

PAH concentrations and seasonal variation in PM₁₀ in the industrial area of an Italian provincial town

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Abstract

A comprehensive campaign was performed from November 2006 to September 2007 in four sites in the industrial area of an Italian provincial town in order to fully understand the state and characteristics of the air pollution. As part of the work, 13 PAHs in PM₁₀ aerosols were chemically characterized in this study by GC/MS. The main aim of this study was identifying the seasonal variation of PAHs concentration and the distribution pattern associated with PM₁₀.

Keywords: PM10, PAHs, seasonal variation, GC/MS, BaP.

1 Introduction

Investigation of the origin of air pollution, its major sources and the importance of pollution from distant regions became increasingly important due to new limits that were set for PM₁₀ concentrations in EC-Directive 99/30/CE [1]. The Italian Ministry of Environment, as a response to the first daughter directive on air quality proposed by the European Commission (96/62/CE [2]), published the DM n. 60/2002 [3] in order to assess PM₁₀ pollution and monitor the ambient air quality in Italy. The new directive proposed the measurement of PM₁₀ concentrations and set limit values to be reached towards health protection. However, it needs to be considered that the chemical composition of particles can also induce health related effects. Polycyclic aromatic hydrocarbons (PAHs) are one of the several hundred organic compounds that have been identified in the particulate matter. PAHs are emitted into the atmosphere by the incomplete combustion of organic materials and fossil fuels such as automobile fuel



combustion, industrial combustion, wood and coal burning etc. PAHs in the atmosphere can be present either in the gaseous phase or adsorbed on atmospheric particles depending on their respective chemical and physical properties. Scientific research has proved that many higher molecular weight PAHs with four or more aromatic rings are carcinogenic and they are mostly attached to the particle phase in the atmosphere [4].

The International Agency for Research in Cancer (IARC) has classified a number of individual PAH compounds as probable human carcinogens and a number of "common mixtures of substances" that include PAH compounds as carcinogenic to humans. Despite this possible carcinogenic character of PAHs, a Directive relative to PAH in air was only recently established. The target value for PAH in air shall be assessed for the level of benzo(a)pyrene (BaP): 1 ng/m^3 , for the total content in the PM_{10} fraction averaged over a calendar year (Directive 2004/107/EC, implemented in Italy in 2007 [5]). With this Directive, it is expected that each Member State shall take all necessary measures to ensure that, as from 31 December 2012, the concentration of BaPs do not exceed this target value. In addition, each Member State shall monitor other relevant PAHs at a limited number of measurement sites to assess the contribution of BaP in ambient air.

2 Experimental

2.1 Sampling

The study was performed in the industrial area of an Italian provincial town where sources of anthropogenic emissions surrounding the sampling sites included industrial chemical plants (production of H_2SO_4 , synthesis of TiO_2 , an electrical energy power plant, a water-treatment system, an incinerator). The environmental survey was designed to monitor the impact caused by the release of air pollutants from industrial plants on the surrounding territory, with particular reference to compounds containing sulphur and nitrogen, which are the most significant for their effects on the population's health and ecosystems.

The work provided the monitoring of ambient air and industrial emissions by measuring the concentration of conventional and unconventional atmospheric pollutants, both in the gaseous phase and in particulate. Sampling was carried out on a monthly basis by means of 52 passive samplers to measure SO_2 , NO_x , NO_2 , O_3 , BTX, H_2S and four active samplers for the simultaneous measurement of PM_{10} in different locations on a daily basis. Along with the particulate, PAHs, metals, anions and cations were also determined. By the means of specific models of spatial interpolation, it was possible to estimate the concentration of SO_2 , NO_x , NO_2 , O_3 , BTX and H_2S in sites where there were no samplers, allowing the establishment of maps of the concentration of pollutants and to identify in these maps which are the areas most subject to high concentrations.

In this study, only the results on particulate PAHs are presented.

The map in Fig. 1 shows the location of the selected 52 sites and the four active sampler sites (P1-P4). Site 1 (P1) is in a residential area; Site 2 (P2) is

situated in the seaside resort of the municipality of Scarlino; Site 3 (P3) is situated in a peripheral industrial area; Site 4 (P4) is situated in an almost rural area.

Air samples were collected in four 30-days campaigns from November 2006 to September 2007 using a Tecora Skypost PM HV air monitor, provided with a PM₁₀ sampling head, which collects airborne particles on a 47mm 2µm pore size Teflon filter. Samples were collected over 24 hour periods (sampling time beginning at midnight) at a flow rate of 38 L/min, yielding sampled air volumes of ~55m³ per day. Among the filters, a part corresponding to a week's sampling was used for the analysis of PAHs.

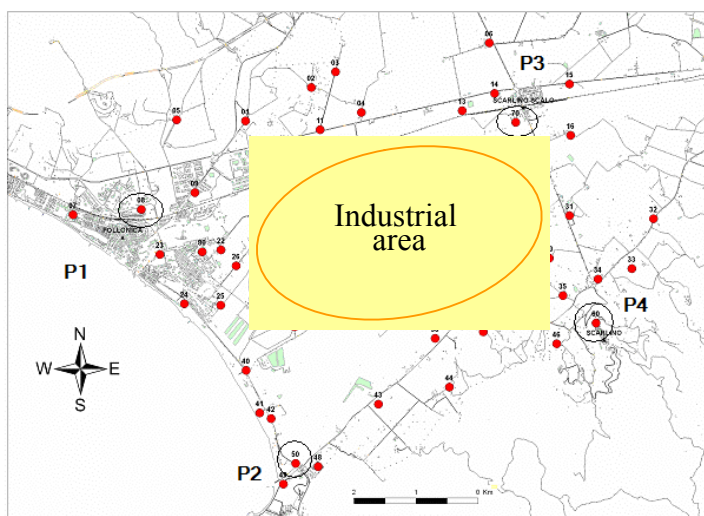


Figure 1: Map of the investigated area showing the position of sampling sites.

2.2 Extraction and analysis

After sampling, the filters were removed from the sampler and stored in a dark and closed chamber at a controlled temperature for 24h. Then they were weighed using a microbalance in order to obtain the mass of PM₁₀ collected.

Each filter was then extracted for PAHs analysis as follows: it was put in an amber vial, with the addition of perpetuated-PAH surrogate standard and extracted with 3ml of DCM:Acetone (4:1) in an ultrasonic bath for 30 min, twice. The extract was transferred to a clean vial, concentrated to about 100µl by a gentle flow of nitrogen and cleaned using solid-liquid chromatography on silica gel. Each sample was placed on the top of the column and hexane was used to elute the n-alkanes fraction and toluene to collect the fraction containing PAHs.

The analysis was performed using a Thermo Trace GC ultra gas chromatograph coupled to a DSQ mass spectrometer detector (electron ionization mode and quadrupole analyser) fitted with a fused silica capillary

column (Restek RxiTM-50 30m x 0.25mm ID x 0.25 μ m df) working in SIM mode. Helium was used as carrier gas at a constant flow of 1ml/min and transfer line was heated at 280°C. All injections were in PTV mode with an injection volume of 1 μ l.

The oven temperature was programmed as follows: 40°C (held 1 min), 30°C/min till 150°C (held 1 min), 8°C/min till 190°C (held 5 min), 6°C/min till 308°C (held 29 min).

The quantifications were performed by using an internal standard method for the following PAHs: phenantrene (PHE, 3-ring), anthracene (AN, 3-ring), fluoranthene (FA, 4-ring), pyrene (PY, 4-ring), benzo[a]anthracene (BaA, 4-ring), chrysene (CHR, 4-ring), benzo[b]fluoranthene (BbFA, 4-ring), benzo[j]fluoranthene (BjFA, 4-ring), benzo[k]fluoranthene (BkFA, 4-ring), benzo[a]pyrene (BaP, 5-ring), dibenzo(ah)anthracene (DBahA, 5-ring), indeno(1,2,3-cd)pyrene (IP, 6-ring), benzo(ghi)perylene (BghiP, 6-ring).

3 Results and discussion

3.1 PM₁₀

Table 1 reports the mean PM₁₀ concentrations and ranges at the four sites in each season. The Italian air quality health guideline for PM₁₀ is a 24-h average concentration of 50 μ g/m³ [3].

The mean daily concentration ranged from 17 to 37 μ g/m³. The highest values were found in the third campaign (23-29 May 2007) at each site. It could be due to the fact that the investigated area is a seaside resort and a major contribution to the concentration is due to inorganic components (salt, sulphates, metals). Moreover, the campaign included a weekend and it could agree with the beginning of holidays. This hypothesis is enhanced by the fact that the highest daily mean value in site P4 (rural area, far away from the sea) is lower than the maximum values of the other sites.

Table 1: The mean, minimum and maximum values of PM₁₀ (μ g/m³).

| | 15-22 Nov 2006 | | | 17-23 Feb 2007 | | | 23-29 May 2007 | | | 5-12 Sep 2007 | | |
|----|----------------|-----|-----|----------------|-----|-----|----------------|-----|-----|---------------|-----|-----|
| | Mean | Min | Max | Mean | Min | Max | Mean | Min | Max | Mean | Min | Max |
| P1 | 25 | 21 | 32 | 18 | 15 | 21 | 35 | 20 | 49 | 35 | 18 | 56 |
| P2 | 22 | 16 | 28 | 31 | 16 | 60 | 37 | 26 | 48 | 26 | 19 | 33 |
| P3 | 21 | 15 | 28 | 19 | 14 | 23 | 33 | 16 | 50 | 27 | 13 | 44 |
| P4 | 21 | 12 | 28 | 17 | 14 | 20 | 32 | 20 | 38 | 25 | 16 | 35 |

3.2 Particulate PAH

Tables 2–5 show mean, minimum and maximum concentrations for each PAH (in ng/m³) over the whole period and in each season and at each site.

The concentration of particulate PAHs exerted distinct seasonal variation presenting a maximum during winter (17–23 February) and a minimum during spring (23–29 May). In winter (mean temperature: 10°C), the atmospheric



condition is rather stagnant due to the frequent occurrence of low inversion layers. Under these conditions, photo-degradation and pollutant dispersion are least, resulting in the accumulation and more gas-to-particle conversion of PAHs. In spring (mean temperature: 21°C), higher temperature and higher mixing height could lead to the shift of PAHs from the particle to the gas phase with increased dispersion of pollutants [6–8].

BaP is considered one of the most powerful mutagens and often used as a general indicator of PAHs and regarded by the World Health Organization (WHO) as a good index for whole PAH carcinogenicity.

BaP, the classical chemical carcinogen, was detected in all samples with average daily values of 0.02–0.46 ng/m³. These values are all below the annual average value of 1 ng/m³ that the Italian regulation indicates as a quality objective.

Table 2: The mean, minimum and maximum values of PAHs in P1 site (ng/m³).

| | 15-22 nov 2006 | | | 17-23 feb 2007 | | | 23-29 may 2007 | | | 5-12 sep 2007 | | |
|-------|----------------|------|------|----------------|------|------|----------------|------|------|---------------|------|------|
| | Mean | Min | Max | Mean | Min | Max | Mean | Min | Max | Mean | Min | Max |
| PHE | 0.07 | 0.04 | 0.12 | 0.23 | 0.14 | 0.32 | 0.32 | 0.28 | 0.39 | 0.18 | 0.06 | 0.24 |
| AN | 0.02 | 0.01 | 0.04 | 0.08 | 0.01 | 0.19 | 0.26 | 0.24 | 0.30 | 0.10 | 0.08 | 0.14 |
| FA | 0.09 | 0.04 | 0.14 | 0.05 | 0.02 | 0.10 | 0.12 | 0.08 | 0.18 | 0.21 | 0.16 | 0.27 |
| PY | 0.09 | 0.04 | 0.14 | 0.06 | 0.02 | 0.10 | 0.13 | 0.10 | 0.19 | 0.33 | 0.28 | 0.37 |
| BaA | 0.09 | 0.03 | 0.14 | 0.14 | 0.04 | 0.31 | 0.06 | 0.05 | 0.06 | 0.14 | 0.06 | 0.24 |
| CHR | 0.16 | 0.08 | 0.21 | 0.21 | 0.07 | 0.43 | 0.08 | 0.05 | 0.11 | 0.27 | 0.21 | 0.35 |
| BbFA | 0.21 | 0.10 | 0.27 | 0.33 | 0.21 | 0.58 | 0.08 | 0.05 | 0.13 | 0.28 | 0.19 | 0.35 |
| BjFA | 0.06 | 0.03 | 0.12 | 0.16 | 0.11 | 0.29 | 0.04 | 0.02 | 0.06 | 0.13 | 0.10 | 0.17 |
| BkFA | 0.09 | 0.04 | 0.18 | 0.20 | 0.12 | 0.31 | 0.06 | 0.04 | 0.08 | 0.19 | 0.16 | 0.25 |
| BaP | 0.14 | 0.04 | 0.25 | 0.34 | 0.27 | 0.46 | 0.03 | 0.01 | 0.06 | 0.22 | 0.15 | 0.35 |
| IP | 0.14 | 0.06 | 0.23 | 0.39 | 0.24 | 0.58 | 0.05 | 0.02 | 0.09 | 0.28 | 0.21 | 0.35 |
| DBAhA | 0.05 | 0.02 | 0.07 | 0.13 | 0.08 | 0.19 | 0.04 | 0.02 | 0.07 | 0.09 | 0.05 | 0.12 |
| BghiP | 0.18 | 0.10 | 0.30 | 0.47 | 0.33 | 0.64 | 0.08 | 0.06 | 0.12 | 0.27 | 0.24 | 0.30 |
| ΣPAHs | 1.38 | 0.76 | 1.80 | 2.79 | 1.77 | 3.95 | 1.34 | 1.05 | 1.69 | 2.70 | 2.45 | 2.92 |

Table 3: The mean, minimum and maximum values of PAHs in P2 site (ng/m³).

| | 15-22 nov 2006 | | | 17-23 feb 2007 | | | 23-29 may 2007 | | | 5-12 sep 2007 | | |
|-------|----------------|------|------|----------------|------|------|----------------|------|------|---------------|------|------|
| | mean | min | max | mean | min | max | mean | min | max | mean | min | max |
| PHE | 0.07 | 0.04 | 0.10 | 0.16 | 0.13 | 0.19 | 0.34 | 0.30 | 0.37 | 0.56 | 0.11 | 1.07 |
| AN | 0.02 | 0.01 | 0.03 | 0.26 | 0.15 | 0.35 | 0.26 | 0.25 | 0.26 | 0.10 | 0.08 | 0.14 |
| FA | 0.10 | 0.06 | 0.14 | 0.10 | 0.04 | 0.14 | 0.21 | 0.15 | 0.26 | 0.56 | 0.00 | 1.08 |
| PY | 0.13 | 0.09 | 0.18 | 0.10 | 0.05 | 0.13 | 0.22 | 0.13 | 0.29 | 0.98 | 0.20 | 1.58 |
| BaA | 0.10 | 0.04 | 0.20 | 0.12 | 0.08 | 0.15 | 0.08 | 0.06 | 0.11 | 0.43 | 0.24 | 0.61 |
| CHR | 0.14 | 0.09 | 0.18 | 0.15 | 0.07 | 0.23 | 0.12 | 0.07 | 0.17 | 0.77 | 0.55 | 1.13 |
| BbFA | 0.20 | 0.14 | 0.36 | 0.38 | 0.25 | 0.52 | 0.10 | 0.05 | 0.18 | 0.63 | 0.50 | 0.98 |
| BjFA | 0.10 | 0.06 | 0.18 | 0.19 | 0.13 | 0.26 | 0.04 | 0.02 | 0.07 | 0.25 | 0.11 | 0.57 |
| BkFA | 0.17 | 0.10 | 0.31 | 0.17 | 0.14 | 0.20 | 0.07 | 0.04 | 0.12 | 0.33 | 0.24 | 0.52 |
| BaP | 0.19 | 0.10 | 0.36 | 0.26 | 0.17 | 0.41 | 0.06 | 0.03 | 0.10 | 0.40 | 0.30 | 0.61 |
| IP | 0.19 | 0.14 | 0.26 | 0.27 | 0.19 | 0.36 | 0.05 | 0.03 | 0.09 | 0.35 | 0.00 | 0.57 |
| DBAhA | 0.05 | 0.03 | 0.09 | 0.13 | 0.08 | 0.17 | 0.04 | 0.02 | 0.07 | 0.04 | 0.02 | 0.06 |
| BghiP | 0.28 | 0.17 | 0.40 | 0.29 | 0.12 | 0.44 | 0.10 | 0.05 | 0.14 | 0.80 | 0.50 | 1.31 |
| ΣPAHs | 1.74 | 1.24 | 2.41 | 2.54 | 2.00 | 3.09 | 1.70 | 1.36 | 2.15 | 6.24 | 3.67 | 8.36 |



Table 4: The mean, minimum and maximum values of PAHs in P3 site (ng/m³).

| | 15-22 nov 2006 | | | 17-23 feb 2007 | | | 23-29 may 2007 | | | 5-12 sep 2007 | | |
|-------|----------------|------|------|----------------|------|------|----------------|------|------|---------------|------|------|
| | mean | min | max | mean | min | max | mean | min | max | mean | min | max |
| PHE | 0.07 | 0.05 | 0.10 | 0.12 | 0.04 | 0.33 | 0.34 | 0.31 | 0.45 | 0.18 | 0.08 | 0.29 |
| AN | 0.02 | 0.01 | 0.03 | 0.04 | 0.00 | 0.14 | 0.32 | 0.27 | 0.51 | 0.10 | 0.08 | 0.14 |
| FA | 0.09 | 0.04 | 0.13 | 0.06 | 0.03 | 0.13 | 0.19 | 0.15 | 0.26 | 0.26 | 0.22 | 0.34 |
| PY | 0.11 | 0.06 | 0.16 | 0.05 | 0.03 | 0.08 | 0.18 | 0.10 | 0.29 | 0.30 | 0.15 | 0.44 |
| BaA | 0.07 | 0.03 | 0.18 | 0.13 | 0.07 | 0.22 | 0.13 | 0.06 | 0.18 | 0.08 | 0.00 | 0.12 |
| CHR | 0.20 | 0.12 | 0.31 | 0.23 | 0.14 | 0.27 | 0.08 | 0.04 | 0.16 | 0.27 | 0.20 | 0.33 |
| BbFA | 0.40 | 0.31 | 0.57 | 0.52 | 0.36 | 0.64 | 0.07 | 0.05 | 0.09 | 0.27 | 0.19 | 0.36 |
| BjFA | 0.23 | 0.16 | 0.32 | 0.26 | 0.18 | 0.32 | 0.05 | 0.03 | 0.07 | 0.10 | 0.05 | 0.18 |
| BkFA | 0.28 | 0.18 | 0.39 | 0.21 | 0.12 | 0.31 | 0.06 | 0.04 | 0.11 | 0.17 | 0.09 | 0.29 |
| BaP | 0.24 | 0.14 | 0.38 | 0.46 | 0.26 | 0.69 | 0.03 | 0.01 | 0.05 | 0.15 | 0.09 | 0.20 |
| IP | 0.29 | 0.21 | 0.34 | 0.35 | 0.24 | 0.46 | 0.03 | 0.02 | 0.05 | 0.18 | 0.10 | 0.28 |
| DBAhA | 0.21 | 0.16 | 0.28 | 0.12 | 0.07 | 0.15 | 0.02 | 0.02 | 0.03 | 0.04 | 0.02 | 0.06 |
| BghiP | 0.38 | 0.13 | 0.66 | 0.43 | 0.31 | 0.64 | 0.07 | 0.05 | 0.13 | 0.27 | 0.15 | 0.36 |
| ΣPAHs | 2.58 | 2.05 | 3.23 | 2.99 | 2.00 | 3.86 | 1.56 | 1.36 | 2.23 | 2.40 | 1.99 | 2.90 |

Table 5: The mean, minimum and maximum values of PAHs in P3 site (ng/m³).

| | 15-22 nov 2006 | | | 17-23 feb 2007 | | | 23-29 may 2007 | | | 5-12 sep 2007 | | |
|-------|----------------|------|------|----------------|------|------|----------------|------|------|---------------|------|------|
| | mean | min | max | mean | min | max | mean | min | max | mean | min | max |
| PHE | 0.05 | 0.03 | 0.07 | 0.16 | 0.13 | 0.18 | 0.32 | 0.29 | 0.39 | 0.14 | 0.10 | 0.21 |
| AN | 0.02 | 0.00 | 0.04 | 0.11 | 0.06 | 0.17 | 0.26 | 0.24 | 0.29 | 0.10 | 0.08 | 0.14 |
| FA | 0.05 | 0.02 | 0.10 | 0.05 | 0.03 | 0.07 | 0.11 | 0.07 | 0.19 | 0.19 | 0.13 | 0.27 |
| PY | 0.06 | 0.02 | 0.09 | 0.04 | 0.02 | 0.06 | 0.13 | 0.09 | 0.21 | 0.24 | 0.16 | 0.27 |
| BaA | 0.05 | 0.01 | 0.12 | 0.14 | 0.02 | 0.28 | 0.05 | 0.05 | 0.07 | 0.09 | 0.05 | 0.17 |
| CHR | 0.10 | 0.05 | 0.17 | 0.14 | 0.04 | 0.20 | 0.07 | 0.04 | 0.12 | 0.24 | 0.14 | 0.33 |
| BbFA | 0.14 | 0.11 | 0.17 | 0.19 | 0.17 | 0.23 | 0.07 | 0.04 | 0.11 | 0.24 | 0.16 | 0.32 |
| BjFA | 0.06 | 0.02 | 0.08 | 0.10 | 0.09 | 0.11 | 0.03 | 0.02 | 0.05 | 0.08 | 0.04 | 0.13 |
| BkFA | 0.11 | 0.07 | 0.18 | 0.20 | 0.16 | 0.29 | 0.05 | 0.04 | 0.06 | 0.09 | 0.05 | 0.13 |
| BaP | 0.10 | 0.07 | 0.14 | 0.23 | 0.13 | 0.32 | 0.02 | 0.01 | 0.04 | 0.13 | 0.10 | 0.18 |
| IP | 0.12 | 0.08 | 0.16 | 0.40 | 0.27 | 0.61 | 0.03 | 0.01 | 0.04 | 0.14 | 0.10 | 0.18 |
| DBAhA | 0.02 | 0.01 | 0.03 | 0.18 | 0.12 | 0.30 | 0.02 | 0.01 | 0.03 | 0.04 | 0.02 | 0.06 |
| BghiP | 0.18 | 0.05 | 0.27 | 0.41 | 0.19 | 0.78 | 0.07 | 0.04 | 0.10 | 0.19 | 0.16 | 0.24 |
| ΣPAHs | 1.05 | 0.78 | 1.30 | 2.38 | 1.69 | 3.34 | 1.22 | 1.03 | 1.67 | 1.93 | 1.44 | 2.33 |

4 Conclusions

In this study, concentration of thirteen ambient air polycyclic aromatic hydrocarbons were identified and quantified in the PM₁₀ during four seasons at four sampling sites. Results showed the concentrations of ΣPAHs ranged from 0.76 to 8.36 ng/m³, with the average ΣPAHs measured highest in winter and lowest in summer. The relative proportions of individual compounds could reflect changes in PAHs emissions sources and/or atmospheric conditions. Daily levels of BaP, the most investigated PAH and often used as an indicator of total PAHs, are in the range of 0.01-0.69 ng/m³, definitively below the annual average value of 1 ng/m³ that the Italian regulation indicates as a quality objective.

References

[1] Directive 1999/30/CE of 22 April 1999 relating to limit values for sulphur dioxide, nitrogen dioxide and oxides of nitrogen, particulate matter and lead in ambient air.



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