**Levels and risk assessment of hydrocarbons and organochlorines in aerosols from
a North African coastal city (Bizerte, Tunisia)**

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Barhoumi, B., Castro-Jiménez, J., Guigue, C., Goutx, M., Sempéré, R., Derouiche, A.,
Achour, A., Touil, S., Driss, M.R., Tedetti, M., 2018. Levels and risk assessment of
hydrocarbons and organochlorines in aerosols from a north African coastal city (Bizerte,
Tunisia). Environmental Pollution, 240, 422-431.

Abstract

The aim of this study was to assess, for the first time, the concentrations, sources, dry deposition and human health risks of polycyclic aromatic hydrocarbons (PAHs), aliphatic hydrocarbons (AHs), polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) in total suspended particle (TSP) samples collected in Bizerte city, Tunisia (North Africa), during one year (March 2015 - January 2016). Concentrations of PAHs, AHs, PCBs and OCPs ranged 0.5-17.8 ng m⁻³, 6.7-126.5 ng m⁻³, 0.3-11 pg m⁻³ and 0.2-3.6 pg m⁻³, respectively, with higher levels of all contaminants measured in winter. A combined analysis revealed AHs originating from both biogenic and petrogenic sources, while diesel vehicle emissions were identified as dominant sources for PAHs. PCB potential sources included electronic, iron, cement, lubricant factories located within or outside Bizerte city. The dominant OCP congeners were *p,p'*-DDT and *p,p'*-DDE, reflecting a current or past use in agriculture. Health risk assessment showed that the lifetime excess cancer risk from exposure to airborne BaP was negligible in Bizerte, except in winter, where a potential risk to the local population may occur.

Keywords: Atmospheric pollution; Total suspended particles; North Africa; Hydrocarbons; Organochlorines

Capsule: Hydrocarbons and organochlorines in aerosols of Bizerte city (Tunisia) displayed the highest concentrations, deposition fluxes and carcinogenic risks in winter.

1. Introduction

Airborne particles (aerosols), which are composed of hundreds of harmful constituents (Azimi et al., 2005), have gained significant attention over past decades due to their impacts on human health and ecosystems (Dockery et al., 2000; WHO, 2000). Among these constituents, hydrocarbons, including polycyclic aromatic (PAHs) and aliphatic hydrocarbons (AHs), as well as organochlorines (OCs), including polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs), have attracted much interest due to their carcinogenic, mutagenic and bioaccumulative effects, as well as their long-range atmospheric transport (particularly OCs) (Kim et al., 2013; Wania and Mackay, 1996).

PAHs are primarily emitted in the atmosphere by biomass and gas burning, incineration of urban wastes, petrol and diesel combustion, as well as industrial processes (Tobiszewski and Namieśnik, 2012), even though natural sources (volcanoes, forest fires) are not negligible (Mazquiarán and de Pinedo, 2007). AHs are also emitted by anthropogenic activities (vehicle emissions, coal, biomass and gas burning) but have significant biogenic sources, such as higher plant waxes, pollen, and microbial activities (Alves et al., 2012; Perrone et al., 2014). PCB and OCP production and use were banned by the mid-1970s in most countries, but these compounds remain present in all environmental media (Haddaoui et al., 2016; Pegoraro et al., 2016; Schröder et al., 2016). Although the primary sources of PCBs are supposed to be controlled (Nizzetto et al., 2010), i.e., transformers and capacitors, hydraulic fluids, additives in paints and pesticides, plastics, landfills, and sludge drying beds (Kim et al., 2013; Lehmler et al., 2010), diffuse sources, such as accidental spills, combustion of different fuels, and re-volatilization may have led to the current input of PCBs to the atmosphere (Breivik et al., 2002; Dyke et al., 2003). OCPs may enter the atmosphere during agricultural field applications and in their evaporation from contaminated soils, water bodies and vegetation (Scholtz and Bidleman, 2006).

PAH, AH, PCB and OCP concentrations have been largely reported in different environments throughout the world (Stern et al., 1997; Valotto et al., 2017; Yao et al., 2002). However, their measurements in aerosols of North African cities remain rare. In Tunisia, only one preliminary study was conducted on PAHs associated with total suspended particles (TSP) in Bizerte city (northern Tunisia) during the winter season (Ben Hassine et al., 2014). In this context, the goal of the present study was to assess the levels, potential sources, dry deposition and human health risks of PAHs, AHs, PCBs and OCPs in aerosols of Bizerte city. Thereby, a one-year monitoring program was carried out for the collection of 60 aerosol samples and the subsequent analysis of 94 organic compounds.

2. Material and methods

2.1. Sampling site

Sampling was conducted on the roof of the Faculty of Sciences of Bizerte (37° 16' 0.5802" N, 9° 52' 49.875" E; 8 m above ground level), approximately 1 km from the Bizerte city center in Northern Tunisia, between the Mediterranean Sea and the Bizerte lagoon (Fig. S1 in the supplementary information (SI)). Surrounding this site are heavily trafficked roads, schools, residential areas and several industries, e.g., a petroleum refinery, cement manufacturing, iron and steel metallurgy and bolt factory. Hence, the sampling site is well representative of the Bizerte urban area (Castro-Jiménez et al., 2017). Bizerte is a medium-sized city (~127,000 inhabitants), with economic activity focused mainly on agriculture, fishing and operations of light and heavy industries, including cementery, plastic, textile,

mechanic and electronic manufacturing, iron and steel metallurgy, petroleum refining and lubricants.

Generally, Bizerte has a humid climate, with an average temperature of 22°C, annual precipitation rates varying between 300 and 800 mm, mainly concentrated in the fall and winter months, and a hot summer and mild spring. The most frequent and strongest winds are from the northwest (Ouakad, 2007).

2.2. Aerosol sampling

Aerosol samples were collected from March 2015 to January 2016 on precombusted (450°C, 6 h) quartz fiber filters (QFFs) (Whatman QMA grade, 20.3 × 25.4 cm) using a high volume air sampler (Tisch Environmental Inc., OH, USA) operating at an average flow of 0.66 m³ min⁻¹ for 48 h. Overall, 60 samples were collected along with five field blanks. Field blanks were obtained by placing QFFs in the air sampler for a few seconds without switching it on (Castro-Jiménez et al., 2016; Gioia et al., 2012). QFFs were then individually wrapped in a double precombusted aluminum foil and stored in a freezer at -20°C before processing. The pre- and post-sampling weights of the QFFs were determined using a microbalance after they were placed in a desiccator (25°C) for 24 h. Each QFF was cut into two equal parts. One half was used for pollutant analysis and the other half for the determination of TSP, organic carbon (OC) and organic nitrogen (ON). Details regarding the sampling dates, meteorological conditions and collected air volumes, as well as data on TSP, OC and ON concentrations for each sample, are given in the SI (Table S1).

2.3. Analysis

Details on analytical procedures are presented in the SI (Text S1). Briefly, QFF filters were cut into small pieces, spiked with a multi-standard mixture containing internal standards for AHs (Hexadecane- d_{34} , tetracosane- d_{50} and hexatriacontane- d_{74}), PAHs (naphthalene- d_8 , fluorene- d_{10} , anthracene- d_{10} and pyrene- d_{12}), PCBs and OCPs (CB30, CB155 and CB198), and extracted by Accelerated Solvent Extraction (ASE). The extracts were then purified using silica-alumina columns and the analysis of native pollutants was subsequently performed using gas chromatography coupled with a mass spectrometer (GC-MS) and an electron capture detector (GC-ECD). The analyzed compounds included 34 PAHs (19 parents and 15 alkylated homologues), 28 AHs, 20 PCBs and 12 OCPs.

The concentrations of TSP in the QFFs were determined gravimetrically using the total and impacted areas of the whole QFF, the area of the weighted QFF subsample, the mass of TSP onto the QFF subsample, and the filtered air volume. OC and ON concentrations were determined by high temperature combustion (CHN analyzer) (Raimbault et al., 2008).

2.4. Quality assurance and quality control (QA/QC)

QA and QC included control/validation of laboratory and field blanks (procedures for analysis and sampling, respectively), method recoveries (extraction, clean-up, analysis), detection limits, analysis of certified reference material, and regular calibrations of the high volume air sampler (each month), following the manufacturer's manual (Tisch Environmental, HIGH VOL+). Blank samples were prepared, processed and analyzed in the same manner as the field samples. Nap was detected in small amounts in the laboratory blanks (< 5% of sample values), whereas CB-18, HCB and AHs (n -C₁₅– n -C₃₇) were detected in field blanks (< 10% of sample values). Blank values for the individual compounds in aerosols are presented in Table S2. Average recoveries for AH, PAH and OC internal standards were 86,

84 and 91%, respectively. Instrument detection limits (IDLs) for all compounds were determined as a signal-to-noise ratio (S/N) of 3 (Wolska, 2002). Method detection limits (MDLs) were derived from the mean plus three times the standard deviation of the concentrations in field blanks (considering an average sampled air volume of 960 m³). For compounds that were not detected in field blanks, MDLs were based on their IDL. The MDLs for hydrocarbons and OCs were in the range of 0.2-8 pg m⁻³ and 0.01-0.6 pg m⁻³, respectively (Table S2). If the concentration of a given compound in a sample was below its MDL/IDL, this compound was considered as not detected in the sample (below the limit of detection, < lod).

The whole analytical procedure was validated by analyzing three replicates (0.1 g) of SRM 1649b (Urban Dust). A good agreement between the analyzed values and certified levels was obtained for all compounds with recoveries varying from 82 to 104% (mean values) (Table S3). All the data reported here were corrected for the blanks (laboratory and field blanks) but not corrected for the recoveries.

2.5. Statistical analysis

Box-and-whisker plots, Pearson correlation matrix and principal component analysis (PCA) were performed using XLSTAT 2013.5.01. No rotation technique was applied to PCA. Non-parametric tests of Mann-Whitney (U-test) and Kruskal-Wallis (H-test), conducted with Stat-View 5.0, were used to compare the distributions of two (U-test) or more than two (H-test) groups.

3. Results and discussion

3.1. Concentrations and molecular distributions

3.1.1. PAHs

The concentrations of Σ_{34} PAHs in aerosols of Bizerte city over the study period displayed a high variability, ranging from 0.5 to 17.8 ng m⁻³ (mean: 2.8 ± 3.4 ng m⁻³; median: 1.7 ng m⁻³) (Table S4), being in most cases < 5 ng m⁻³, while the highest value was recorded on 11 December (Fig. 1A). In the same area, Ben Hassine et al. (2014) recorded a Σ_{14} PAH concentration of 25.4 ng m⁻³ in winter, which is higher than those measured in the present study at the same season, very likely due a sampling site much more close to direct vehicular traffic emissions. The measured concentrations in Bizerte were comparable with those reported in Northwestern Mediterranean coastal cities (Chofre et al., 2016) and in the Western and Southeastern Mediterranean Sea (Castro-Jiménez et al., 2012). However, they were lower than those found in another north African coastal city, Algiers, Algeria (Yassaa et al., 2001), in urban areas of the Eastern Mediterranean (Chrysikou and Samara, 2009; Ozcan and Aydin, 2009) and in Asian cities (Masih et al., 2010; Wu et al., 2014) (Table S5). Overall, PAH concentrations found in Bizerte were lower than those recorded in other urban areas. This could be explained by lower consumption of wood and fossil fuels for house heating and/or less pronounced urban activities in Bizerte compared to the other sites.

The most abundant PAHs were BbF, BeP, IcdP and BghiP (Table S4; Fig. S2A). They accounted for 38% of Σ_{34} PAHs (Fig. S3A). Logically, the annual ring distribution pattern shows the dominance of high molecular weight PAHs (HMW-PAHs) (67.3–76.9%), followed by medium molecular weight PAHs (MMW-PAHs) (17.7–27.3%), while low molecular weight PAHs (LMW-PAHs), known to be preferentially present in the air gaseous phase (Zheng et al., 2005), were a minority (7%) (Fig. S2B).

Σ_{34} PAH concentrations showed marked seasonal differences (H-test, $p < 0.05$), with significantly higher values in winter (mean: $8.7 \pm 6.5 \text{ ng m}^{-3}$; median: 7.9 ng m^{-3}), and significantly lower in summer (mean: $1.2 \pm 1.0 \text{ ng m}^{-3}$; median: 0.9 ng m^{-3}), compared to the other three seasons (U-test, $p < 0.05$) (Fig. S4A). The lower concentrations in summer may be due to higher temperatures and solar irradiance, which favor PAH evaporation and photodegradation (Masiol et al., 2013). In contrast, during the winter, the increase in domestic and vehicular emissions along with lower dispersion conditions and a decrease in photochemical reactions may promote the accumulation of PAHs at the lower atmosphere (Wan et al., 2006). Most of individual PAHs exhibited higher concentrations in winter and lower in summer (Fig. S2A). As a result, LMW-PAHs presented the largest contribution in summer (7.5%) and the smallest contribution in winter (3.6%), while the contributions of MMW- (30.9%) and HMW-PAHs (65.4%) remain large in winter (Fig. S2B). This seasonal ring distribution pattern has been already observed in other urban areas (Kishida et al., 2009; Ramírez et al., 2011).

3.1.2. AHs

The concentrations of Σ_{28} AHs over the study period ranged from 6.7 to 126.5 ng m^{-3} (mean: $30.2 \pm 21.1 \text{ ng m}^{-3}$; median: 25.1 ng m^{-3}) (Fig. 1B; Table S4). The highest concentrations were recorded on 7 and 14 May (125.8 and 88.2 ng m^{-3}), while during the rest of the year, they were mainly $< 55 \text{ ng m}^{-3}$, suggesting that the May peaks were caused by a specific event (see below). These AH concentrations were within the range of those reported in Prato, Italy (Cincinelli et al., 2003), Algiers (Yassaa et al., 2001) and Hong Kong, China (Zheng et al., 2000), but significantly lower than those observed in northwestern and Eastern Mediterranean coastal cities (Gogou et al., 1994; Karanasiou et al., 2007), and in Qingdao, China (Guo et al., 2003) (Table S5).

The most abundant AHs were *n*-C₂₉, followed by *n*-C₂₇, *n*-C₃₁ and *n*-C₂₅ (Table S4; Fig. S5). These four congeners accounted for 55% of the total AHs (Fig. S3B). The mean concentration of HMW AHs (*n*-C₂₂–*n*-C₄₀) (28.9 ng m⁻³) was significantly higher (U-test, *p* < 0.05) than that of LMW AHs (*n*-C₁₅–*n*-C₂₁) (1.0 ng m⁻³), and concentrations of the HMW AHs with an odd-number of carbon atoms were higher than those with an even-number of carbon atoms (Figs. S3B and S5). This molecular distribution profile, characterized by the dominance of *n*-C₂₅–*n*-C₃₁, no odd/even predominance in the range of *n*-C₁₅–*n*-C₂₁ and odd carbon number predominance in the range *n*-C₂₂–*n*-C₄₀ (Fig. S3B), was similar to that found in the urban areas of Nanjing, China (Wang et al., 2006) and Rio de Janeiro, Brazil (Maioli et al., 2009) and was indicative of mixed petrogenic and biogenic sources (Rogge et al., 1993a, 1993b, 1996).

The AH concentrations in spring (mean: 36.4 ± 30.0 ng m⁻³; median: 25.1 ng m⁻³), summer (mean: 24.0 ± 13.6 ng m⁻³; median: 19.8 ng m⁻³), autumn (mean: 24.4 ± 12.8 ng m⁻³; median: 22.5 ng m⁻³) and winter (mean: 38.6 ± 18.5 ng m⁻³; median: 38.3 ng m⁻³) were not significantly different from each others (H-test, U-test, *p* > 0.05) (Fig. S4B). The concentrations of individual AHs in the ranges *n*-C₁₅–*n*-C₂₆ and *n*-C₃₃–*n*-C₄₀ were rather higher in winter and spring, and lower in summer and autumn (Fig. S5). *n*-C₂₇, *n*-C₂₉ and *n*-C₃₁ concentrations displayed a strong increase in winter, summer/spring and spring, respectively. The higher levels of the biogenic *n*-C₂₉ and *n*-C₃₁ during spring and summer could be due to the higher contribution of terrestrial vegetation through the mechanical abrasion of higher plants, leaf waxes, vegetation debris, and soil erosion, while the highest concentration of the biogenic *n*-C₂₇ in winter remains quite peculiar (Rogge et al., 1993b; Górka et al., 2014).

3.1.3. PCBs and OCPs

The concentration of $\sum_{20}\text{PCBs}$ averaged $3.5 \pm 2.4 \text{ pg m}^{-3}$ with a median value of 3.6 pg m^{-3} (Fig. 1C; Table S6). The highest $\sum_{20}\text{PCB}$ concentration was found on 11 June (11.0 pg m^{-3}), and the lowest (0.3 pg m^{-3}) on 10 July. Total PCB concentrations measured were within the range of those reported for other Mediterranean coastal sites (Castro-Jiménez et al., 2011; 2017; Mandalakis et al., 2005) and some European inland areas (Castro-Jiménez et al., 2009; Landlová et al., 2014), but they were lower than those recorded over the Mediterranean and Black Seas (Berrojalbiz et al., 2014) and in highly urbanized Mediterranean and Asian areas (Gregoris et al., 2014; Mandalakis et al., 2002; Ozcan and Aydin, 2009; Yeo et al., 2004) (Table S5).

The most abundant PCB congeners were CB-180, -138 and -153 (Table S6; Fig. S6A), accounting for 48% of $\sum_{20}\text{PCBs}$ (Fig. S3C). Hence, the dominant PCB groups were Hexa-CBs, Hepta-CBs and Penta-CBs (Table S6; Fig. S6B). This pattern of homolog profiles had already been observed in Kyonggi-do, South Korea (Yeo et al., 2004).

Among the 12 analyzed OCPs, only 6 pesticides were detected in Bizerte aerosols (HCB, γ -HCH, δ -HCH, Hepchl, p,p' -DDE and p,p' -DDT). The $\sum_6\text{OCP}$ concentrations ranged from 0.2 to 3.6 pg m^{-3} (mean: $1.1 \pm 0.84 \text{ pg m}^{-3}$; median: 0.76 pg m^{-3}) (Table S6). The highest concentrations were observed on 18 March and 23 December (Fig. 1D). Interestingly, March and December are land laboring and cereal treatment periods, respectively, potentially favoring soil-atmosphere pesticide transfer. $\sum_6\text{OCP}$ concentrations determined in Bizerte were generally lower than those observed in other urban areas (Table S5). The most abundant compounds were DDTs, including p,p' -DDT and p,p' -DDE, and Hepchl, accounting for 69 and 10% of $\sum\text{OCPs}$, respectively (Fig. S3D).

The highest $\sum_{20}\text{PCB}$ and $\sum_6\text{OCP}$ concentrations were measured in winter (mean: $5.0 \pm 2.6 \text{ pg m}^{-3}$, median: 5.0 pg m^{-3} for PCBs; mean $2.1 \pm 1.0 \text{ pg m}^{-3}$, median: 2.2 pg m^{-3} for OCPs) and the lowest in autumn for PCBs (mean $3.1 \pm 1.4 \text{ pg m}^{-3}$, median: 2.7 pg m^{-3}) and in

summer for OCPs (mean $0.7 \pm 0.4 \text{ pg m}^{-3}$, median: 0.6 pg m^{-3}) (Fig. S4C and D). Nevertheless, whereas no significant seasonal difference was found for $\Sigma_{20}\text{PCB}$ concentrations (H-test, U-test, $p > 0.05$) (Fig. S4C), $\Sigma_6\text{OCP}$ concentrations were significantly higher in winter compared to the other three seasons (H-test, U-test, $p < 0.05$) (Fig. S4D). Most individual PCBs and OCPs also exhibited higher concentrations in winter (Fig. S6A and S7).

3.2. Influence of air mass origin and meteorological parameters

Wind sector and backward trajectory analyses were carried out to assess the local and long-range atmospheric transport of pollutants, respectively (Fig. 2). The dominant wind directions were from the west-north-west (WNW) in spring, the WNW and the north-west (NW) in summer and autumn, and the south-east (SE) in winter. This suggests that local emissions from downtown Bizerte (vehicular exhaust), Bizerte harbor and the cement factory, located NW of the site, and from Zarzouna area (petroleum refinery, the Tunisian Company of Lubricants (SOTULUB)) and Menzel Jemil city (electronic, plastic, and textile industries), located SE of the site, are the most likely to influence the pollutant levels observed in aerosols (Fig. S1). In all cases, the highest concentrations occurred in winter when winds were from the SE.

Back-trajectories were calculated using the NOAA Hysplit Model (Draxler and Rolph, 2011). As shown in Fig. 2, most of the air masses which reached the sampling site were of oceanic origin with limited passage through the European continent. Although there is a combined effect of remote air masses and local winds, the contribution of local sources and neighboring cities to the contamination observed here is likely more important. Actually, in addition to the apparent clean nature of the oceanic air masses, high wind speeds above the Mediterranean Sea can disperse pollutants before they reach the sampling site. Indeed, we

observe a significant inverse relationship between wind speed (WS) and PAH/OCP concentrations (Table S7). This suggests the predominance of local sources, as strong winds flush pollutants out of the study area whereas weak winds allow pollutants to accumulate over time (Hong et al., 2007).

Besides wind, it has been recognized that TSP amount, ambient temperature (AT) and relative humidity (RH), may strongly affect pollutant concentrations in aerosols (Park et al., 2002). In this region, AT was higher in summer/autumn and lower in spring/winter, while RH showed little variation among the seasons. TSP concentrations ranged from 9.6 to 119.1 $\mu\text{g m}^{-3}$ (mean: 62.0 $\mu\text{g m}^{-3}$) (Table S1). A significant positive correlation was observed between PAH/OCP concentrations and RH (Table S7), suggesting that the latter can play an important role in pollutant condensation on particulate matter. Mastral et al. (2003) showed that RH influenced the PAH concentrations in aerosols possibly through its impact on PAH gas-particle partitioning. Significant negative correlations were found between PAH/OCP concentrations and AT (Table S7), indicating a possible temperature dependence on atmospheric pollutants. Low temperatures may indeed stimulate the transfer of pollutants from the gaseous to particulate phase, and inversely (Masiol et al., 2013). This observation is in accordance with the aforementioned results, that is the highest and the lowest PAH/OCP concentrations were recorded in winter and summer, respectively (Fig. S4).

PCA was carried out to obtain a picture of the relationships between all the measured parameters (Fig. 3). Samples collected in winter had the highest Factor 1 scores, indicating that PAHs, PCBs and OCPs were the dominant compounds in winter and were associated with RH, OC and ON (Table S7). Samples collected in summer displayed the highest Factor 2 scores, suggesting that AT and WS were probably important parameters driving the low levels of PAHs, PCBs and OCPs during the warm season. Some samples collected in spring were

loading on Factor 3, suggesting that AHs were important in spring due to biogenic activities, as previously described.

3.3. Potential sources

3.3.1. PAHs

Molecular diagnostic ratios used to investigate PAH emission sources are reported in Table 1. These ratios have to be taken with caution for the evaluation of PAH sources since they may be modified with degradation and weathering of PAHs occurring from the source point to the collection site (Tobiszewski and Namiesnik, 2012). The cross plots of BaA/(BaA + Chr) (0.06-0.40) and IcdP/(IcdP + BghiP) (0.23-0.52) ratios and of Ant/(Ant + Phe) (0.00 to 0.31) and Flu/(Flu + Pyr) (0.25-0.67) ratios (Table 1 for values but cross plots not shown) revealed a mixed source of PAHs (petrogenic and pyrogenic), with a strong contribution of liquid fossil fuel combustion (Mai et al., 2003; Yunker et al., 2002), as well as a small contribution of biomass combustion (Ravindra et al., 2008; Tang et al., 2005). Albeit no industry using coal as fuel source (or coal burning for house heating) is present in the study area, open burning of biomass is a common procedure in Bizerte for crop and forest residue disposal and for land preparation.

The ratio of combustion PAHs (CPAHs, i.e., the sum of Flu, Pyr, BaA, Chr, BbF, BkF, BaP, IcdP, BghiP) over $\Sigma 16$ US EPA PAHs (CPAHs/ $\Sigma 16$ US EPA PAHs) was ~ 1 , while the BbF/BkF ratio was > 0.5 for all samples (Table 1). Their cross plot (not shown) suggested the dominant contribution of diesel combustion. In addition, our BbF/BkF ratios, all higher than 0.5 (1.74–12.43), our IcdP/(IcdP + BghiP) ratios, mostly between 0.35 and 0.70, as well as some Flu/(Flu + Pyr) ratios higher than 0.5 indicate diesel emissions (Mai et al., 2003; Manoli et al., 2004; Mirante et al., 2013; Ravindra et al., 2008). Indeed, extensive vehicular emissions

of heavy and light cars have been observed coming from the highway at 400 m from the sampling site. Overall, these diagnostic ratios underline that PAHs in Bizerte aerosols are mainly originating from vehicular traffic emissions and diesel combustion.

3.3.2. AHs

The calculated CPI, %Wax, UCM and Pr/Phy values are listed in Table 1. CPI computed as the ratio of odd to even numbered homologues, is an indicator of anthropogenic (CPI ~ 1) or biogenic AHs (CPI higher than 3) (Gong et al., 2011). Table 1 shows values for CPI₁ (whole range, *n*-C₁₅–*n*-C₄₀), CPI₂ (petrogenic AHs, *n*-C₁₅–*n*-C₂₅), and CPI₃ (biogenic AHs, *n*-C₂₅–*n*-C₃₆) for the entire study period and four seasons. CPI₁ annually ranged 1.1–6.1, which was very close to the range determined in Guangzhou, China (Choi et al., 2016) but higher than that found in Rouiba (Algiers) and Wroclaw (Poland) (Górka et al., 2014; Moussaoui et al., 2013), likely because of a larger input from biogenic sources in Bizerte. CPI₁ was closer to 3 in spring and summer than in autumn and winter, suggesting a higher contribution of biogenic sources during the warmer seasons. CPI₂ ranged 0.96–8.4 over the study period (Table 1), and the fact that almost all values were between 1 and 2 revealed a petrogenic fingerprint. CPI₃ (1.2–8.8) displayed, as for CPI₁, higher values (higher than 3) in spring and summer (Table 1), underscoring the influence of biogenic emissions from season-to-season. CPI₂ and CPI₃ values determined in Bizerte are similar to those observed in Lhasa, China (Gong et al., 2011) but higher than those in Nanjing, China (Wang et al., 2006). The plant wax contribution to the total mass of the measured AHs (%Wax) in Bizerte aerosols was on average 39.9, 45.0, 22.9 and 23.4% in spring, summer, autumn and winter, respectively (Table 1). This indicated a higher input from leaf epicuticular waxes within the AH pool during the warmer seasons. A highly significant positive correlation was found between %Wax and CPI₁ at the annual level ($r = 0.93$, $p < 0.05$) showing that these two indices were

relevant in the source assignment of AHs (He et al., 2010). The stronger contributions of biogenic sources in spring and summer may be due to growth of leaves, photosynthesis, blooming, fungi and pollen spreading (Choi et al., 2016). Indeed, the study site is surrounded by a varied vegetation cover, and mountains rich with deciduous and coniferous trees, which may represent the main biogenic sources.

Unresolved complex mixture (UCM) has been identified in all samples ($22.5\text{--}262.5\text{ ng m}^{-3}$) (Table 1), denoting the presence of vehicular residues (Rogge et al., 1993a, b). It exhibits higher concentrations in winter and spring, suggesting more fossil fuel utilization during the cold seasons. Additionally, the presence of UCM together with isoprenoids Pr and Phy confirms petroleum residue contamination (Andreou et al., 2008). However, in summer, the highest Pr/Phy ratio (> 1.5), along with the lowest UCM values, may reflect the more important contribution of biogenic sources.

3.3.3. PCBs

PCBs have been widely used in Tunisia since the 1970s, and despite an import ban in 1986 of any equipment containing PCBs, they can still be detected in Bizerte aerosols. Several authors reported that the PCB pattern was directly related to meteorological conditions and air mass transport (Diesch et al., 2012; Piazza et al., 2013; Yeo et al., 2003). Wania and Mackay (1996) assumed that the heaviest homologues could easily be deposited on plants, soils and surface waters, while the lightest ones, more volatile, were mostly present in the gaseous phase and strongly affected by long-range atmospheric transport. The distribution of Penta-, Hexa-, Hepta- and Tri-CBs in the Bizerte aerosols (Fig. S6B, Table S6) could be the result of both short and long-range atmospheric transport. The high concentrations of the heaviest homologues (Hexa- and Hepta-CBs) might be influenced by industrial emissions (the cement factory) and intense shipping activities (Bizerte harbor), both very close to the sampling site

(to the NW). Previous studies have recorded PCBs in sediment and fish in the same area (Barhoumi et al., 2014a, b). The presence of tetrachloro- (CB66), pentachloro- (CB101, CB118, CB126), hexachloro- (CB128, CB138, CB153) and heptachloro-congeners (CB180) in our samples is consistent with a contribution of commercial PCB mixtures Aroclor 1248, 1254 and 1260/1262 (Takasuga et al., 2006), which have been widely used in transformers and electrical equipment in several countries (Gregoris et al., 2014). A large number of transformers are still used or presently stored in unsatisfactory conditions, promoting their atmospheric dispersion. In 2004, a study identified 1,079 PCB-contaminated transformers in Tunisia, representing 720 tons of liquid PCBs (APEK, 2005). In view of industrial activities around the sampling site (to the NW, SE and SW), it is assumed that the plastic, tire, mechanic and electronic factories in Menzel Jemil city, the iron factory in Menzel Bourguiba city (to the SW), the Bizerte cement factory, SOTULUB in Zarzouna area, the incineration of contaminated equipment, and the combustion of different fuels were significant sources of PCBs in Bizerte aerosols.

3.3.4. OCPs

As previously discussed, HCB, *p,p'*-DDT and *p,p'*-DDE showed the highest frequency of detection in aerosols, despite their ban since 1984 (APEK, 2005). HCB occurrence may be ascribed not only to its past use as a fungicide treatment for seeds, but also to the fact that it can be released from certain thermal processes in the metallurgical industry and at oil refineries, and from waste incineration and motor vehicles. It may also be present as impurity in other OCPs (Barber et al., 2005). HCB has also been measured in the same region in breast milk (Hassine et al., 2012). Higher concentrations of *p,p'*-DDT compared to their metabolite *p,p'*-DDE are known to indicate recent DDT input (Iwata et al., 1995). This is the case in Bizerte with *p,p'*-DDT/*p,p'*-DDE ratios > 1 (mean: 3.2). This is consistent with the fact that

large amounts of DDT have been recently detected in Menzel Bourguiba city located 24 km SW the sampling site. Hence, some DDT measured in Bizerte aerosols would be likely derived from different regional sources *via* long-range transport. According to wind directions and backward trajectories (Fig. 2), a transportation of DDT from Menzel Bourguiba may occur in winter. In Tunisia, works conducted in 1997 revealed the existence of a number of obsolete stocks of pesticides, containing mostly HCH, DDT (45 tons) and other organochlorines. These pesticides are currently stored in unsatisfactory conditions and can easily disperse into the atmosphere. The ratio of *o,p'*-DDT/*p,p'*-DDT can be used to distinguish technical DDT (low ratio) from “dicofol-type DDT” (high ratio) (Gong et al., 2010). In our case, the *o,p'*-DDT was not detected in any samples, indicating that technical DDT was the main DDT source in the Bizerte aerosols. Similar results were observed by Barhoumi et al. (2014b) in the Bizerte lagoon sediments. Hepchl is the second most abundant compound in our samples, accounting for 10.4% of $\sum_6\text{OCPs}$. Their detection may be related to their use against termites, ants and soil insects, in seed grains and on crops, and in houses (Wang et al., 2008).

3.4. Dry deposition and cancer risk assessment

The estimation of dry deposition fluxes is relevant to assess the budget of pollutants in the environment and their human health effects (Valotto et al., 2017; Vardar et al., 2002). Detailed information on the dry deposition flux calculation ($F, \text{ng m}^{-2} \text{d}^{-1}$) can be found in the SI (Text S2).

For the study period, the average dry deposition fluxes varied from 83.4 to 3070 $\text{ng m}^{-2} \text{d}^{-1}$ and from 1157 to 21850 $\text{ng m}^{-2} \text{d}^{-1}$ for $\sum_{34}\text{PAHs}$ and $\sum_{28}\text{AHs}$, respectively. For $\sum_{20}\text{PCBs}$ and $\sum_6\text{OCPs}$ they varied from 60.6 to 1895 $\text{pg m}^{-2} \text{d}^{-1}$ and from 38.2 to 620 $\text{pg m}^{-2} \text{d}^{-1}$, respectively

(Table S8). Average daily fluxes were in the range of those reported in other sites (Table S9). The total integrated dry deposition flux ($\sum_{34}\text{PAH}+\sum_{28}\text{AH}+\sum_{20}\text{PCB}+\sum_6\text{OCP}$) in the Bizerte area varied from 158 to 22 078 $\text{ng m}^{-2} \text{ day}^{-1}$ (Fig. S8). Considering the surface of the Bizerte lagoon as $1.28 \times 10^8 \text{ m}^2$ (Barhoumi et al., 2016), approximately 250 kg yr^{-1} of these chemicals can be deposited to surface waters through aerosols.

In this study, inhalation of contaminated aerosols was considered for health risk assessment of PAHs and PCBs. Benzo[a]pyrene (BaP) has been regarded by the World Health Organization (WHO) as the most appropriate indicator to evaluate the carcinogenicity of PAHs in air. Equations used to calculate the total daily carcinogenic potential ($\sum\text{BaP}_{\text{TEQ}}$) of the PAH mixture and lifetime excess cancer risk (ECR) are described in detail in the SI (Text S2).

Fig. 4 shows the annual evolution of $\sum\text{BaP}_{\text{TEQ}}$ and ECR for $\Sigma_8\text{PAHs}$. The mean $\sum\text{BaP}_{\text{TEQ}}$ for the whole period was 0.19 ng m^{-3} and was 10 times higher in winter (mean: 0.70 ng m^{-3} ; maximal value of 1.49 ng m^{-3} in December) than in summer (mean: 0.07 ng m^{-3} ; minimal value of 0.05 ng m^{-3} in July), indicating a higher health risk during the cold season. BaP was the highest carcinogenic contributor with 37% of the $\sum\text{BaP}_{\text{TEQ}}$, followed by DahA (21%) and BbF (17%). Table S10 shows a comparison of the derived $\sum\text{BaP}_{\text{TEQ}}$ values with those observed in other regions. The $\sum\text{BaP}_{\text{TEQ}}$ values in Bizerte were similar to those in Elche and Zaragoza, Spain (Chofre et al., 2016; Mastral et al., 2003), and lower than those in Algiers (Yassaa et al., 2001), and Venice, Italy (Gregoris et al., 2014). The ECR for a lifetime of 70 years ranged from 9×10^{-9} to 1.6×10^{-6} with a mean of 2.1×10^{-7} (Fig. 4), indicating that the lifetime cancer risk from exposure to BaP is negligible in Bizerte ($\text{ECR} < 10^{-6}$), except in winter ($\text{ECR} > 10^{-6}$). These ECR values are much lower than those observed in Beijing and South China (Bandowe et al., 2014).

4. Conclusions

For the first time hydrocarbons and organochlorines have been simultaneously measured in aerosol samples from a North African coastal city during one year. Overall, the generated data set is relevant to understand the contribution of the atmospheric pathway to the pollution budget in Bizerte city and very valuable for future evaluations in an area for which little information is available on the atmospheric occurrence and risks of the target contaminants. Further investigations using finer fractions of atmospheric aerosols (PM_{2.5} and PM₁₀) are needed in North African countries such as Tunisia, which have a significantly increasing number of motor vehicles.

Acknowledgements

This work received the financial support of the Institut de Recherche pour le Développement (IRD), through the International Joint Laboratory (LMI) “COSYS-Med”, the Tunisian Ministry of Higher Education and Scientific Research, the PACA region “Particule” project, the IRD-MIO Action Sud “AEROBIZ” project, and the Labex OT-Med (no. ANR-11-LABX-0061) – MEDPOP, funded by the French Government “Investissements d’Avenir” (ANR) through the A*MIDEX project (no ANR-11-IDEX-0001-02). This study is also a contribution to MERMEX/MISTRALS program. We thank the MIO core parameter analytical platform (PAPB) for performing OC and ON analyses. Four anonymous reviewers and associate editor are greatly acknowledged for their constructive comments on the manuscript.

Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version.

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Figure captions

Figure 1. Total PAH (A), AH (B), PCB (C) and OCP (D) concentrations in aerosol samples of Bizerte city from March 2015 to January 2016.

Figure 2. The dominant wind directions and five day backward trajectories in Bizerte city during the four seasons (for backward trajectories, colors denote different air-mass movement and the figures in the lower frames are altitude in meters).

Figure 3. Pearson principal component analysis (loading plots (A) and score plots (B)) for TSP, OC, ON, chemical ($\sum_{34}$ PAHs, $\sum_{28}$ AHs, $\sum_{20}$ PCBs, $\sum_6$ OCPs) and meteorological (AT, WS, RH) variables for aerosol samples of Bizerte city. TSP – total suspended particles, OC – organic carbon, ON – organic nitrogen, WS –wind speed, RH – relative humidity, AT – ambient temperature, AHs – aliphatic hydrocarbons, PAHs – polycyclic aromatic hydrocarbons, PCBs – polychlorinated biphenyls, OCPs – organochlorine pesticides. Green, blue, black and red colors indicate the seasons of spring, summer, autumn and winter, respectively.

Figure 4. $\sum$ BaP_{TEQ} and excess cancer risk (ECR) in Bizerte city from March 2015 to January 2016.

812 **Table captions**

813

814 **Table 1.** Diagnostic indices and ratios of PAHs and AHs for aerosol samples of Bizerte city at

815 the four seasons.

816

817

818

Figure 1

(A)

(B)

(C)

(D)

Figure 2

Figure 3

Figure 4

Table 1. Diagnostic indices and ratios of PAHs and AHs for aerosol samples of Bizerte city at the four seasons.

Index or ratio	Spring		Summer		Autumn		Winter		Annual	
	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range
PAHs										
Ant/(Ant + Phe)	0.11	0.00–0.31	0.14	0.00–0.25	0.11	0.03–0.18	0.10	0.06–0.12	0.12	0.00–0.31
BaA/(BaA + Chr)	0.18	0.08–0.24	0.24	0.06–0.40	0.27	0.17–0.39	0.24	0.17–0.29	0.23	0.06–0.40
Flu/(Flu + Pyr)	0.47	0.28–0.67	0.41	0.25–0.48	0.44	0.36–0.52	0.46	0.43–0.51	0.44	0.25–0.67
IcdP/(IcdP + BghiP)	0.39	0.28–0.49	0.40	0.23–0.49	0.39	0.31–0.52	0.41	0.36–0.46	0.39	0.23–0.52
BbF/BkF	3.05	2.26–4.25	3.93	1.74–12.4	3.85	3.29–4.75	3.93	3.11–4.63	3.63	1.74–12.4
CPAHs/ $\sum_{16}$ US EPA PAHs ^a	0.91	0.83–0.95	0.89	0.84–0.92	0.91	0.84–0.93	0.94	0.91–0.96	0.91	0.83–0.96
AHs										
CPI ₁ ^b	2.49	1.38–6.12	2.76	1.69–5.91	1.58	1.07–2.38	1.84	1.27–5.04	2.29	1.07–6.12
CPI ₂ ^c	1.57	1.06–2.23	1.72	0.96–8.40	1.71	1.47–1.94	1.44	1.32–1.70	1.63	0.96–8.40
CPI ₃ ^d	3.64	2.11–7.96	3.70	1.91–8.84	1.81	1.21–2.85	2.46	1.62–7.07	3.10	1.21–8.84
%Wax ^e	39.9	19.3–72.8	45.0	27.3–73.0	22.9	5.9–42.0	23.4	13.1–67.9	35.6	5.9–73.0
UCM (ng m ⁻³)	118.0	24.8–262.5	71.7	22.6–109.1	81.6	22.5–169.3	153.9	32.1–254.9	99.6	22.5–262.5
Pr/Phy	0.95	0.00–2.10	1.59	0.00–6.77	1.40	0.00–14.6	0.03	0.00–0.25	1.13	0.00–14.6

^aCPAHs = combustion PAHs = Flu+Pyr+BaA+Chr+BbF+BkF+BaP+IcdP+BghiP.

^bCPI₁ = $\Sigma(n\text{-}C_{15}\text{--}n\text{-}C_{39})/\Sigma(n\text{-}C_{16}\text{--}n\text{-}C_{40})$, CPI for the whole range.

^cCPI₂ = $\Sigma(n\text{-}C_{15}\text{--}n\text{-}C_{25})/\Sigma(n\text{-}C_{16}\text{--}n\text{-}C_{24})$, CPI for petrogenic *n*-alkanes.

^dCPI₃ = $\Sigma(n\text{-}C_{25}\text{--}n\text{-}C_{35})/\Sigma(n\text{-}C_{26}\text{--}n\text{-}C_{36})$, CPI for biogenic *n*-alkanes.

^eWax $C_n = [C_n] - [C_{n+1} + C_{n-1}] \times 0.5$ (1), %Wax = $(\Sigma \text{Wax } C_n \times 100)/\Sigma C_n$, negative values of C_n were replaced by zero.