4
Limit of detection (LOD) and limit of quantification (LOQ) for all investigated NPAHs in solution (pg/ml) and in atmosphere (ng/m^3). Relative standard deviation (R.S.D.%) and recovery percentage for triplicate extractions on six concentrations levels.

Compounds	LOD ng/mL	LOQ ng/mL	LOD ng/m^3	LOQ ng/m^3	RSD% Max - min	Recovery % (0.25–10 ng/L)	R^2 (N:30)
2 - Nitrofluorene	0.049	0.16	0.018	0.059	7.2–1.6	≥95%	0.999
9 - Nitroanthracene	0.049	0.16	0.018	0.059	3.2–0.7	≥96%	0.999
9 - Nitrophenanthrene	0.036	0.12	0.013	0.043	4.2–0.6	≥96%	0.999
3 - Nitrophenanthrene	0.085	0.28	0.031	0.10	5.6–0.1	≥98%	0.999
2 - Nnitroanthracene	0.040	0.132	0.014	0.048	5.9–0.7	≥98%	0.999
3 - Nitrofluoranthene	0.012	0.041	0.004	0.015	3.3–1.1	≥96%	0.998
1 - Nitropyrene	0.016	0.055	0.006	0.020	3.6–0.1	≥99%	0.999
2,7 - Dinitrofluorene	0.084	0.28	0.030	0.10	12.8–0.8	≥98%	0.998
7 - Nitrobenz[a]anthracene	0.068	0.23	0.025	0.083	10.1–2.4	≥99%	0.999
6 - Nitrochrysene	0.053	0.18	0.019	0.064	7.9–1.4	≥98%	0.999
1,3 - Dinitropyrene	0.57	1.9	0.21	0.68	12.6–7.5	≥95%	0.999
1,8 - Dinitropyrene	1.4	4.6	0.498	1.7	9.4–5.7	≥95%	0.996
1,6 - Dinitropyrene	1.8	6.9	0.7	2.2	14.4–13.9	≥95%	0.993
6 - Nitrobenz[a]pyrene	1.4	4.5	0.5	1.6	6.8–2.8	≥96%	0.996

R^2 values for linear regression obtained by extracted standards analysis.
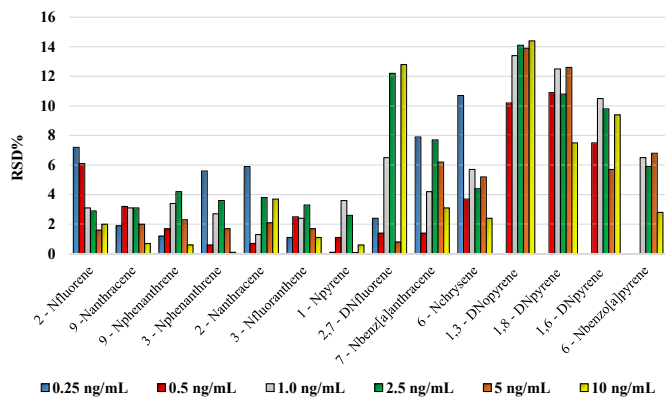
Fig. 2. Repeatability of NAPHs determination method, expressed as standard deviations percentage (RSD%) of five determinations of a spiked sample over the range between 2.25 ng/mL and 10 ng/mL.

Fig. 3. Average daily concentrations of sum of detected nitro-PAHs ($\sum$ NPAHs) at industrial (Cimitero, Machiavelli, Eni, Cementir) and urban (Alto Adige) sites of Taranto.

Fig. 4. Temporal trend of average daily concentrations of sum of nitro-PAHs ($\sum$ NPAHs) and PAHs ($\sum$ PAHs) at Cimitero site.

the high sensitivity of the proposed method allowed NPAH analyses by using a half of the 47 mm-diameter filter.

Finally, the method was applied to PM10 samples collected from 25 to 31 May 2011 at five sites of Taranto. Table 5 shows that PM10 concentrations exceeding the daily limit value (50 μg/m^3) were detected at Cimitero (25th and 29th May 2011) and Cementir sites (25th and 28th May 2011). The daily concentrations of NPAHs, the sum of NPAHs ($\sum$ NPAHs) and PAHs ($\sum$ PAHs) were determined for each sampling site (see Table 6). Cimitero site showed the highest NPAH concentrations with two maximums on 26 and 29 May 2011 (Fig. 3). Total NPAHs ranged from 1.27 to 5.43 ng/m^3 for the site nearest the steel plant (Cimitero) and from 0.63 to 0.84 ng/m^3 in the city center. Both these values were higher than those determined at industrial site Qingyuan (0.3–0.7 ng/m^3) in China (Wei et al., 2012) and at urban sites as Xi'an (0.3–2.5 ng/m^3) and Beijing (0.07–3 ng/m^3) in China (Bandowe et al., 2014; Wang et al., 2011), Sao Paulo (0.2–1.2 ng/m^3) in Brasil (de Castro Vasconcellos et al., 2008) and Paris (0.03–0.18 ng/m^3) in France (Ringuet et al., 2012b). The daily NPAH concentrations at Machiavelli site were lower than at Cimitero but higher than those measured at the industrial sites as ENI and Cementir and in Taranto center (Alto
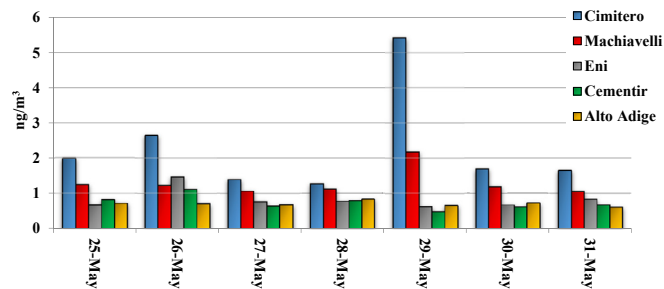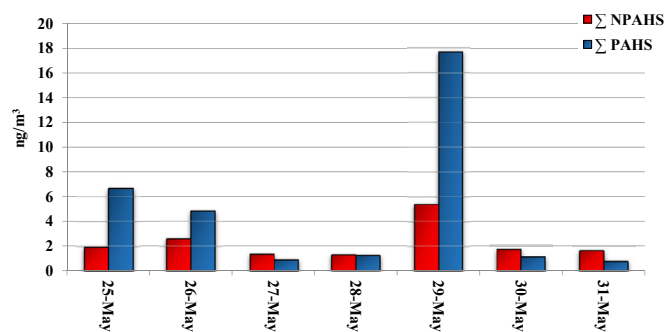
Adige), which showed comparable levels. Cimitero and Machiavelli sites probably suffered the proximity to steel plant (see Fig. 1). The high correlation between individual congeners (correlation coefficient > 0.85 with the exception of 2-nitroanthracene) suggested that most NPAHs have similar behavior in the atmosphere or were emitted from common sources. Similar temporal trend of the daily concentrations of nitro-PAHs and PAHs was found at Cimitero site (Fig. 4). Moreover, comparable daily concentrations occurred during other investigated days. This first finding suggested the presence of a common primary source for both pollutant classes.

Table 5
Daily PM10 concentrations measured for each sampling site.

	PM10 (μg/m^3) Cimitero	PM10 (μg/m^3) Machiavelli	PM10 (μg/m^3) Alto Adige	PM10 (μg/m^3) Cementir	PM10 (μg/m^3) Eni
25 May 2011	51.5	45.4	26.2	66.4	35.6
26 May 2011	44.6	38.2	28.9	77.6	48.7
27 May 2011	41.7	39.5	28.4	46.4	35.4
28 May 2011	35.6	36.8	26.8	58.2	45.8
29 May 2011	58.2	38.4	22.5	24.6	20.8
30 May 2011	31.8	24.9	20.4	27.4	22.2
31 May 2011	26.8	31.6	28.3	31.1	38.5

Table 6
Daily concentrations of the sum of NPAHs ($\sum$ NPAHs) and of PAHs ($\sum$ PAHs) for each sampling site.

	$\sum$ NPAHS (ng/m^3)					$\sum$ PAHS (ng/m^3)				
	Cimitero	Machiavelli	Alto Adige	Cementir	Eni	Cimitero	Machiavelli	Alto Adige	Cementir	Eni
25 May 2011	1.99	1.25	0.73	0.83	0.69	6.66	3.40	0.74	2.83	1.85
26 May 2011	2.65	1.25	0.72	1.12	1.48	4.86	1.55	0.76	5.29	7.68
27 May 2011	1.39	1.08	0.69	0.65	0.77	0.96	0.39	0.36	0.39	0.52
28 May 2011	1.27	1.14	0.84	0.81	0.78	1.22	0.74	0.59	1.63	0.67
29 May 2011	5.43	2.19	0.67	0.49	0.64	17.71	9.56	1.59	0.61	0.50
30 May 2011	1.70	1.21	0.74	0.62	0.69	1.15	0.59	2.16	0.22	0.62
31 May 2011	1.65	1.07	0.63	0.69	0.85	0.83	0.56	0.85	0.57	2.02

Table 7
Minimum (Min) and maximum (Max) of NPAHs daily concentrations for each sampling sites.

Daily concentration (ng/m^3)	Cimitero		Machiavelli		Alto Adige		Cementir		Eni	
	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max
2 - Nitrofluorene	0.97	2.64	0.23	0.91	0.07	0.17	0.10	0.37	0.09	0.46
9 - Nitroanthracene	0.07	0.18	0.07	0.12	<LOQ	0.07	<LOQ	0.08	<LOQ	0.08
9 - Nitrophenanthrene	0.14	0.38	0.10	0.09	0.05	0.08	0.05	0.10	0.05	0.14
3- Nitrofluoranthene	0.02	0.17	0.21	0.08	<LOQ	0.03	0.07	0.23	0.03	0.04
1 - Nitropyrene	0.02	0.06	0.04	0.13	0.03	0.04	0.03	0.04	0.03	0.05
2,7 - Dinitrofluorene	0.16	0.25	0.17	0.83	0.15	0.22	0.06	0.14	0.16	0.30
7 - Nitrobenz[a]anthracene	<LOQ	1.25	0.10	0.16	<LOQ	0.17	0.08	0.13	<LOQ	0.29
6 - Nitrochrysene	0.03	0.42	0.05	0.06	0.06	0.18	0.03	0.08	0.04	0.11

Furthermore, 2-nitrofluorene showed the highest concentration values among the NPAHs for all industrial sites reaching at Cimitero site 1.28 ng/m^3 and 2.64 ng/m^3 on the two peak days (see Table 7). The study of wind speed and direction highlighted that on 26th and 29th May the wind blew at high speed from N-NW direction, transporting micro-pollutants from the steel plant to Cimitero and Machiavelli sites. Thus, coal combustion processes in steel plant was probably the main source of both PAHs and NPAHs in Taranto under certain weather conditions.

Finally, according to Bandowe et al., 2014, in this study the ratio of the concentration of 3-nitrofluoranthene/1-Nitropyrene has been used to evaluate primary and secondary sources of nitro-PAHs. In fact, the first one is mainly formed by atmospheric photochemical reactions while the second originates mainly from primary emissions. At all sites investigated these ratio were lower than 5 (range from 0.8 to 2.5) suggesting that primary emissions are the main source of the atmospheric nitro-PAHs (Albinet et al., 2007, 2008; Bamford and Baker, 2003; Ciccioli et al., 1996).

4. Conclusions

The analytical method developed and validated in this study, enabled to determine ambient particle-bound NPAHs collected on a half of the sampled filter. In fact, the QQQ detector in MRM mode ensures high repeatability and sensitivity for this purpose. The main advantages using this analytical technique are the lower time-consumption for micro-pollutants determinations and the availability of the other half filter for the PM characterization (heavy metals, organic carbon, ions, etc.). The study of PAHs concentrations and meteorological data highlighted the impact of the industrial area of Taranto on NPAHs concentrations measured in urban area.

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