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One year intensive $PM_{2.5}$ bound polycyclic aromatic hydrocarbons monitoring in the area of Tuscany, Italy. Concentrations, source understanding and implications

Tania Martellini [a], Martina Giannoni [a], Luciano Lepri [a], Athanasios Katsoyiannis [b], Alessandra Cincinelli [a,b,*]

[a] Department of Chemistry, University of Florence, Via della Lastruccia, 3, 50019 Sesto Fiorentino, Florence, Italy
[b] Lancaster Environment Centre, Lancaster University, Bailrigg, LA14YQ Lancaster, United Kingdom

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ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) associated to $PM_{2.5}$ particles were monitored at three sites in the region of Tuscany, Italy, during the period March 2009–March 2010. PAH concentrations ranged between 0.92 ng m^{-3} and 13 ng m^{-3}. The spatial and seasonal differences observed at the three sites are discussed and attributed to specific PAH sources.

Benzo[a]Pyrene average annual values were below the EU limit value of 1.0 ng m^{-3}. The results of this study suggest that emissions from commuting and work related traffic play an important role for the city of Florence, whereas for the city of Livorno, the harbor activities seem to impact the PAH burden substantially, as well. The PAH cancer risk (expressed as the "BaPE index") has shown a 6-fold decline compared to early 1990's concentrations and 2- to 3-fold decline compared to the late 1990's.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous pollutants that enter the environment as a result of a number of anthropogenic (i.e. combustion of organic matter), but also natural activities (like volcanic eruptions, biogenic formation, etc. Nikolaou et al., 1984) resulting in global annual emissions that exceed 500 Gg (520 Gg was the estimation for 2004 by Zhang and Tao (2009)). Due to their toxic, mutagenic and carcinogenic properties, 16 PAHs have been identified as priority pollutants by United States Environmental Protection Agency (USEPA) and seven of them are considered as some of the strongest known carcinogenic compounds (IARC, 1991). The most toxic of all PAHs is Benzo-a-Pyrene (BaP), which is used as ΣPAH indicator by the 4th European Daughter Directive on Air Quality (Directive 2004/107/EC), according to which, the annual average value should not exceed 1 ng m^{-3}. Mantis et al. (2005) mentioned also the long-term objective of 0.1 ng m^{-3} to be met by the 1st January of 2010.

PAHs are very hydrophobic and tend to bind on particles (Cai et al., 2007; Ratola et al., 2011) and due to their resistance to degradation processes (especially when bound on particles), PAHs are subject to long range transport, being that way detected even in remote areas, where primary emissions are limited.

In urban atmospheres, PAHs are expected to derive as a result of heating and cooking activities, from motor vehicles, from industrial activities, or waste incineration (Bjorseth and Ramdahl, 1985). Once in the atmosphere, PAHs will partition between the gas and particulate phase, with the heavier and more hydrophobic ones tending to sorb exclusively on particles (Vasilakos et al., 2007). Especially the five- and hexa-ring PAHs are expected to sorb on particles with aerodynamic diameter (d) of 0.5–1.0 μm, because the latter deposit very slowly and stay in atmospheric dispersion for days (Mantis et al., 2005; Venkataraman and Friedlander, 1994). The atmospheric particulate matter is a complex mixture of material that is either directly emitted from sources, or formed in the atmosphere through vapor nucleation or condensation. The most important fraction of airborne particles is the fraction of $d < 2.5$ μm, because it is the respirable fraction and has been associated with cardiopulmonary diseases and lung cancer (Berico et al., 1997; Gemenetzis et al., 2006).

The region of Tuscany is one of the most picturesque areas in Europe with a very important cultural heritage and a big number of monuments. It is estimated that >10 million tourists visit annually this region. In addition to tourism, more than 300,000 car trips take

* Corresponding author.
E-mail address: acincinelli@unifi.it (A. Cincinelli).

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place daily only within/to/from the city of Florence for work commuting/work related trips/leisure (Fondelli et al., 2008) and thus, concerns about environmental/atmospheric, pollution are frequently risen, both for the impact of the latter to humans, but also for their potential effects on monuments. The Florence vehicular traffic is also said to contribute 40% of the total PM_{10} burden (Fondelli et al., 2008).

In line with the afore-mentioned concerns, and driven also by the 2010 BaP objective of the European daughter Directive on air quality, this study was designed to assess the occurrence of PAHs over a year of intensive monitoring in Florence and Livorno, the former being the most important metropolitan area of Tuscany, whilst the latter is a medium sized city and the most busy harbor of this region. It should also be underlined that in the international literature there are only scarce data about the occurrence of PAHs in Tuscany (Lodovici et al., 2003; Cincinelli et al., 2003, 2004, 2007; the latter three studied the area of Prato, a city 25 km to the north-west of Florence).

2. Experimental

2.1. Sample collection

An extensive aerosol sampling campaign was carried out from March 2009 to March 2010 at three locations in Tuscany, Italy, to investigate the aerosol sources and trace their contributions to $PM_{2.5}$. This study is a part of PATOS 2 project (Particolato Atmosferico in TOScana) funded by the Regional Government of Tuscany.

The first site in Florence (urban traffic, FIG; 43°46′N, 11°16′E – FIG) is located close to a heavily polluted major traffic junction in the city centre, whereas the second Florence site (urban background, FIB; 43°47′N, 11°17′E – FIB) is located in a small "green" public area surrounded by residential buildings, and about 50 m away from a moderately-trafficked road (secondary city road). The third site was located in the park "Villa Maurogordato" in Livorno (suburban-background, LMG; 43°30′N, 10°20′E – LMG). The latter is located far from the main traffic and industrial city zones.

$PM_{2.5}$ samples were collected on Quartz Fiber filters (Schleicher & Schuell, QMA 126 grade, diameter 47 mm), previously baked at 450 °C for 12 h and stored in a desiccators cabinet until use, using a low-volume Hydra Dual Samplers (FAI Instruments s.r.l., Italy) operating at a constant volumetric flow rate of 2.3 $m^3\ h^{-1}$ for 24 h. $PM_{2.5}$ daily mass concentrations were evaluated by weighing the filters before and after sampling at ambient temperature (20 ± 3 °C) and relative humidity of 38 ± 4% by an electronic analytical balance (Orma, Italy) with a sensitivity of 1 μg. Once $PM_{2.5}$ mass concentrations were obtained by this standard gravimetric method, the filters were stored at −20 °C in a desiccator cabinet until analysis.

The following PAHs were determined: fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fla), pyrene (Pyr), benzo(a)anthracene (BaA), chrysene (Chr), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(e) pyrene (BeP), benzo(a)pyrene (BaP), perylene (Per), indeno(1,2,3cd)pyrene (IPy), dibenzo(a,h)anthracene (DbA), benzo(g,h,i)perylene (BPe) and coronene (Cor).

2.2. Analytical procedure and QA/QC

The protocols used for the analysis of PAHs and other parameters as well as all the details about QA/QC are given as Supporting material (paragraphs S1–S2).

3. Results and discussion

3.1. $PM_{2.5}$ and PAH concentrations

Table 1 summarizes the PAH and $PM_{2.5}$ concentrations measured at the three sites during warm and cold periods. The two Florence sites represent one site impacted by traffic (FIG) and one urban background site (FIB); their difference can be seen already by the $PM_{2.5}$ concentrations that were twice as high in FIG, comparing to FIB during both cold and warm periods. The third site, LMG, is a suburban-background site in the city of Livorno, located in a public green park, affected by land and sea breeze due to its proximity to the seacoast; its location justifies the low $PM_{2.5}$ concentration levels. The LMG site exhibited higher average $PM_{2.5}$ concentrations during the warm period, suggesting that the main

Table 1
Descriptive statistics of PAH concentrations (ng m^{-3}) and $PM_{2.5}$ (μg m^{-3}) in FIB, FIG and LMG during warm and cold seasons.

	FIB cold				FIB warm				FIG cold				FIG warm				LMG cold				LMG warm			
	Avrg	Max	Min	Med	Avrg	Max	Min	Med	Avrg	Max	Min	Med	Avrg	Max	Min	Med	Avrg	Max	Min	Med	Avrg	Max	Min	Med
Flu	0.05	1.1	ND	ND	0.014	0.22	ND	0.01	0.04	0.25	ND	0.03	0.03	0.12	ND	0.02	0.03	0.20	ND	ND	0.01	0.06	ND	ND
Phe	0.15	1.1	ND	0.01	0.11	1.1	ND	0.07	0.48	2.9	0.12	0.26	0.38	1.7	0.03	0.25	0.07	0.23	ND	0.05	0.06	0.38	ND	0.04
Ant	0.19	1.5	ND	0.07	0.013	0.19	ND	ND	0.63	4.5	ND	0.41	0.09	0.48	ND	0.06	0.16	1.4	ND	ND	0.001	0.03	ND	ND
Fla	0.24	0.80	0.02	0.18	0.14	0.81	0.04	0.11	0.58	2.2	0.04	0.45	0.69	3.3	0.06	0.46	0.15	0.54	ND	0.07	0.10	0.60	ND	0.07
Pyr	0.26	0.84	ND	0.20	0.11	1.9	ND	0.10	0.88	6.2	0.23	0.72	0.81	3.7	ND	0.63	0.16	0.89	0.01	0.07	0.07	0.50	ND	0.04
BaA	0.34	1.6	ND	0.22	0.069	0.37	ND	0.05	1.2	2.5	0.24	1.2	0.83	4.0	0.05	0.73	0.10	0.55	ND	0.05	0.02	0.25	ND	ND
Chr	0.40	1.5	0.00	0.27	0.13	1.2	ND	0.08	1.2	2.3	0.28	1.2	0.84	5.0	0.13	0.68	0.16	0.65	ND	0.12	0.05	0.19	ND	0.04
BbF	0.54	2.1	0.06	0.38	0.14	1.1	0.02	0.13	1.3	2.8	0.34	1.2	0.40	2.0	ND	0.34	0.25	1.2	ND	0.17	0.10	0.56	ND	0.06
BkF	0.50	2.6	ND	0.36	0.085	1.2	ND	0.06	1.1	3.0	0.10	0.95	0.33	1.9	ND	0.30	0.18	0.73	ND	0.10	0.01	0.10	ND	ND
BeP	1.2	5.8	ND	0.68	0.51	3.3	0.08	0.38	0.56	4.3	0.01	0.40	1.3	3.4	ND	1.2	0.80	3.5	ND	0.48	0.33	1.8	0.01	0.29
BaP	0.47	1.8	0.01	0.29	0.049	0.53	0.01	0.03	1.0	2.8	0.05	0.89	0.21	1.1	0.01	0.15	0.20	0.72	0.01	0.14	0.02	0.19	ND	0.02
Per	0.46	3.3	ND	0.06	0.042	0.90	ND	ND	0.93	3.0	0.01	0.99	0.29	1.9	ND	0.13	0.16	1.6	ND	ND	0.06	2.0	ND	ND
IPy	0.50	2.6	ND	0.30	0.062	0.97	ND	0.04	0.92	2.8	0.06	0.77	0.14	0.85	ND	0.11	0.25	0.98	ND	0.16	0.03	0.26	ND	0.02
DbA	0.41	1.7	0.01	0.17	0.065	0.93	ND	0.04	0.79	2.4	0.03	0.56	0.23	1.2	ND	0.16	0.11	0.48	ND	0.06	0.01	0.19	ND	ND
BPe	0.13	1.3	ND	ND	0.003	0.12	ND	ND	0.46	2.1	0.02	0.02	0.01	0.32	ND	0.00	0.22	0.92	ND	0.11	0.04	0.27	0.01	0.02
Cor	0.89	5.4	ND	0.37	0.23	1.5	ND	0.07	1.2	3.9	0.14	1.1	0.56	1.7	ND	0.45	0.62	2.9	ND	0.30	0.01	0.28	ND	ND
ΣPAHs	6.7	17	0.76	5.4	1.7	10	0.46	1.4	13	24	3.5	13	7.2	15	1.8	6.8	3.6	15	0.12	2.4	0.92	3.4	0.20	0.65
$PM_{2.5}$	18.2	51.2	3.27	15.1	16.4	24.6	4.21	16.2	29.6	73.5	14.4	29.6	26.2	45.8	14.5	25.7	13.6	28.3	2.99	13.8	15.4	28.2	2.99	15.5

BaA, BbF, BkF, BaP, IPy, DbA (in bold); Cancerogenic PAHs, ND: Not detected.