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

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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.

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., 1993; 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.,

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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 m^3 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-C_{15}–n-C_{37}) 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 m^3). 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})