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Levels of organic compounds in interiors (school, home, university and hospital) of Ouargla city, Algeria

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HIGHLIGHTS

- *n*-Alkanes and PAHs were investigated in indoor air in Ouargla, Algeria.
- *n*-Alkanes were of twin origin (anthropogenic and biogenic). Indoor PAHs in Ouargla ranged from 17 to 182 ng/m^3.
- As for dust, the home was more PAH polluted than the hospital, university and school.
- Phthalates, caffeine, nicotine, nonylphenols and cannabinol affected interiors of Ouargla.

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ABSTRACT

Indoor environments are affected by a number of organic contaminants, whose concentrations can exceed by orders of magnitude those found outdoors in external air. At this regard, polycyclic aromatic hydrocarbons (PAHs) deserve a special concern. PAHs occur in the air both in the gaseous and particulate forms; they are associated to fine aerosols and soil dust, and deposit on surfaces. Nonetheless, scarce information exists about the PAH pollution of indoor locations in Northern Africa. PAHs were first investigated in dust of interiors in Ouargla (Saharan Algeria), concurrently with *n*-alkanes and polar organics. Settled dust was collected from pre-cleaned surfaces (0.5 m^2 each) at 7 internal locations in total from a school, the city hospital and university, and a home. Three sample series were collected 15, 30 days and random after the preliminary cleaning of surfaces. Contemporarily, organic compounds were collected at 15 locations of the target sites by deploying diffusive samplers over the whole study period to obtain molecular signatures of semi-volatile organic fraction. A consolidated procedure consisting of ultra-sonic bath extraction, semi-preparative column chromatography and gas chromatographic - mass spectrometric analysis was applied for chemical characterization of dusts. *n*-Alkanes ranged from 3.8 to 41 μg/m^2 in dust and 0.17–2.42 μg/m^3 in gas phase. PAHs concentrations were 17–89 ng/m^2 and 45–182 ng/m^3, respectively. Caffeine and nicotine were found both in dust (63–2,02 ng/m^2 and 7–284 ng/m^2, respectively) and as vapors in air (4–416 ng/m^3 and 3.5–60 ng/m^3). Two sites were affected by cannabinoids, while traces of nonylphenols occurred at all locations. External air was, on the average, more affected by PAHs than the interiors of school and hospital, but not of university. The compound concentrations show that Ouargla city is seriously polluted and requires actions to improve air quality.

1. Introduction

Biogenic and anthropogenic sources concur to release huge amounts of chemicals harmful for humans (WHO, 2014). Toxicants exist both in the particulate form (aerosols and settled dust) and as gases; in particular, most organic substances partition between the two aggregation modes, according to total concentrations they reach and to environmental contour, e.g., ambient temperature and relative humidity, levels and nature of suspended particulate matter, pH, etc. (Simoneit, 1989; Pio et al., 2001; Alves et al., 2012; Balducci et al., 2014).

Organic substances occur everywhere in the world, independently of the features of site investigated, e.g. urban, industrial, remote, rural, and marine (Moussaoui et al., 2010, 2013; Canha

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et al., 2014; Ladji et al., 2014; Xie et al., 2014). The organic mixture comprises a number of compounds such as linear and branched hydrocarbons, *n*-alkanols, *n*-alkanoic acids, polycyclic aromatic hydrocarbons (PAHs), pesticides, halogenated toxicants like polychlorobiphenyls (PCBs), dioxins and furans (PCDD/Fs), phthalate and phosphate esters, licit and illicit drugs (Yassaa et al., 2001a; Ladji et al., 2010; Moussaoui et al., 2012). These substances affect both internal and external locations, with distinct levels and pathways (Cecinato et al., 2009; Sangiorgi et al., 2013; Kliucininkas et al., 2014).

Airborne *n*-alkanes originate naturally from living organisms, high plants, and from forest fires. The common process leading to their release into the atmosphere is combustion of organic matter like biomass used for heating or agricultural purposes, petrol-derived mixtures to fuel vehicles, industrial plants, kitchens, power generators. Another relevant source is methane and oil spill from pipelines, tanks and natural deposits. Biogenic and anthropogenic emissions are characterized by distinct *n*-alkane homologue signatures. Particulate exhausts coming from petroleum-derived fuels show a mono-modal percent composition, with the maximum usually centered between C_{17} and C_{26}, depending on ambient temperature; by contrast, high vegetation emits overall odd-carbon numbered *n*-alkanes, with maximum in the correspondence of C_{29} or C_{31}. Thus, the relative importance of the two source types can be estimated by means of dedicated indexes, like Carbon Preference Indexes (CPIs) or Natural Wax Percentage (Yassaa et al., 2001a; Wang et al., 2009; Wingfors et al., 2011; Chen et al., 2014). The non-polar organic fraction of particulates is also characterized by variable percentages of branched hydrocarbons (e.g., steranes, hopanes), typically associated to fuels and lubricating oils, which further put in the evidence the impact of man's activities (Perrone et al., 2014).

The principal source of airborne polycyclic aromatic hydrocarbons is, by far, combustion of organic matter. Though PAHs are present in petrol formulations and can originate from soil resuspension, brake and tire consumption, and natural synthesis by biota, however most of the total budget outcomes from combustion for transport (automobiles, ships and airplanes) (Fromme et al., 1998; Cecinato, 2014; Kliucininkas et al., 2014; Perrone et al., 2014; Vojtisek-Lom et al., 2015), heating and cooking (natural gas, heating oil), refuse disposal, pipelines (Orecchio et al., 2010) industry and power plants (Alam et al., 2013), as well as from biomass burning (forest fires) (Cecinato et al., 2014). Relatively scarce in terms of global budget, but very important with regards to impact on humans, is the presence of PAHs in tobacco smoke (Hoh et al., 2012). PAHs have been extensively investigated in open and indoor air (Pio et al., 2001; Boonyatumanond et al., 2007; Lu et al., 2008; Chen et al., 2014; Romagnoli et al., 2014), overall to preserve health and verify the fulfillment of normative (EC, 2008). Though depending on meteorology, the PAH concentrations in air are overall regulated by year seasons (Boonyatumanond et al., 2007; Sklorz et al., 2007) and are over 10 times higher in the winter than in the summer (Castellano et al., 2003; Agudelo-Castañeda and Teixeira, 2014). The environmental monitoring of PAHs is oriented by toxicity, which depends drastically on compounds (Slezakova et al., 2009). Indeed, most attention is paid to 4-, 5- and 6- benzene-ring congeners, and benzo[*a*]pyrene is regarded as the most important one (IARC, 2014) and indicator of the whole group (EC, 2008).

As key toxicants, halogenated organic substances are studied since long time and extensively monitored in emissions and environment. “Old” and “new” groups of compounds belong to this class; the most important ones are polychlorobiphenyls (PCBs), polychlorodibenzodioxins and furans (PCDD/Fs), halogenated pesticides (e.g., chlordane, DDT, DDE, HBB) and flame retardants (e.g. polybromodiphenyl ethers [PBDEs]) (Montone et al., 2002; Zhu et al., 2015). Internal environments are often affected by huge concentrations of nicotine originated by tobacco smoking, as well as by traces ($\approx$ng/m^3) of psychotropic substances and emerging contaminants (phthalates, phenols, plasticizers) (Fromme and Schober, 2014).

Measurements of particulate *n*-alkanes and PAHs have been already performed in Algeria, both in Algiers and in other urban and rural localities. Investigations have been somewhere extended to fatty acids and polar organics (Yassaa et al., 2001a, b, c; Moussaoui et al., 2012, 2013; Ladji et al., 2014).

In this study *n*-alkanes, PAHs and polar organic compounds were monitored at several locations in Ouargla city, Algeria, by collecting settled dust from surfaces, and gas phase contaminants by means of passive sampling devices. The distinct neat concentrations of compounds and the respective distributions between particulate and gas phase could be evaluated. Finally, insights about the impact of natural and anthropogenic sources could be drawn.

2. Experimental

2.1. Air sampling sites and protocols

Two monitoring networks were implemented in our study; the former was dedicated to dust (sampling points N = 7), and the latter to semi-volatile substances (N = 15), with some points in common. All sampling points lied in Ouargla city, Algeria, or its neighborhoods (Fig. 1), and belonged to four main environments, i.e., university, hospital, school and home.

Six locations (two outdoors and four indoors including offices and laboratories) were investigated in the university, five in the hospital (patient treatment and service rooms), four in the school (classrooms and common areas), and one in the home (dining room); school and home were not in downtown but in its proximities (at Ain Beida, ca. 10 km E of Ouargla) (Table 1).

The protocol in-field experiment was conducted between October 2014 and January 2015. To collect dust, horizontal surfaces (in marble or furniture matter, each equal to 0.50 m^2, located $\geq$1 m above floor and $\geq$1 m from vertical surfaces) were polished with pre-cleaned cotton wads (sterile swab stick, 13 × 155 mm, purchased from Ningbo Greetmed Medical Instruments Co., Ltd., Ningbo, China R.P.) without using organic solvents or cleaning products, then they were exposed to particle deposition; after 15 or 31 days, surfaces were cleaned again and dust was retained in cotton wads. Before chemically characterizing dusts, the analytical procedure was tested by means of analogous samples collected without exactly recording the deposition times, to draw preliminary information. Dust loaded cottons were wrapped with aluminum foils, sealed into plastic bags and stored at low temperature (~4 °C) until analysis.

Passive samplers (14 cm diameter; 1.35 cm thick; surface area, 365 cm^2; volume, 207 cm^3; density, 0.0213 g cm^{-3}; purchased from PacWill Environmental, Beamsville, ON, USA) were deployed in interiors 2 m above soil and 1.5 m away from vertical walls, and exposed to ambient contaminants from October 28 to December 28, 2014 (61 days). Afterwards, the devices were removed and PUF cartridges were sealed and stored at low temperature until analysis. Unused cotton wads and PUF cartridges were examined for blank subtraction.

2.2. Sample treatment

The analytical procedures were adapted from the studies of Moussaoui et al. (2010) and Ladji et al. (2014), after testing for quality controls (detector linearity, lack of interferences and matrix