Monitoring of Polycyclic Aromatic Hydrocarbons in Atmospheric Aerosols of Algiers City Area: Occurrence and Size Distribution

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Abstract. The distribution of polycyclic aromatic hydrocarbons (PAHs) in particulate matter with aerodynamic diameter smaller than 10 μm (PM_{10}) and total suspended particles (TSP) is reported. It has been determined during the period from December 2009 to April 2010 in a busy urban area located in Algiers. The airborne particulate matter was enriched onto glass fibre filters by using a medium-volume sampler with or without a size-selective inlet for PM10 and TSP, respectively. Extractable organics were recovered by refluxing the aerosol-enriched filters in soxhlet using a dichloromethane–acetone mixture for 16h. The PAHs were analyzed by using a gas chromatograph coupled to a mass spectrometer (GC/MS). The potential emission sources of airborne contaminants were reconciled by combining the values of diagnostic ratios of PAHs, calculated in both PM_{10} and TSP. Carcinogenic and mutagenic potencies associated to PAHs were evaluated by multiplying the concentrations of "active" compounds times the corresponding potency factors normalized vs. benzo(a)pyrene (BaP), and were found both acceptable. The total PAH concentrations ranged from 33 to 387 ng m^{-3} in PM_{10} particles suspended in the atmosphere of Algiers urban area.

Keywords: Polycyclic aromatic hydrocarbons, total suspended particles, air pollution, size distribution.

1. Introduction

Particulate organic matter (POM) has gained a big environmental concern among atmospheric pollutants due to the high mutagenic and carcinogenic potency displayed by its components, which improves the *physical* adverse impact on human health caused by the ambient aerosol dimensions. In fact, particles usually accumulate into the inhalable size range and about 95% of total polycyclic aromatic hydrocarbons (PAH) is associated with the size fraction characterised by aerodynamic diameters lesser than 3 μm. PAH arise naturally from reductive processes, which transform biomass into fossil fuels such as peat, lignite, crude oil and hard coal. Nevertheless, most of the atmospheric PAH are the consequences of *anthropogenic emission*, related to motor vehicles, domestic heating, coke and power production. *Motor vehicle exhaust*, in particular, is recognized to account for a main portion of POM and to be responsible for its recent accumulation in the atmosphere in rich regions as well as in the developing countries. Through any ambient media, anthropogenic POM is capable of contaminating vegetables and other foodstuffs and affecting human health.

For several decades, a considerable amount of research has focused on characterizing ambient levels of polycyclic aromatic hydrocarbons (PAHs), which are well-known for their carcinogenicity and/or mutagenicity. Among PAH exposures, benzo[a]pyrene (BAP) is considered as the most toxic, and is known to induce lung cancer and DNA binding.

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In this work, we present the distribution of PAH concentrations between PM_{10} and TSP present in the atmosphere at busy urban area of Algiers.

2. Experimental

2.1. Site description

Fig. 1 provides the general view of Algiers Bay as well as a detailed position of the site investigated. The sampling site is pretty close to traffic influence and located in the student residence of University of Bab-Ezzouar (CUB1), 15 km south-east from Algiers city center. This site can be considered as an urban area because of its strong population density (45000 hab/ Km^2). This residence is occupied by more than 2000 students and covers an area of 10 ha. It is highly impacted by busy traffic circulation as well as by the bus station used to transport students. The samplings were carried out at 4 meters above ground level and 10 m close to the main road.
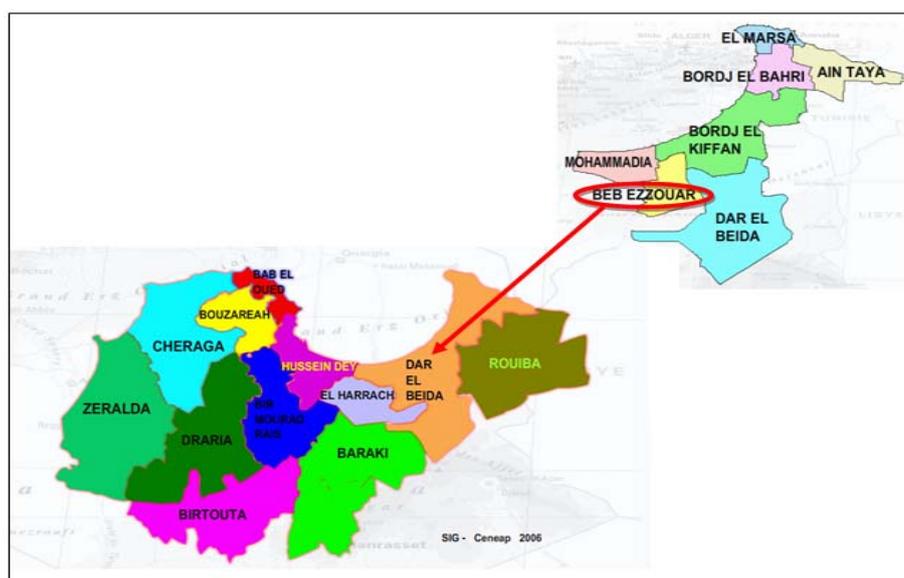

Fig. 1: General view of Algiers Bay as well as detailed position of the sampling site investigated in CUB1 student residence.

2.2. Collection materials and sampling protocols

The coarse fraction TSP of organics were collected using medium-volume samplers operating at 39 L min^{-1} flow rates and equipped with electronic volume counters. Particles were collected on 47 mm diameter quartz filter membranes for 24 h with the sampling period starting at 8:00 h in the morning. The fine particle PM_{10} was collected using the same sampling device but the inlet was equipped with PM_{10} size selector.

2.3. Sample extraction and clean-up

Chemical determination of organic aerosols was performed by applying a procedure described extensively elsewhere [1,2]. Briefly, samples were spiked with a solution containing internal reference compounds for the analysis i.e. phenanthrene-d10, pyrene-d10, chrysene-d12 and perylene-d12.

The particle samples were extracted by refluxing with a mixture of dichloromethane–acetone (4:1, v/v) in a Soxhlet apparatus for 16 h. Solvent was reduced to low volume by means of a Kuderna–Danish device and transferred onto a neutral Alumina column. The PAHs were collected by passing dichloromethane-acetone through the column. Solvent was evaporated under a gentle high-purity N_2 stream. All sample fractions were stored in the dark at low temperature (4 °C) until the analysis.

2.4. Gas chromatography/mass spectrometry analysis

PAHs were characterized by gas chromatography/mass spectrometry. Compound identification was based upon comparison of eluted peaks with authentic analyte standards, GC retention times, mass spectra

derived from reference (NIST) as well as home-made libraries and interpretation of mass spectrometric fragmentation patterns.

3. Results and discussion

PAHs are the class of particulate organic compounds the most studied. They are formed from the incomplete combustions of organic matter, mainly from combustion of petroleum, coal and gas [3]. Indeed, the prevalence of the relative contribution of vehicle emissions, home heating and other urban sources were related to various compositions of the fraction of PAHs [4].

Among the PAHs studied, the most volatile aromatic compounds such as: phenanthrene (PHE), methylated phenanthrenes/anthracenes, the Acenaphtene(ACE) and the Fluorene(FL) are the most abundant PAHs, although their concentrations in air are to some degree underestimated because PAHs with 2-4 aromatic rings have a high volatility so they accumulate in the gas phase rather than in the particulate phase under ambient conditions. By contrast, the high molecular weight PAH (indeno(1,2,3-cd) pyrene [IPY] and Dibenzopyrene and the Coronene) are present in low concentrations.

The principal PAH congeners detected in this study were phenanthrene (PHE), anthracene (AN), methylated phenanthrenes/anthracenes (Me-PHE/AN), fluoranthene (FA) and pyrene (PY). While 3- and 4-ring PAHs were at concentration levels of tens of ng per cubic meter, the less volatile congeners were one or two order of magnitude less.

Table.1 and Fig. 2 include the individual PAH concentrations recorded at CUB1 for both size classes studied. PAHs are richer in TSP particles with about 75% (3 times higher than PM10). It is interesting to point that the same distribution patterns of PAHs were observed in both types of particles. For instance, while fluorene (26.74 ng/m^3 in TSP and 4.06 ng/m^3 in PM10) and acenaphtene (21.17 ng/m^3 in TSP and 2.45 ng/m^3 in PM10) are the principal PAHs in both TSP and PM10, the methylated fluoranthene / Pyrene (Me-FL/PYR) (0.44 ng/m^3 in TSP and 0.33 ng/m^3 in PM10) and Perylene (0.15 ng/m^3 in TSP and not detected in PM10) are the minor PAHs in both classes of particles.

The PAH levels resulting at the CUB1 in winter 2010 were higher than those reported in the atmosphere of Prato, Italy (concentrations ranging from 5.6 to 14 ng per cubic meter) [5] however, they are lower than those measured in Thessaloniki, Greece (30.8-137 ng/ m^3) [6].

The approach of "diagnostic ratios" between selected PAH congeners (DRPAH) was attempted in the aim of identifying the principal sources of airborne particulates of CUB1. This approach relies on the peculiarity of ratio rates with respect to nature of emission and the concurrent influence of atmospheric reactivity versus target pollutants.

The ratio [FA] / ([FA] + [PY]) around 0.5 for both classes is comparable to the emission of exhaust pipes of old cars not equipped with catalytic converters which very likely the case in Algeria. This is confirmed by the CPAH/ΣPAH ratio which is close to 0.3 suggesting vehicular emission without passing by catalytic converters.

The ratio ([BaPY]/([BaPY]+[BePY]) around 0.68 in TSP and 0.63 in the PM10, suggests that new emissions of PAHs were accounting for losses by photochemical decomposition.

The ratio ([BaP]/[BghiP]) were around 0.92 and 0.42 in TSP and PM10, respectively. While values calculated in PM10 are indicative of car emissions, those evaluated in TSP imply that another source other than traffic road contributes to the enrichment of these pollutants in the coarse particles.

Table 1: Average PAH concentrations (pg m^{-3}) measured in CUB1, January 2010 and their respective diagnostic ratios.

Compounds	Formulas	m/z	TSP	PM10
ACY	$C_{12}H_8$	152, 151, 153	13.52	2.13
ACE	$C_{12}H_{10}$	154, 153, 155	21.17	2.45
FL	$C_{13}H_{10}$	166, 165, 167	26.74	4.06
PHE	$C_{14}H_{10}$	178, 177, 179	5.54	2.21
ANT	$C_{14}H_{10}$	178, 177, 179	2.17	1.14

Me-PHE/ANT	$C_{15}H_{12}$	192, 177, 193	7.61	1.47
FLU	$C_{16}H_{10}$	202, 201, 203	4.40	1.90
PYR	$C_{16}H_{10}$	202, 201, 203	4.46	1.84
Me-FLU/ PYR	$C_{17}H_{12}$	216, 201, 217	0.44	0.33
BcPHE	$C_{18}H_{10}$	226, 225, 227	0.62	0.28
BaA	$C_{18}H_{12}$	228, 227, 229	1.72	0.98
CHR	$C_{18}H_{12}$	228, 227, 229	2.16	1.52
BbF	$C_{20}H_{12}$	252, 251, 253	2.41	1.66
BkjF	$C_{20}H_{12}$	252, 251, 253	1.35	1.37
BePY	$C_{20}H_{12}$	252, 251, 253	0.76	0.85
BaPY	$C_{20}H_{12}$	252, 251, 253	1.61	1.43
PERY	$C_{20}H_{12}$	252, 251, 253	n.d.	0.15
IcdF	$C_{22}H_{12}$	276, 275,277	n.d.	0.41
IcdP	$C_{22}H_{12}$	276, 275,277	1.58	2.17
DahA	$C_{22}H_{14}$	278, 277, 279	1.17	1.12
BghiP	$C_{22}H_{12}$	276, 275, 277	1.75	3.34
CO	$C_{24}H_{12}$	300, 299, 301	n.d.	0.92
DBaiPY	$C_{24}H_{14}$	302, 301, 303	1.52	0.55
∑PAH	**-**	**-**	**102.72**	**34.27**
CPAH	**-**	**-**	**27.58**	**17.38**
CPAH/∑PAH	**-**	**-**	**0.27**	**0.24**
PHE/(PHE+ANT)	**-**	**-**	**0.72**	**0.66**
BaPY/BghiPY	**-**	**-**	**0.92**	**0.42**
BaP/(BaP+BeP)	**-**	**-**	**0.68**	**0.63**
FLU/(FLU+PYR)	**-**	**-**	**0.50**	**0.51**
IcdP/(IcdP+BghiP)	**-**	**-**	**0.48**	**0.39**

[a] BaPE=BaA*0.06+BF* 0.07+BaP+DBahA* 0.6+IcdP*0.08 **[1]**.
[b] CPAH: total concentration of the nine "combustion-derived PAHs", namely fluoranthene, pyrene, benz(a)anthracene, chrysene, benzofluoranthenes (sum), benzo(e)pyrene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene and benzo(ghi)perylene.

The levels of benzo[a]pyrene which is usually considered a good indicator of the overall carcinogenicity of PAHs reached 1.61 ng/m^3 in TSP and 1.43 ng/m^3 in PM10. For sake of comparison, these concentration values in both size classes are above the guideline value fixed by the Italian Ministry of the Environment (1.0 ng/m^3).
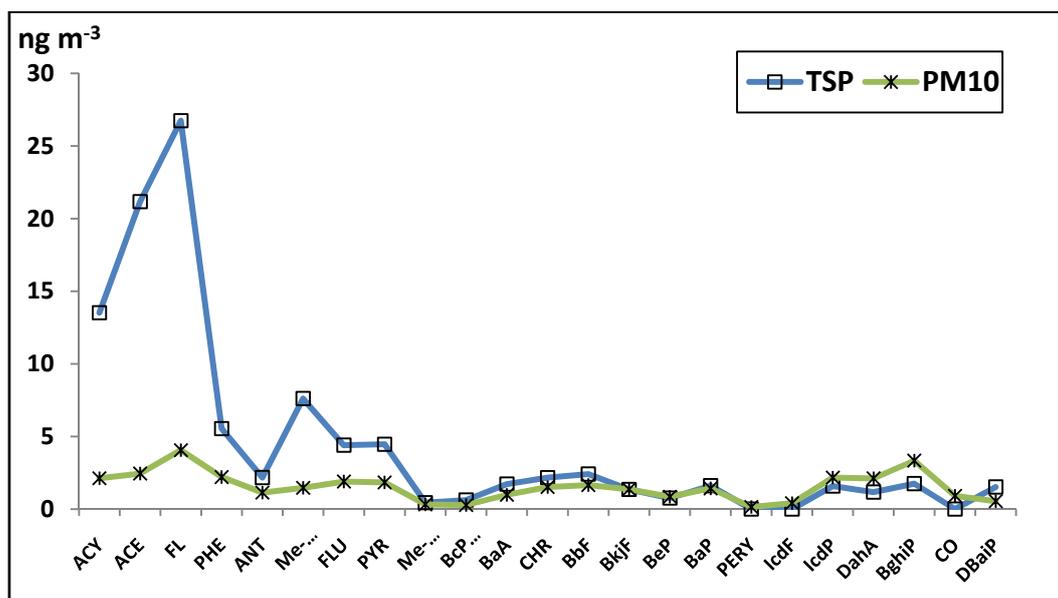

Fig. 3: Distribution profile of PAHs in PM10 and TSP (pg m^{-3}) in the Student Residence of University of Bab- Ezzouar (CUB1).

4. Conclusion

The partition of more than 23 organic contaminants including PAHs and Me-PAHs between the fine (PM$_{10}$) and coarse (TSP) airborne particulates was determined in the atmosphere of the Student Residence of Bab-Ezzouar, commonly named CUB1. High concentrations of these toxic substances were found in TSP.

Thanks to diagnostic ratios of speciated PAHs, motor vehicles were found to be the main source of particulate organic matter in Algiers.

Long term campaigns are planned in order to investigate the seasonal and topographic variations of airborne particulate in different Algiers areas. A special concern would be given to PAHs and their derivatives, with respect to their potential carcinogenic and mutagenic properties.

5. References

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