Exposure levels and health risk of PAHs associated with fine and ultrafine aerosols in an urban site in northern Algeria

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Received: 17 November 2020 / Accepted: 8 April 2021 / Published online: 16 April 2021
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Abstract
Size distribution of toxicants in airborne particulates remains insufficiently investigated in Algeria. A 1-year campaign was performed at Bab Ezzouar, Algiers (Algeria), aimed at characterizing particulates for their physical and chemical features. For this purpose, scanning electronic microscopy (SEM), Raman spectroscopy (RaS), and GC-MS methodologies were applied. The samples were collected on daily basis by means of a high-volume sampling (HVS) system equipped with cascade impactor separating three size fractions, i.e., particles with aerodynamic diameters \( d < 1.0 \mu m (PM_{1}) \), \( 1.0 \mu m < d < 2.5 \mu m (PM_{2.5}) \), and \( 2.5 \mu m < d < 10 \mu m (PM_{10}) \), respectively. The organic fraction was recovered from substrate through solvent extraction in an ultrasonic bath, separated and purified by column chromatography, then analyzed by gas chromatography coupled with mass spectrometry (GC-MS). Investigation was focused on polycyclic aromatic hydrocarbons (PAHs) and the concentration ratios suitable to investigate the source nature. Further information was drawn from SEM and Raman analyses. Total PAH concentrations ranged broadly throughout the study period (namely, from 4.1 to 59.7 ng m\(^{-3}\) for \( PM_{1} \), from 2.72 to 32.3 ng m\(^{-3}\) for \( PM_{2.5} \), and from 3.30 to 32.7 ng m\(^{-3}\) for \( PM_{10} \)). Both approaches and principal component analysis (PCA) of data revealed that emission from vehicles was the most important PAH source, while tobacco smoke provided an additional contribution.

Keywords Airborne particulate, · Polycyclic aromatic hydrocarbons (PAHs), · PAH diagnostic ratios, · Principal component analysis (PCA), · Health risk, · Algeria

Introduction
Air quality degradation is one of the important consequences of rapid industrialization and urbanization, particularly in developing countries. Consequently, in the last few years, air quality has become a subject of health and environmental concern around the world (Gadi et al. 2018).

Fine particulate matter (PM) is listed among the principal indicators of air quality. In Algeria, the annual exposure to fine particles \( (PM_{1}+PM_{2.5}) \) was about 39 \( \mu g m^{-3} \) (WB 2017). This value is four times higher than the standard value of 10 \( \mu g m^{-3} \) set by the World Health Organization (WHO). Fine particles present, at the same time, a serious risk due to small size, which helps them to reach the deeper respiratory ways and settle in the lungs (WB 2017).

Organic particulate is released by both biogenic and anthropogenic sources, i.e., living organisms and human activities, respectively (Stephanou and Stratigakis 1993). Biogenic sources include the direct suspension of pollen, micro-organisms, insects, and fragments of epicuticular waxes of vascular plants; on the other hand, man-made sources comprise the combustion of fossil fuels, industrial and house activities, agricultural debris, and wood burning (Kadowaki 1994).

Among the components of particulate organic matter (POM), polycyclic aromatic hydrocarbons (PAHs) are of...
great concern, due to their ascertained carcinogenic and 
mutagenic potency. The four primary sources of airborne 
PAHs are motor vehicles (mobile: diesel and gasoline en-
gine exhausts), home emissions, manufacturing (station-
ary: steel and power plants), and emissions from forest, 
agricultural burning and uncontrolled waste incineration. 
The toxicity of PAHs has been demonstrated conclusively 
by assays on bacterial and human cells (Mukherji et al. 
2002). Besides, PAHs are direct precursors of oxy- and 
nitro-PAHs, the latter resulting up to 10 times more carci-
nogenic and 10E5 times more mutagenic than the corre-
ponding native compounds (Durant et al. 1996).

The emission sources of organic particles can be identi-

died by using many analytical techniques and statistical 
methods, the former including high-performance liquid 
 chromatography (Eisenberg 1978) and gas chromatogra-
phy coupled to mass spectrometry (Cautreels and Van 
Cauwenbergh 1976) applied to solvent-extractable com-
ponents, and surface characterization of particles (i.e., 
morphology) through SEM and RaS (Bharti et al. 2017). 
According to literature, the spherical shape matches soot 
particles associated with fuel combustion, which highlights 
the influence of road traffic (Huda et al. 2018; Talbi et al. 
2018).

On the other hand, PCA is the most used statistical ap-

droach for dimensional reduction of source matrix. PCA con-
verts a high number of features of the original data set by using 
projection into few non-correlated features. Previous PCA 
studies undertaken in Algeria on fine particulates identified 
five principal emission sources of organic compounds such 
as alkanes, PAHs, and phthalates, namely vehicles, plastic 
burning, biomass burning, cooking, and mixed sources 
(Gadi et al. 2019).

Until today, airborne particulates have been studied in 
various regions of Algeria, including cities (Yassaa et al. 
2001b; Ladji et al. 2009a; Moussaoui et al. 2010; Kerchich 
et al. 2016; Talbi et al. 2018), rural areas (Moussaoui et al. 
2010), and forests (Ladji et al. 2009b; Moussaoui et al. 
2013a; Khedidji et al. 2017). Both organic carbon and 
extractable organic matter such as n-alkanes, PAHs, nitro-
PAHs, organic acids, and polar compounds were studied 
(Yassaa et al. 2001a, 2001c, 2001d; Moussaoui et al. 
2013b). In addition, the distribution of organic solvent 
particulate matter was shortly investigated in ultra-fine size 
(PM1) and coarse fraction (PM10) at urban and forest areas 
(Ladji et al. 2009b), but no study has been reported for 
organic solvent particulate matter of fine size (PM2.5), 
nor studies were conducted over one whole year. This 
gap was partly resolved with this study, focused on PAH 
assessment in PM1, PM2.5, and PM10 at Bab Ezzouar, 
Algiers, combined with PM characterization by means of 
scanning electron microscopy (SEM) and Raman spectro-
copy (RaS).

Materials and methods

Study area

For our experiments, atmospheric particulates were 
collected over the terrace of the Medical-Social Center of 
Civil Protection (ca. 5 m over soil) at Bab Ezzouar city, 
Algiers (36° 43′ 00″ N, 3° 11′ 00″ E, see Fig. 1). Bab 
Ezzouar city is one of Algiers’ fastest-growing municipal-
ities, characterized by a high population density (12,045 
inhabitants/km2; NOS 2008). It includes many hotels and 
malls. The city is served by the Algiers train and tramway 
lines, the former having a station near to collection point 
(<100 m). Moreover, Bab Ezzouar lies very close to the 
Algiers international airport, and includes one of the largest 
universities in Africa, University of Science and 
Technology Houary Boumedienne of Bab Ezzouar, 
USTHB. Moreover, the study area is surrounded by many 
industrial districts, such as the Oued Smar and Dar El 
Beida. Finally, the sampling site is characterized by huge 
road traffic.

Meteorological data records were obtained from the 
weather station DAAG (36° 68′ N, 3° 25′ E), located at 
Dar El Beida, approximately 2 km from our study site 
(NOM 2019). The meteorological data included wind 
speed, relative humidity, and temperature (Table 1). 
Several studies have shown the influence of meteorologi-
cal conditions on the characteristics and dispersion of fine 
particles. In this study, specific meteorological factors 
were chosen, including wind speed, relative humidity and 
temperature, as wind data can be used to determine the area 
of emissions and identify the source of pollutants. 
Temperature, solar radiation, and relative humidity play 
an important role in many chemical and photochemical 
reactions in the atmosphere. High and low temperature 
are linked with intensive and decreased convection of pol-
lutants respectively which resulting in increased concentra-
tions of particles in the atmosphere. In addition, higher 
orates of RH lead to higher PM concentrations, so air pol-
lution events such as thermal inversion and days with high 
pollutant concentrations can be predicted. Meteorological 
parameters were studied in order to investigate seasonal 
variations in PM (Deng et al. 2012).

Sampling period and methodology

Particles were collected daily in three fractions on glass 
fiber filters (GFF, Whatman) of different sizes (20.3 × 
25.4 cm2 for PM1 and 10 × 12 cm2 for PM2.5 and PM10) 
using a HVS (Model VFC, Anderson, USA) with a PM10 
head equipped with a cascade impactor. The sampling pe-
riod lasted one year from January 2018 to January 2019. 
Particles had collected over 24-h intervals at the 1.1
m$^3$.min$^{-1}$ flow rate. The fiber filters had previously backed in a chamber at constant temperature and relative humidity. Each filter was enveloped in aluminum foil (USEPA-Method IO-3.1 1999). The glass fiber filters used for particulate matter collection had weighted before and after sampling at the same percentage relative humidity (RH). The PM-enriched filters were enveloped aluminum foils and stored at a low temperature (4 °C) until analysis to preserve analytes from decomposition.

**Extraction and cleanup of PAHs**

Before analysis, the samples were fortified with an internal standard solution of perdeuterated homologues of analytes, used as reference compounds for quantification. The standard solution contained fluoranthene, phenanthrene, chrysene, benzo(a)anthracene, benzo(a)pyrene, perylene, benzo(ghi)perylene, and dibenz(a,h)anthracene. Filters were extracted three times for 20 min in an ultrasonic bath using a mixture of dichloromethane, acetone, and methanol (45:45:10 % v/v).

The extract was first evaporated under a gentle stream of nitrogen and purified by liquid chromatography on a neutral alumina column (6 g, deactivated with 2.5% water), then PAHs were recovered through elution with dichloromethane:isooctane (40:60 in volume, 15 mL); the eluate was reduced close to dryness under nitrogen, dissolved with toluene and analyzed by GC-MS.

**Table 1** Meteorological data for the year 2018

| Month | $T_{\text{max}}$(°C) | $T_{\text{min}}$(°C) | $T_{\text{ave}}$(°C) | Relative humidity (%) | Wind speed (km h$^{-1}$) |
|-------|---------------------|---------------------|---------------------|----------------------|------------------------|
| Jan.18| 24                  | 02                  | 11.4                | 75.9                 | 09.0                   |
| Feb.18| 26                  | 00                  | 10.2                | 77.0                 | 10.5                   |
| Mar.18| 29                  | 02                  | 14.0                | 72.8                 | 14.2                   |
| Apr.18| 29                  | 04                  | 16.0                | 74.5                 | 11.5                   |
| May.18| 33                  | 05                  | 17.5                | 79.2                 | 10.1                   |
| Jul.18| 36                  | 15                  | 26.2                | 65.3                 | 10.8                   |
| Aug.18| 37                  | 16.5                | 26.5                | 67.5                 | 10.2                   |
| Sep.18| 36                  | 16                  | 24.6                | 72.2                 | 10.0                   |
| Oct.18| 33                  | 08                  | 19.7                | 71.6                 | 10.2                   |
| Nov.18| 28                  | 03                  | 15.7                | 71.2                 | 10.6                   |
| Dec.18| 25                  | 02                  | 11.9                | 81.6                 | 06.6                   |
| Jan.19| 20                  | 00                  | 09.9                | 79.0                 | 10.9                   |
GC/MS analysis

Individual PAHs were characterized using a gas chromatograph equipped with a mass spectrometer (Trace-GC and Trace Q MS) and controlled by the proprietary software Excalibur (all from Thermo Fisher, Rodano MI, Italy). The analytes were separated applying a temperature gradient from 90 up to 290°C to a 25-m-long RT5MS type column (i.d. = 250 μm, film thickness = 0.33 μm, Superchrom, Milan, Italy), under a Helium constant flow of 1.0 mL min⁻¹. For identification, the combination of relative retention times, mass spectra and ion trace ratios of the peaks was compared with that of authentic PAH standards. For quantitative purposes, the peak area of each compound had compared with that of its perdeuterated homologue or the closest internal reference in the chromatogram (isotopic dilution method). The quantitative data were kept as reliable when the resulting concentrations lied within the operating ranges of the detector, i.e., 3.3 to ~1000 times the respective detection limits.

Filter blanks were included in the chromatograms in the correspondence; in the cases of phenanthrene and pyrene (light PAH congeners), blanks were quite important and accounted for in the quantitative determinations. The recovery rates varied between 83% and 106% (±9%), and the accuracy was better than 11% for all species.

Results and discussion

SEM analysis

The results of SEM indicated a variety of particle shapes and sizes; the morphology of the particles studied was widely variable and corresponded to irregular, aggregate, spherical, or spheroidal shapes (Fig. 2). Three types of particulate matter were observed, i.e., soot, inorganic compounds, tar balls, in addition to the fourth group of non-identified particles. The shape and size of the particles changed according to their way of formation and distance from the source. For instance, the aggregated and spherical shapes that refer to soot particles generated by fuel combustion showed the impact of road traffic on the sampling site, while the coarser particles had the tendency to approach the source. According to studies previously published dealing with particle morphology, irregular and spherical shapes refer to inorganic compounds and tar balls, respectively (Cong et al. 2010; Bharti et al. 2017; Talbi et al. 2018).

Raman spectroscopy (RaS) analysis

Analyses, carried out on three particle fractions (PM₁₀, PM₂.₅, and PM₁), showed the presence of a number of bands linked to metal oxides, sulfates, and organic compounds. Table 2 illustrates a summary of the molecular composition of the characterized PM.

Figure 3 shows characteristic Raman spectra of PM₁₀, PM₂.₅, and PM₁, samples. All of them were characterized by pronounced peaks at ~1350 cm⁻¹ and ~1600 cm⁻¹. Both identified bands were identical to those of standard graphite, in particular activated carbon, as well as to bands typical of inorganic compounds. A small peak at 470 cm⁻¹, probably quartz, a large peak between 600 and 800 cm⁻¹, attributed to hematite Fe₂O₃, the peaks at 420 and 1008 cm⁻¹, indicating the existence of gypsum (CaSO₄•2H₂O), and finally the peak at 1000 cm⁻¹, possibly associated with celestine (SrSO₄) as representative of sulfate mixture, were also observed.

Particulate matter mass concentration

Particulate matter size distribution

As shown in Fig. 4, the daily mass concentrations of PM₁₀, PM₂.₅, and PM₁ ranged from 22.6 to 260 μg m⁻³, from 12.7 to 180 μg m⁻³, and from 8.7 to 155 μg m⁻³, respectively. The daily evolution of particulate matter reveals important fluctuations for all the three size fractions, with standard deviations.
The concentrations of PM10 and PM2.5 respectively is about 93% and 91% of days during 1 year of campaign were greater than WHO Guidelines, which indicates that the population is exposed to high levels of fine particle pollution.

Two tests were performed with the statistical software R which are Student’s tests $t$-test and Mann-Whitney $U$-tests (MWU) to compare the data sets and determine if they were statistically different from each other. Both tests were performed with a significance level of 0.05 (95% confidence).

Paired-Student $t$-tests were performed between paired measurements (PM$_{10}$ and PM$_1$, PM$_{10}$ and PM$_{2.5}$, PM$_{2.5}$ and PM$_1$). The $p$-values were $< 2.2 \times 10^{-16}$ for all paired measurements, the mean value of the difference was 48.50 for PM$_{10}$ and PM$_{2.5}$, 15.15 for PM$_{2.5}$ and PM$_1$ and 63.64 for PM$_{10}$ and PM$_1$. The results showed that the mean difference between paired measurements is significant different, this result is confirmed by $U$-test ($P < 10^{-14}$) with a $p$-value < 0.05 indicating significant differences between the paired measurements.

The monthly average mass concentrations varied from 68 to 140 $\mu$g m$^{-3}$, 30–76 $\mu$g m$^{-3}$, and from 16.6–56 $\mu$g m$^{-3}$, respectively, for PM$_{10}$, PM$_{2.5}$, and PM$_1$ (Fig. 5). The $p$-values of $t$-test were $< 1.21 \times 10^{-7}$ for PM$_{10}$ and PM$_{2.5}$, the same value for PM$_1$ and PM$_{2.5}$ and $8.47 \times 10^{-8}$ for PM$_{10}$ and PM$_1$, the mean value of the difference was 49.33 for PM$_{10}$ and PM$_{2.5}$, 15.62 for PM$_{2.5}$ and PM$_1$ and 64.94 for PM$_{10}$ and PM$_1$.
Two main factors seemed to influence the time fluctuations of SPM (Suspended Particulate Matter), i.e., the daily road traffic rate and weather. Indeed, the maximum concentration was recorded in December; this can be explained by the combination of various sources, in particular the extension of the Algiers metro line up to 100 m away from the sampling site and unfavorable weather conditions (this month was characterized by weak wind speeds and high humidity).

The annual average of mass concentrations reached $94.8 \pm 11.4 \, \mu g \, m^{-3}$ for PM$_{10}$, $46.3 \pm 7.3 \, \mu g \, m^{-3}$ for PM$_{2.5}$, and $31.1 \pm 6.4 \, \mu g \, m^{-3}$ for PM$_1$. Therefore, all of the annual average limits of $80 \, \mu g \, m^{-3}$, $40 \, \mu g \, m^{-3}$, and $20 \, \mu g \, m^{-3}$ fixed for PM$_{10}$ by the Algerian air quality standard, the EU Air Quality Directive, and the WHO guidelines, respectively, were exceeded. Besides, the three fractions cumulatively reached $169 \, \mu g \, m^{-3}$ as yearly average ($119–272 \, \mu g \, m^{-3}$, $\sigma = 47 \, \mu g \, m^{-3}$), which means over 3 times the limit established by European normative (European Union 2008) to preserve human health. As for PM$_{2.5}$, the mean concentration was over four times higher than the WHO guideline. This level of pollution appears as a cause for health concern, overall because of the strong presence of very fine particles, where PM$_1$ represents ca 1/3 of PM$_{10}$.

The weather in Algiers is of Mediterranean type characterized by hot and dry summers, wet and cool winters.

Figure 6 presents the seasonal mean profiles of PM$_{10}$, PM$_{2.5}$, and PM$_1$. A weak seasonal fluctuation was observed for PM$_{2.5}$ and PM$_1$; by contrast, an important seasonal behavior had found for PM$_{10}$. As pictured in Fig. 6, the highest concentrations were typically found in the winter, may be associated with important factors that promote the accumulation of particles in the atmosphere and limit particle dispersion, i.e., combustion of fossil fuels and coal, resuspension of road dust and a shallower mixing layer, while the lowest concentrations were detected in the autumn. These low concentrations are probably due to the winds formed during the heat exchanges that occur between cold air masses and warm air masses during the fall. This season is particularly marked by frequent windy and rainy weather, resulting in good dispersion of pollutants.

The annual mean concentrations of PM$_{10}$ were in agreement with those resulting from previous studies conducted in
Algeria (Oucher and Kerbachi 2012; Terrouche and Ali-khodja 2015; Talbi et al. 2018); at the same time, they exceeded those observed in European countries (WHO 2014), e.g., in Spain, Italy, and Portugal (varied between 22 and 40 μg m⁻³), but were lesser than those of countries known for their high pollution rates, such as United Arab Emirates (160 μg m⁻³), Palestine (175 μg m⁻³), and Egypt (108–450 μg m⁻³) (Jodeh et al. 2018; Zahran et al. 2018).

Similarities existed among the levels of PM₂.₅ found in this study and those reported from India (46 μg m⁻³) and Turkey (43 μg m⁻³) (WHO 2014), but our rates were higher than those detected in Malaysia and Brazil (28 and 11 μg m⁻³, respectively; Amil et al. 2016; Franzin et al. 2020), and lower than those of China (56 μg m⁻³; Chen et al. 2017). The concentrations of PM₂.₅ in the megacities Delhi in India during the CoViD-19 lockdown were as high as 38 μg m⁻³ (ca 52 μg m⁻³ off from normal situation). According to that, it is expected that also in Bab Ezzouar pollution was reduced during pandemic period (Mahato et al. 2020).

The measured concentrations of PM₁ (31.1± 6.4 μg m⁻³) are higher than those reported from Czech Republic (17 μg m⁻³) (Kozáková et al. 2018) and Poland (14 μg m⁻³) (Rogula-Kozłowska et al. 2019) in the urban area.

### Statistical parameters of the particulate matter studied

Table 3 presents the Pearson correlations between the mean concentrations of airborne particles and mean meteorological factors. Throughout the study, a p-value of <0.05 was regarded as statistically significant. The resulting correlations rates were poor, pointing out that no relationship existed between atmospheric particle concentrations and temperature, relative humidity, and wind speed. A possible explanation for this is the short distance from the sampling site to road traffic (<5 m), which means that the influence of meteorological conditions on the PM is barely visible.

On the other hand, the correlation coefficients between the next respective pairs of PM fractions, i.e., PM₁₀–PM₂.₅ (p = 2.22·10⁻⁶), PM₁₀–PM₁ (p = 2.14·10⁻⁴), and PM₂.₅–PM₁ (p = 1.05·10⁻⁶) indicate meaningful correlations among all fractions. These findings are in accordance with previous researches carried out in Algiers (Talbi et al. 2018).

The PM₁/PM₁₀, PM₁/PM₂.₅, and PM₂.₅/PM₁₀ ratios are shown in Fig. 7. The annual averages recorded in this study were 0.29, 0.63, and 0.46, respectively, for PM₁/PM₁₀, PM₁/PM₂.₅, and PM₂.₅/PM₁₀; hence, in the average PM₁, PM₂.₅, and PM₁₀ accounted for 21%, 29%, and 60% of the total (SPM = PM₁+PM₂.₅+PM₁₀) over the whole year. The PM₁/PM₁₀, PM₁/PM₂.₅, and PM₂.₅/PM₁₀ ratios were analogous to those previously found in Algiers, i.e., 0.30, 0.58, and 0.51, respectively (Talbi et al. 2018). The ratio PM₂.₅/PM₁₀ ratio was about 0.5, indicating that coarse particles from road dust
| Compounds                      | Abbreviation | Unit  | 01/18 | 02/18 | 03/18 | 04/18 | 05/18 | 07/18 | 08/18 | 09/18 | 10/18 | 11/18 | 12/18 | 01/19 |
|-------------------------------|--------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| PM                            | PM<sub>10</sub> | μg m<sup>3</sup> | 137.08 | 106.56 | 106.22 | 98.21 | 74.81 | 83.27 | 83.37 | 75.42 | 76.86 | 75.95 | 139.67 | 81.18 |
| Phenanthrene                  | PHE          | ng m<sup>3</sup> | 0.51 | 0.12 | 0.09 | 0.14 | 0.06 | 0.1 | 0.19 | 0.09 | 0.1 | 0.09 | 0.28 | 0.18 |
| Anthracene                    | AN           | ng m<sup>3</sup> | 0.04 | 0.01 | 0.01 | 0.02 | 0.01 | 0.01 | 0.02 | 0.01 | 0.01 | 0.01 | 0.04 | 0.02 |
| methyl Phenanthrene/anthracene| MeP/A        | ng m<sup>3</sup> | 0.49 | 0.17 | 0.17 | 0.24 | 0.1 | 0.13 | 0.19 | 0.12 | 0.13 | 0.12 | 0.36 | 0.21 |
| dimethyl-Phenanthrene/anthracene| DMeP/A      | ng m<sup>3</sup> | 0.39 | 0.2 | 0.26 | 0.29 | 0.11 | 0.2 | 0.19 | 0.18 | 0.15 | 0.18 | 0.51 | 0.33 |
| Fluorantheine                 | FA           | ng m<sup>3</sup> | 0.3 | 0.11 | 0.08 | 0.1 | 0.04 | 0.07 | 0.13 | 0.09 | 0.12 | 0.1 | 0.35 | 0.23 |
| Pyrene                        | PY           | ng m<sup>3</sup> | 0.32 | 0.12 | 0.09 | 0.13 | 0.04 | 0.08 | 0.13 | 0.09 | 0.12 | 0.12 | 0.48 | 0.26 |
| Methyl-Fluorantheine/pyrene   | MeF/P        | ng m<sup>3</sup> | 0.29 | 0.11 | 0.08 | 0.12 | 0.05 | 0.06 | 0.15 | 0.07 | 0.08 | 0.1 | 0.52 | 0.23 |
| Benzo[ghi]fluoranthene        | BghiF        | ng m<sup>3</sup> | 0.49 | 0.45 | 0.11 | 0.16 | 0.04 | 0.05 | 0.08 | 0.07 | 0.09 | 0.12 | 0.76 | 0.31 |
| Benzo(c)phenanthrene          | BcP          | ng m<sup>3</sup> | 0.08 | 0.06 | 0.02 | 0.02 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.02 | 0.12 | 0.05 |
| Cyclopenta(c,d)pyrene         | CPP          | ng m<sup>3</sup> | 0.19 | 0.07 | 0.04 | 0.08 | 0.01 | 0.03 | 0.05 | 0.03 | 0.05 | 0.05 | 0.49 | 0.21 |
| Benz[a]anthracene             | BaA          | ng m<sup>3</sup> | 0.51 | 0.14 | 0.09 | 0.14 | 0.04 | 0.05 | 0.09 | 0.06 | 0.06 | 0.12 | 0.99 | 0.35 |
| Chrysene+trifenilene          | CH+TR        | ng m<sup>3</sup> | 1.4 | 0.62 | 0.34 | 0.46 | 0.18 | 0.17 | 0.27 | 0.25 | 0.23 | 0.35 | 2.2 | 0.79 |
| Benzo[b]fluoranthene          | BbF          | ng m<sup>3</sup> | 2.61 | 1.3 | 0.55 | 0.83 | 0.25 | 0.39 | 0.54 | 0.42 | 0.41 | 0.57 | 3.09 | 1.49 |
| Benzo[j]fluoranthene          | BjF          | ng m<sup>3</sup> | 2.94 | 0.91 | 0.7 | 1.01 | 0.37 | 0.52 | 0.68 | 0.56 | 0.54 | 0.71 | 3.48 | 1.78 |
| Benzo[e]pyrene                | BeP          | ng m<sup>3</sup> | 3.35 | 2.54 | 0.77 | 1.04 | 0.32 | 0.58 | 0.79 | 0.55 | 0.57 | 0.68 | 3.37 | 1.75 |
| Benzo[a]pyrene                | BaP          | ng m<sup>3</sup> | 1.64 | 0.47 | 0.26 | 0.42 | 0.09 | 0.16 | 0.24 | 0.14 | 0.17 | 0.21 | 2.2 | 1.15 |
| Perylene                      | PE           | ng m<sup>3</sup> | 0.28 | 0.13 | 0.05 | 0.08 | 0.02 | 0.03 | 0.04 | 0.02 | 0.03 | 0.03 | 0.36 | 0.19 |
| Indeno[1.2.3-cd]pyrene        | IP           | ng m<sup>3</sup> | 3.87 | 1.25 | 1.21 | 1.72 | 0.48 | 0.86 | 1.12 | 0.79 | 0.79 | 0.89 | 4.53 | 2.84 |
| Benzo[ghi]perylene            | BPE          | ng m<sup>3</sup> | 6.9 | 5.25 | 2.67 | 3.99 | 0.97 | 1.71 | 2.29 | 1.61 | 1.75 | 1.87 | 7.82 | 4.59 |
| Dibenzo[a,h]anthracene        | DBahA        | ng m<sup>3</sup> | 0.63 | 0.15 | 0.19 | 0.23 | 0.16 | 0.15 | 0.19 | 0.12 | 0.11 | 0.12 | 0.71 | 0.4 |
| Total PAHs                    | ng m<sup>3</sup> |       | 27.2 | 14.2 | 7.8 | 11.2 | 3.3 | 5.4 | 7.4 | 5.3 | 5.5 | 12.1 | 32.7 | 17.4 |
Table 5  Concentration of PAHs identified in PM$_{2.5}$ from January 2018 for January 2019

| Compounds                        | Abbreviation | Unit       | 01/18 | 02/18 | 03/18 | 04/18 | 05/18 | 07/18 | 08/18 | 09/18 | 10/18 | 11/18 | 12/18 | 01/19 |
|----------------------------------|--------------|------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| PM                               | PM$_{2.5}$   | μg m$^{-3}$| 61.17 | 49.58 | 51.20 | 50.50 | 29.99 | 41.55 | 38.47 | 34.42 | 30.86 | 41.72 | 76.37 | 36.42 |
| Phenanthrene                     | PHE          | ng m$^{-3}$| 0.37  | 0.09  | 0.07  | 0.11  | 0.04  | 0.08  | 0.15  | 0.07  | 0.08  | 0.07  | 0.24  | 0.16  |
| Anthracene                       | AN           | ng m$^{-3}$| 0.03  | 0.01  | 0.01  | 0.02  | 0       | 0.01  | 0       | 0.01  | 0.01  | 0.01  | 0.04  | 0.02  |
| methyl-Phenanthrene/anthracene   | MeP/A        | ng m$^{-3}$| 0.35  | 0.12  | 0.12  | 0.19  | 0.07  | 0.11  | 0.15  | 0.09  | 0.1   | 0.09  | 0.28  | 0.18  |
| dimethyl-Phenanthrene/anthracene | DMeP/A       | ng m$^{-3}$| 0.39  | 0.2   | 0.18  | 0.29  | 0.11  | 0.16  | 0.19  | 0.13  | 0.15  | 0.12  | 0.39  | 0.27  |
| Fluoranthene                     | FA           | ng m$^{-3}$| 0.24  | 0.09  | 0.06  | 0.08  | 0.03  | 0.06  | 0.1   | 0.07  | 0.09  | 0.07  | 0.29  | 0.21  |
| Pyrene                           | PY           | ng m$^{-3}$| 0.26  | 0.1   | 0.07  | 0.12  | 0.03  | 0.07  | 0.11  | 0.07  | 0.11  | 0.09  | 0.41  | 0.23  |
| methyl-Fluoranthene/pyrene       | MeF/P        | ng m$^{-3}$| 0.23  | 0.08  | 0.06  | 0.1   | 0.04  | 0.05  | 0.07  | 0.06  | 0.07  | 0.07  | 0.41  | 0.19  |
| Benzo[g,h,i]fluoranthene         | BghiF        | ng m$^{-3}$| 0.35  | 0.14  | 0.08  | 0.13  | 0.03  | 0.04  | 0.07  | 0.06  | 0.07  | 0.09  | 0.6   | 0.27  |
| Benzo[j]phenanthrene             | BcP          | ng m$^{-3}$| 0.06  | 0.02  | 0.01  | 0.02  | 0.01  | 0.01  | 0.01  | 0.01  | 0.01  | 0.1   | 0.04  |        |
| Cyclopenta(c,d)pyrene            | CPP          | ng m$^{-3}$| 0.17  | 0.05  | 0.04  | 0.08  | 0.01  | 0.03  | 0.05  | 0.03  | 0.05  | 0.04  | 0.44  | 0.2   |
| Benzo[a]anthracene               | BaA          | ng m$^{-3}$| 0.39  | 0.11  | 0.07  | 0.12  | 0.03  | 0.04  | 0.08  | 0.05  | 0.05  | 0.09  | 0.79  | 0.31  |
| Chrysene+trifilenene             | CH+TR        | ng m$^{-3}$| 0.97  | 0.35  | 0.23  | 0.37  | 0.13  | 0.15  | 0.22  | 0.2   | 0.18  | 0.24  | 1.71  | 0.68  |
| Benzo[b]fluoranthene             | BbF          | ng m$^{-3}$| 1.97  | 1.02  | 0.43  | 0.71  | 0.18  | 0.34  | 0.48  | 0.34  | 0.35  | 0.45  | 2.55  | 1.35  |
| Benzo[j,k]fluoranthene           | BjkF         | ng m$^{-3}$| 2.1   | 0.51  | 0.51  | 0.84  | 0.27  | 0.45  | 0.58  | 0.45  | 0.43  | 0.57  | 2.79  | 1.59  |
| Benzo[e]pyrene                   | BeP          | ng m$^{-3}$| 2.51  | 2.13  | 0.57  | 0.87  | 0.23  | 0.5   | 0.65  | 0.44  | 0.45  | 0.54  | 2.84  | 1.59  |
| Benzo[a]pyrene                   | BaP          | ng m$^{-3}$| 1.33  | 0.36  | 0.22  | 0.38  | 0.08  | 0.15  | 0.23  | 0.12  | 0.15  | 0.18  | 1.93  | 1.08  |
| Perylene                         | PE           | ng m$^{-3}$| 0.22  | 0.11  | 0.04  | 0.07  | 0.01  | 0.03  | 0.04  | 0.02  | 0.02  | 0.03  | 0.32  | 0.18  |
| Indeno[1,2,3-cd]pyrene            | IP           | ng m$^{-3}$| 3.5   | 1.07  | 1.12  | 1.58  | 0.43  | 0.82  | 1.03  | 0.69  | 0.72  | 0.81  | 4.24  | 2.71  |
| Benzo[g,h]perylenel               | BPE          | ng m$^{-3}$| 6.2   | 4.85  | 2.45  | 3.64  | 0.84  | 1.62  | 2.01  | 1.39  | 1.57  | 1.68  | 7.29  | 4.35  |
| Dibenzo[a,h]anthracene           | DBahA        | ng m$^{-3}$| 0.56  | 0.12  | 0.17  | 0.21  | 0.14  | 0.14  | 0.17  | 0.11  | 0.1   | 0.1   | 0.66  | 0.38  |
| Total PAHs                        |              | ng m$^{-3}$| 22.21 | 11.52 | 6.51  | 9.95  | 2.72  | 4.88  | 6.39  | 4.39  | 4.77  | 5.37  | 28.33 | 16.02 |
resuspension and abrasion processes are the dominant fraction of the particulates.

PAHs

GC/MS analysis

Twenty PAHs had identified and quantified in PM$_{10}$, PM$_{2.5}$, and PM$_{1}$ (Tables 4, 5, 6). The mean concentration of individual PAHs ranged from 0.02±0.01 to 3.45±1.27 ng m$^{-3}$, from 0.01±0.06 to 3.16±1.19 ng m$^{-3}$, and from 0.04±0.003 to 7.88±2.63 ng m$^{-3}$ for PM$_{10}$, PM$_{2.5}$, and PM$_{1}$, respectively. The most volatile among the 20 PAHs analyzed (Fig. 8), namely naphthalene, acenaphthene, and fluorene, were not detected in airborne particles, because the 2/3-ring aromatic molecules occur predominantly in the gaseous phase of atmosphere, at ambient temperatures typical of North Western Africa. The results are in accordance with other studies conducted in that region (Jamhari et al. 2014).

The mean concentrations of total PAHs (T-PAHs) in PM$_{1}$, PM$_{2.5}$, and PM$_{10}$ were equal to 24.9±9.9 ng m$^{-3}$ (4.1-59.7 ng m$^{-3}$), 10.3±4.5 ng m$^{-3}$ (2.72-28.3 ng m$^{-3}$), and 12.5±5.2 ng m$^{-3}$ (3.3-32.7 ng m$^{-3}$), respectively. Cumulatively, T-PAHs reached 47.6±34.5 ng m$^{-3}$ over the measurement period. As for size distribution, T-PAHs were preferably associated to PM$_{1}$ fraction (52.2±5.5%), the remaining being almost equally partitioned between PM$_{2.5}$ and PM$_{10}$ (21.3±2.6% and 26.4±4.6%, respectively), with minor differences among the months. The important content of PAHs in PM$_{1}$ was that typically originated by organic fuel combustion, known as producing ultrafine particles heavily affected by PAHs (Landkocz et al. 2017). Indeed, T-PAHs accounted for 790±420 p.p.m. in mass of PM$_{1}$, 210±120 ppm of PM$_{2.5}$ and 120±60 p.p.m. of PM$_{10}$. Nonetheless, some monthly variability in the relative abundance of PAHs in the three fraction was observed, with percentages in PM$_{10}$ peaking in May and November. The reasons of is behaviour are still unknown and seems to merit further investigation, though presumably related with nature of sources. As shown in Fig. 9, ~50% of T-PAHs were associated with particles <0.95 μm, and up to 90% with particles <2.5  μm. Noteworthy, PAHs accumulate mainly in the form of fine and ultrafine particles, which could pose a potential health risk. Finally, most of particulate PAHs (~88% of the total) belong to high molecular weight range (MW ≥276), however the percentage of low molecular weight PAHs (2–3 ring congeners) is relatively more abundant in the warm season (~16% July to September vs. ~9% December to February). This pattern, apparently inconsistent with ambient temperature profile that should promote the passage of PAHs into the gas phase, has been associated to emission from asphalts and uncontrolled fires (e.g., vegetation) (Cecinato et al. 2014).

The PM$_{10}$-bound PAH concentrations reported in our study were much lower than those previously recorded in urban areas, such as 97 to 137 ng m$^{-3}$ in Tehran (Hoseini et al. 2016) and 14 to 420 ng m$^{-3}$ in Alexandria, Egypt (Khairy and Lohmann 2013). The results of this study were also higher than the 2.8 ng m$^{-3}$ recorded for Bizerte, Tunisia (Barhoumi et al. 2018) and the average of 3 ng m$^{-3}$ in Boumerdes, Algeria (Ladj et al. 2009b) and in agreement with those recorded in Bab el Ouied and Ben Aknoun (Algiers, Algeria), ranging from 8.4 ng m$^{-3}$ to 19 ng m$^{-3}$ (Ladj et al. 2009a).

The measured concentrations of T-PAHs for PM$_{2.5}$ and PM$_{1}$ were higher than those reported in Athens (Greece), which ranged from 0.43 to 1.56 ng m$^{-3}$ and from 0.21 to 0.9 ng m$^{-3}$, respectively (Pateraki et al. 2019). On the other hand, these latter were lower than those recorded in Kigali (Rwanda), which varied from 19.3 ng m$^{-3}$ to 54.9 ng m$^{-3}$ for PM$_{2.5}$ (Kalisa et al. 2018), and those recorded at Porto (Brazil), which ranged from 1.32 to 3.05 ng m$^{-3}$ for PM$_{1}$ (Agudelo-Castañeda and Teixeira 2014), and comparable with those found in Brno and Slapanice (Czech Republic), where a concentration of 22.2 ng m$^{-3}$ was recorded in winter time in PM$_{1}$ (Krumal et al. 2013).

The average concentrations of the PM$_{10}$- and PM$_{2.5}$-bound class 1 carcinogen BaP were 0.60±0.34 ng m$^{-3}$ and 0.52±0.29 ng m$^{-3}$, respectively, whereas the average in the PM$_{1}$-bound fraction was 1.26 ng m$^{-3}$, exceeding 1 ng m$^{-3}$. Cumulatively, BaP reached 2.38 ng m$^{-3}$ and exceeded by far the EU reference value of 1 ng m$^{-3}$ averaged over the calendar year.

The concentrations of PAHs in all three fractions were clearly higher during the cold vs. the warm season. This pattern is primarily the result of emission rate increase from year time modulated sources, like residential heating and motor vehicle traffic. In the colder months, there is also the concurrent impact of atmospheric conditions, characterized by frequent thermal inversions, low mixed layer and considerably reduced atmospheric dispersion. Conversely, the hot period experienced reduced PAH levels thanks to stop of heating plant emissions and to meteorological conditions promoting the gas-phase partition and photo-degradation of PAHs; moreover, PAH concentrations could drop due to photo-oxidation promoted by solar radiation and induced by numerous atmospheric oxidants, namely free radicals such as OH, NO$_3$, NO$_2$ and ozone (Manoli et al. 2015).

BPE and IP were the most abundant PAHs in the three fractions; according to previous studies, relatively high concentration of BPE and IP are associated with exhausts of gasoline-powered vehicles, while lower PAHs including FA, PHE, PY, and CH are overall associated to diesel-powered vehicles (Jamhari et al. 2014).

The principal PAHs in all three fractions of particulate matter were BbF, BjkF, CH, FA, IP, BeP, and BPE, which cumulatively accounted for > 80% of the T-PAHs. This seemed
### Table 6
Concentration of PAHs identified in PM$_1$ from January 2018 for January 2019

| Compounds                                      | Abbreviation | Unit     | 01/18 | 02/18 | 03/18 | 04/18 | 05/18 | 07/18 | 08/18 | 09/18 | 10/18 | 11/18 | 12/18 | 01/19 |
|------------------------------------------------|--------------|----------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| PM                                             | PM$_1$       | $\mu$g m$^{-3}$ | 39.97 | 32.96 | 30.27 | 33.63 | 33.63 | 32.08 | 24.43 | 21.24 | 20.00 | 26.37 | 56.42 | 23.01 |
| Phenanthrene                                   | PHE          | ng m$^{-3}$   | 0.85  | 0.2   | 0.15  | 0.32  | 0.06  | 0.25  | 0.41  | 0.16  | 0.2   | 0.19  | 0.5   | 0.34 |
| Anthracene                                     | AN           | ng m$^{-3}$   | 0.05  | 0.05  | 0.05  | 0.05  | 0.05  | 0.05  | 0.05  | 0.05  | 0.05  | 0.02  | 0.05  | 0.05 |
| methyl-phenanthrene/anthracene                 | MeP/A        | ng m$^{-3}$   | 0.8   | 0.29  | 0.24  | 0.53  | 0.09  | 0.32  | 0.39  | 0.23  | 0.26  | 0.24  | 0.6   | 0.37 |
| dimethyl-Phenanthrene/anthracene               | DMeP/A       | ng m$^{-3}$   | 0.85  | 0.49  | 0.35  | 0.77  | 0.12  | 0.46  | 0.51  | 0.34  | 0.38  | 0.33  | 0.84  | 0.55 |
| Fluoranthene                                   | FA           | ng m$^{-3}$   | 0.55  | 0.21  | 0.14  | 0.22  | 0.04  | 0.18  | 0.25  | 0.15  | 0.21  | 0.19  | 0.58  | 0.43 |
| Pyrene                                         | PY           | ng m$^{-3}$   | 0.62  | 0.25  | 0.17  | 0.34  | 0.04  | 0.22  | 0.29  | 0.18  | 0.28  | 0.26  | 0.91  | 0.5   |
| methyl-Fluoranthene/pyrene                     | MeF/P        | ng m$^{-3}$   | 0.53  | 0.22  | 0.13  | 0.29  | 0.05  | 0.15  | 0.18  | 0.14  | 0.18  | 0.18  | 0.81  | 0.43 |
| Benzo(ghi)fluoranthene                         | BghiF        | ng m$^{-3}$   | 0.82  | 0.34  | 0.2   | 0.38  | 0.04  | 0.14  | 0.18  | 0.15  | 0.2   | 0.25  | 1.24  | 0.65 |
| Benzo(c)phenanthrene                           | BcP          | ng m$^{-3}$   | 0.12  | 0.05  | 0.03  | 0.05  | 0.01  | 0.02  | 0.03  | 0.02  | 0.03  | 0.18  | 0.1   | 0.1   |
| Cyclopenta(c,d)pyrene                          | CPP          | ng m$^{-3}$   | 0.5   | 0.15  | 0.11  | 0.26  | 0.02  | 0.11  | 0.16  | 0.09  | 0.16  | 0.16  | 1.15  | 0.57 |
| Benzo[a]anthracene                             | BaA          | ng m$^{-3}$   | 0.9   | 0.28  | 0.17  | 0.36  | 0.03  | 0.13  | 0.2   | 0.12  | 0.16  | 0.22  | 1.63  | 0.74 |
| Chrysene+trifilenic                            | CH+TR        | ng m$^{-3}$   | 2.21  | 0.85  | 0.54  | 1.07  | 0.15  | 0.44  | 0.55  | 0.47  | 0.49  | 0.62  | 3.5   | 1.6   |
| Benzo[b]fluoranthene                           | Bbf          | ng m$^{-3}$   | 4.95  | 1.75  | 1.06  | 2.13  | 0.23  | 1.09  | 1.26  | 0.84  | 0.99  | 1.25  | 5.61  | 3.43  |
| Benzo[j,k]fluoranthene                         | BjkF         | ng m$^{-3}$   | 5.3   | 2.03  | 1.27  | 2.5   | 0.42  | 1.43  | 1.52  | 1.14  | 1.19  | 1.59  | 5.91  | 3.87  |
| Benzo[e]pyrene                                 | BeP          | ng m$^{-3}$   | 6.06  | 2.22  | 1.36  | 2.53  | 0.32  | 1.52  | 1.76  | 1.11  | 1.28  | 1.52  | 6.04  | 3.88  |
| Benzo[a]pyrene                                 | BaP          | ng m$^{-3}$   | 3.47  | 0.86  | 0.55  | 1.13  | 0.07  | 0.5   | 0.63  | 0.28  | 0.45  | 0.53  | 4.03  | 2.66  |
| Perylene                                       | PE           | ng m$^{-3}$   | 0.52  | 0.16  | 0.1   | 0.21  | 0.01  | 0.11  | 0.05  | 0.07  | 0.08  | 0.65  | 0.39  | 0.39  |
| Indeno[1.2.3-cd]pyrene                         | IP           | ng m$^{-3}$   | 8.25  | 3.83  | 2.77  | 4.51  | 0.66  | 2.63  | 2.65  | 1.6   | 1.93  | 2.19  | 8.4   | 6.92  |
| Benzo[ghi]perylene                             | BPE          | ng m$^{-3}$   | 15.36 | 7.89  | 6.8   | 11.26 | 1.54  | 5.19  | 5.57  | 3.53  | 4.62  | 5.13  | 15.88 | 11.8  |
| Dibenz[a,h]anthracene                          | DBahA        | ng m$^{-3}$   | 1.18  | 0.47  | 0.38  | 0.53  | 0.17  | 0.41  | 0.39  | 0.21  | 0.25  | 0.26  | 1.16  | 0.89  |
| Total PAHs                                      |              | ng m$^{-3}$   | 53.96 | 22.58 | 16.56 | 29.45 | 4.12  | 15.35 | 17.1  | 10.85 | 13.38 | 15.28 | 59.66 | 40.17 |

**Note:** Concentration values are given in micrograms per cubic meter ($\mu$g m$^{-3}$) for each compound and month from January 2018 to January 2019.
indicative of high impact of vehicle exhausts on air quality; indeed, BeP and BPE associated to particulate matter are used to recognize emission from gasoline- and diesel-powered engines (He et al. 2014), suggesting the presence of local pollution and low photo-degradation (Romagnoli et al. 2019).

Figure 10 presents the PAH ring number distribution in PM$_{10}$. According to pie chart, the contribution of high molecular weight congeners (5/6-ring PAHs) in PM$_{10}$ is up to 88%. On the other hand, medium (4-ring) and low molecular weight PAHs (2/3-ring) accounted for 10% and 2% of the total PAHs, respectively. The high percentage of high molecular weight PAHs indicates the sources are high-temperature processes, e.g., fuel combustion in engines (Jamhari et al. 2014).

Emission source identification

**PAHs diagnostic ratios** PAH diagnostic ratios are a practical tool for the identification of probable sources on the basis of the concentrations of specific PAH compounds or groups and have been developed and used by a number of environmental researchers.

The values of calculated diagnostic ratios for the particulate matter studied and characteristic diagnostic ratios obtained from preceding literature are reported in Table 7. From the comparison of the diagnostic ratios shown in Table 7, the majority of the calculated diagnostic ratios were within the range of gasoline, diesel, and coal emissions.

In this study, the FA/PY, IP/BPE, BaP/BeP, and BaP/BPE ratios were equal to 0.90, 0.48, 0.37, and 0.14, respectively. According to them, diesel vehicles were the principal source of emissions. Other emission sources were identified looking to (BaP/BPE) and (BaP/BeP) ratios, i.e., clay plant, urban incinerators, fumes from landfill and tobacco smoke, which also could be important. Finally, fresh emissions seemed to characterize the air at the sampling site, as resulting from the BaP/BeP ratio rates.

**Principal components analysis (PCA)** Principal component analysis (PCA), a multivariate statistical method, has applied to identify emission sources and carried out with the statistical software R. The resulting loads and percentages of variance calculated for each of the components are shown in Table 8.
Only those variables with a factor load higher than 0.5 have considered in order to characterize the source of pollution.

Two components have identified in PM1, PM2.5, and PM10, which probably represented vehicle emissions categories and stationary combustion sources.

The major components (PC1) and (PC2), respectively, accounted for 88% and 5.4% of the total variance for PM1, 92.8% and 3.7% for PM2.5, and 91.6% and 3.9% for PM10.

The high loading factors of FA, PY, BbF, BjkF, BeP, BaP, BaA, IP, and CH for Factor 1 in all fractions confirmed that vehicle emissions were one of the main sources of PAHs.

For Factor 2, only AN had the loading factor >0.50 in PM1, suggesting that this compound was linked to sources other than vehicles. AN had been found in coal combustion, wood combustion, and coke production by several studies (Guo et al. 2003; He et al. 2014).

All fractions of PM-bound PAHs in Bab Ezzouar city were mainly affected by vehicle exhaust and coal/coke sources.

### Health risk assessment

PAHs associated with particulate matter have diverse harmful effects on human health. To assess the potential health risks of inhalation associated with human exposure to PAHs, two approaches have applied, i.e., calculation of aerial concentration of benzo[a]pyrene equivalents ([BaPeq]) and of the incremental lifetime cancer risk (ILCR) rate associated to PAHs.

Taking into account not only BaP, BaPeq was estimated as reliable to parameterize carcinogenicity associated to PAHs and is frequently applied as an indicator of human exposure to PAHs (WHO). For this purpose, neat carcinogenicity of every PAH calculated in this study was expressed in toxic equivalents relative to benzo[a]pyrene; the PAH concentrations were converted into [BaPeq] and summed using the following relationship:

\[
\text{[BaPeq]} = \text{[PAH]} \times \text{Carcinogenicity factor of PAH}
\]

#### Table 7  PAH diagnostic ratio

| Sources                  | PAH ratio | FA/PY | IP/BPE | BaP/BPE | BaP/BeP | Reference                                           |
|--------------------------|-----------|-------|--------|---------|---------|----------------------------------------------------|
| **Vehicles**             | Mixed     | 0.60  | 0.55   |         |         | Ravindra et al. 2008; Rotatori et al. 2005         |
|                          | leaded gasoline | 0.50  | 0.37   | 0.45    | 0.95    | Bourrotte et al. 2005; Ravindra et al. 2008; Rogge et al. 1993; Rotatori et al. 2005 |
|                          | unleaded gasoline | 0.54  | 0.2-0.35 | 0.35  | 0.95  | Bourrotte et al. 2005; Ravindra et al. 2008; Rogge et al. 1993; Rotatori et al. 2005 |
|                          | diesel     | 0.8-1.1 | 0.65-1.1 | 0.8-1.1  | 0.50  | Bourrotte et al. 2005; Ravindra et al. 2008; Rogge et al. 1993; Rotatori et al. 2005 |
| **Domestic heating**     | coal       | 0.9-1.3 | 1.57   | 2.10    |         | Cecinato et al. 2005                               |
|                          | wood, pine | 0.18  | 1.1-1.6 | 1.94    | 1.77    | Schmidl et al. 2008                                |
|                          | wood, oak  | 0.15  | 1.2-1.6 | 1.77    | 0.52    | Schmidl et al. 2008                                |
|                          | synthetic fuel | 1.19  | 1.10   | 1.91    |         | Cecinato et al. 2005                                |
|                          | heavy oil  | 0.83  | 1.61   | 0.81    |         | Cecinato et al. 2005                                |
| **Iron/steel plant**     | coke (coal) | 0.30  | 1.21   | 0.78    | 1.65    | Cecinato et al. 2005 and Yang et al. 1998          |
|                          | power plant (coal) | 0.66  | 2.01   | 0.88    | 2.57    | Cecinato et al. 2005 and Yang et al. 1998          |
| **Tobacco smoke**        | particulate | 0.96  | 0.18   | 0.23    | 0.38    | Lu and Zhu 2007                                    |
| **Landfill**             | fumes      | 1.30  | 0.76   | 0.70    | 0.55    | Cecinato et al. 2005                                |
| **Clay plant**           | fumes      | ~2.65 | 1.82   | 0.14    | 0.02    | Cecinato et al. 2005                                |
| **Urban incinerator**    | fumes      | ~17   | 0.92   | ~0.12   | 0.01    | Bourrotte et al. 2005; Cecinato et al. 2005; Salzano et al. 2008 |
| **This study**           | PM10       | 0.90  | 0.48   | 0.14    | 0.37    |                                                     |
Total \( \text{BaPeq} = \sum C_i \times \text{TEF}_i \)

where \( C_i \) is the concentration of each \( i \)-PAH, and \( \text{TEF}_i \) is the corresponding toxic equivalency factor. In this study, the values established in the literature for the PAH TEFs have been used (Lagoy and Nisbet 1992). The BaPeq for individual PAHs and total BaPeq for 13 PAHs have reported in Table 9.

The average of BaPeq in PM1 was twice that in PM2.5 and PM10; the association of PM1 with carcinogenic PAHs raises the harmful impact on humans due to the capacity of these submicronic particles to settle in the lungs.

### Table 8 PCA analysis of PAHs in PM1, PM2.5, and PM10

| PAHs   | PM1 Factor1 | Factor2 | PM2.5 Factor1 | Factor2 | PM10 Factor1 | Factor2 |
|--------|-------------|---------|---------------|---------|--------------|---------|
| PHE    | 0.831       |         | 0.850         | 0.475   | 0.807        | 0.561   |
| AN     | -           | 0.814   | 0.975         | -       | 0.970        | -       |
| FA     | 0.977       | -       | 0.977         | -       | 0.974        | -       |
| PY     | 0.976       | -       | 0.983         | -       | 0.978        | -       |
| CH     | 0.977       | -       | 0.982         | -       | 0.985        | -       |
| BbF    | 0.997       | -       | 0.990         | -       | 0.993        | -       |
| BjkF   | 0.997       | -       | 0.992         | -       | 0.995        | -       |
| BeP    | 0.928       | -       | 0.909         | -       | 0.928        | -       |
| BaP    | 0.994       | -       | 0.994         | -       | 0.994        | -       |
| PE     | 0.995       | -       | 0.989         | -       | 0.993        | -       |
| IP     | 0.979       | -       | 0.992         | -       | 0.988        | -       |
| DBahA  | 0.981       | -       | 0.977         | -       | 0.976        | -       |
| Eigen value | 17.62    | 1.08   | 18.58         | 0.76    | 18.34        | 0.79    |
| % of variance | 88.08  | 5.41   | 92.89         | 3.78    | 91.69        | 3.94    |
| Cumulative % | 88.08  | 93.50  | 92.89         | 96.67   | 91.69        | 95.63   |
| Source | Source Vehicular emission | Stationary combustion source | Source Vehicular emission | Stationary combustion source | Source Vehicular emission | Stationary combustion source |

### Table 9 [BaPE] and toxic equivalency factor for total PAHs and seven carcinogenic PAHs

| Compound | Toxic equivalency factor (Lagoy and Nisbet 1992) | Toxic equivalency quotients TEQ |
|----------|-----------------------------------------------|---------------------------------|
|          |                                               | PM1        | PM2.5      | PM10       |
| PHE      | 0.001                                         | 0.000302   | 0.00013    | 0.000162   |
| AN       | 0.01                                          | 0.000437   | 0.000146   | 0.000173   |
| FA       | 0.001                                         | 0.000264   | 0.000124   | 0.00015    |
| PY       | 0.001                                         | 0.000339   | 0.000146   | 0.000174   |
| CPP      | 0.1                                           | 0.028746   | 0.010849   | 0.011753   |
| BaA      | 0.1                                           | 0.040979   | 0.018752   | 0.022965   |
| CH       | 0.01                                          | 0.01042    | 0.004697   | 0.006198   |
| BbF      | 0.1                                           | 0.205094   | 0.08865    | 0.107209   |
| BjkF     | 0.1                                           | 0.234589   | 0.097616   | 0.12288    |
| BaP      | 1                                              | 1.262647   | 0.561011   | 0.638223   |
| IP       | 0.1                                           | 0.387053   | 0.16484    | 0.17846    |
| BPE      | 0.01                                          | 0.078815   | 0.032496   | 0.035389   |
| DBahA    | 1                                             | 0.527328   | 0.251108   | 0.275204   |
| Total BaPE | 2.78                      | 1.23       | 1.40       |            |
Table 10  Risk parameters for different age groups

| Symbol | Age         | Units | Infants | Children | Adults |
|--------|-------------|-------|---------|----------|--------|
| C      |             | Year  | 0–1     | 2–18     | 19–70  |
| BW     | Body weight | kg    | 9.1     | 29.7     | 71.05  |
| IR     | Inhalation rate | m³/day | 5.36   | 11.41    | 15.73  |
| EF     | Exposure Frequency | Days/year | 350   | 350      | 350    |
| ED     | Exposure duration | Year   | 0–1     | 0–17     | 0–52   |
| AT     | Averaging time | Days   | 25550   | 25550    | 25550  |
| AT     |             |       |         |          |        |

BaPeq values in Bab Ezzouar were similar to those recorded in Algiers (Yassaa et al. 2001c) and higher than those reported in Bizerte (Barhoumi et al. 2018) and Naples (Di Vaio et al. 2016).

The ILRC has measured by multiplication of the lifetime average daily dose (LADD) by the slope factor BaPeq. The lifetime has divided into three periods as follows: infants (0–1 year), children (2–18 years), and adults (19–70 years). The global LADD has computed by summation of the LADD values of the three age groups. The following equations have used to estimate LADD and ILRC:

\[
\text{LADD} = \frac{C \times EF \times ED \times IR}{AT \times BW} \\
\text{ILRC} = \text{LADD} \times \left( \frac{CSF \times BW}{70} \right)^{1/2} \times cf
\]

where:
- \( C \) is the concentration of [BaPeq] in air (ng m⁻³),
- \( EF \) is the exposure frequency (day year⁻¹),
- \( ED \) is the exposure duration (years),
- \( IR \) is the air inhalation rate (m³ day⁻¹),
- \( AT \) is the average lifetime of carcinogens (days),
- \( BW \) is the body weight (kg),
- \( CSF \) is the cancer slope factor (mg kg⁻¹ day⁻¹), and
- \( cf \) is the conversion factor (10⁻⁶) (Moya et al. 2011).

Table 10 presents the selected parameters chosen for the calculation of ILRC. The CSFs of B[a]P for the inhalation pathway have taken from the published literature (CSF = 3.14 mg kg⁻¹ day⁻¹) (Hoseini et al. 2016). Residents have estimated as exposed 350 days a year during their life span.

The mean ILRC was 2 × 10⁻⁶, 8.87 × 10⁻⁶, and 10⁻⁶ for PM₁, PM₂.₅, and PM₁₀, respectively. The results obtained did not exceed the tolerable level fixed by USEPA of 10⁻⁶ for the general population for PM₂.₅ and PM₁₀, and so the risk to human health was therefore low for the citizens of Bab Ezzouar. The ILRC for PM₁ is twice as high as the USEPA tolerable level of 10⁻⁶.

Conclusion

Twenty polycyclic aromatic hydrocarbons in PM₁, PM₂.₅, and PM₁₀ were identified and quantified at an urban site in Bab Ezzouar city (Algeria), to draw information about their abundance in the atmosphere and distribution among PM size fractions, which influences the carcinogenic risk for humans. SEM and RaS analyses revealed that most particles were carbonaceous. The annual average concentrations of particulate matter of different sizes exceeded by far the guidelines set forth by the WHO (10 µg m⁻³) and EU (25 µg m⁻³) for PM₂.₅ and by more than four times and twice those of the WHO (20 µg m⁻³) and EU (40 µg m⁻³) for PM₁₀. In addition, the annual mean concentration of PM₁ (31.1± 6.4 µg m⁻³) recorded at the sampling site was very high and seemed to present a serious risk, regardless of their potential chemical toxicity, hence the need to introduce some regulation in national normative. Wide seasonal variations were observed of PAH concentrations in the three fractions of particulate matter, all peaking during the winter. Diagnostic ratios and PCA indicate that vehicular emissions with diesel fuel were the predominant source of PAHs. Additional sources from landfills, clay plants, and tobacco smoke were not negligible.

Though the ILRC from exposure to airborne BaPeq seemed negligible for the coarse and the fine particulates, it was important when ultrafine particles and cumulative particulates were considered. Hence, the carcinogenic risk for population residing in the study area was important. These results will contribute to the elaboration and implementation of appropriate pollution mitigation actions in Bab Ezzouar city by the political decision-makers.

Acknowledgements  The authors would like to thank the medical-social center of the Civil Protection at Bab Ezzouar City for the opportunity and support provided to collect the samples needed for this study. This work was also supported by DGRSDT (Direction Générale de la Recherche Scientifique et du Développement Technologique, Algeria).

Declarations

Competing interests  The authors declare no competing interests.

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