Biogenic and anthropogenic organic components of Saharan sands

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HIGHLIGHTS

- Both natural and anthropogenic sources affect organic fraction of Saharan sands.
- Biogenic contribution results quantitatively heavier than the anthropogenic one.
- Sand of the two regions investigated show two different molecular signatures.
- Unlike the other groups, dicarboxylic acids came out in part from a secondary source.

ARTICLE INFO

ABSTRACT

Till now, the Sahara desert sands have scarcely characterized for their organic contents, despite they are known to heavily affect Europe and America when transported by winds. In this study, the composition of sands collected in ten oasis lying in two regions of the Algerian Sahara during 2011 was investigated with regards to organic fraction. Attention was paid to anthropogenic and biogenic sources of organics associated to sands, through the characterization of *n*-alkanes, *n*-alkanoic and *n*-alkanedioic acids, *n*-alkanols, sterols, PAHs and caffeine. The organic fraction load on sands associable to natural sources was higher in the Region of Biskra than in that of Ouargla. The biogenic contribution to the total amount of organics in sands exceeded that of the anthropogenic sources. The composition of sands from Hassi Messaoud, compared to that observed there in 2006, showed that the anthropic impact over the region was not changed.

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1. Introduction

Aerosols are extensively investigated since they play a key role with regards to the multitude of reactions regulating the Earth's equilibrium. Indeed, they are involved in climate change through inducing both direct and indirect effects on the Earth's radiation budget and impact global ecosystem, affecting processes such as the biogeochemical cycle of oceans (Koren et al., 2005; Hatch and Grassian, 2008; Washington et al., 2009; Chaâbane et al., 2012). Besides, epidemiological studies have consistently demonstrated adverse effects of particulate matter on humans (WHO 2013). Desert sands are not equal *tout-court* to aerosols, displaying different size, shape and composition. Nonetheless, as demonstrated by several studies (Washington et al., 2009), huge amounts of atmospheric particulate are made up of soil dust raised by winds in arid

regions, and transported across long distances. It has been estimated that from 900 to 3000 Tg of soil dusts are annually involved in the regional or long-range transport (Ndour et al., 2009). Hence, windblown dust accounts for a large percentage of Earth's suspended particulate. Sahara desert is the major global source of windblown dust, producing about half of the worldwide release (Engelstaedter et al., 2006). Saharan dusts are frequently driven over Mediterranean as well as Caribbean Sea and Atlantic Ocean (Moulin et al., 1997; Prospero, 1999; Griffin, 2007; Karanasiou et al., 2012). It was estimated that approximately 12% of the Saharan dust moves northwards to Europe, 28% westwards to the Americas, and 60% southwards to the Gulf of Guinea (Engelstaedter et al., 2006). African dust intrusions impact air quality so heavily that, for instance, they appear as responsible for over 70% of PM_{10} exceedances recorded in most EMEP sites classified as regional background in Spain, according to daily limit value fixed by the 2008/50/CE European Directive. Member States can even subtract the contribution of Saharan dust, measured or computed by modeling,

when assessing compliance with European air quality standards (Gobbi et al., 2007; Mallone et al., 2011; Karanasiou et al., 2012).

Desert dusts are mainly comprised of inorganic components; thus, most chemical characterizations have been focused on this fraction (Hatch and Grassian, 2008; Karanasiou et al., 2012; Dupart et al., 2012). Nevertheless, biogenic and anthropogenic sources enrich windblown dust with a number of organic substances. These compounds should be further considered if the global and regional aftermaths of the Saharan windblown dust want to be better clarified (Prospero, 1999; Dubovik et al., 2002; Kirchstetter et al., 2004; George et al., 2005; Stemmler et al., 2006; Andreae and Gelencsér, 2006; Hatch and Grassian, 2008; Hatch et al., 2008; Karanasiou et al., 2012; Bahadur et al., 2012). As for the epidemiologic effects, dust transported over long distances usually has a mass median diameter lower than 10 μm (Prospero, 1999) and can represent a threat for human health due to pesticides contents, industrial byproducts, plant detritus or microorganisms, all increasing the toxic, allergenic and inflammatory properties of soot (Mallone et al., 2011; Karanasiou et al., 2012). About the effects on the global equilibriums (i) recent studies suggest that organic coating associated to mineral dust significantly enhances the cloud condensation nuclei action of aerosols (Prospero, 1999; Andreae and Gelencsér, 2006; Hatch and Grassian, 2008); (ii) the photochemistry of organics highly promotes the HONO production during daytime (George et al., 2005; Stemmler et al., 2006; Ndour et al., 2009); (iii) many components of organic matter (defined as *brown carbon*) absorb visible and UV light (Andreae and Gelencsér, 2006; Hatch et al., 2008); and (iv) both the uptake of HONO on dust and the extinction of ultraviolet sunlight can affect the equilibrium of the tropospheric ozone. Even taking in account the low percentage of organic fraction occurring in desert sands, its effect could be relevant because of the huge amounts of dust annually raised and spread by winds. In fact, laboratory and remote sensing measurements have shown that aerosols over desert regions appreciably absorb light at blue and shorter wavelengths (i.e., wavelengths less than 500 nm), which are typical of many polar and aromatic organic compounds.

Small wind-borne soil particles are submitted to duty modification processes during their transit across atmosphere; their physical and chemical properties will depend overall on the weathering history they had at the source region (Prospero, 1999). Very few investigations have been carried out till now on the organic matter composition of desert sands (Al Mutlaq et al., 2002; Ladji et al., 2010). This study reports the characterization of organic constituents of sands collected at ten Algerian Sahara oases experiencing different human and environmental contours. *n*-Alkanes, *n*-alkanoic and *n*-alkanedioic acids, *n*-alkanols, sterols, PAHs and caffeine were investigated. Almost 100 compounds were quantified, and the observed chemical fingerprints appeared helpful to picture the relative impacts of anthropogenic, microbial and plants sources on the desert sands load.

2. Materials and methods

2.1. Sites and samples collection

Sands were collected during March 2011 in Sahara desert areas belonging to two Algerian regions, i.e. Biskra and Ouargla (see Fig. 1). Ten sites were investigated, namely: (i) in the Biskra Region, Biskra city (BK) and the villages of El Ghrous (EG), Tolga (TO), Bir Naam (BN), and Oumache (OU); (ii) in the Ouargla Region, Hassi Messaoud (HM), Hassi Ben Abdellah (HB), and three localities around the province capital, namely Aïn Beïda (AB), Sidi Khouiled (SK) and Rouissat (RO). Table 1 provides the geographical coordinates of sites.
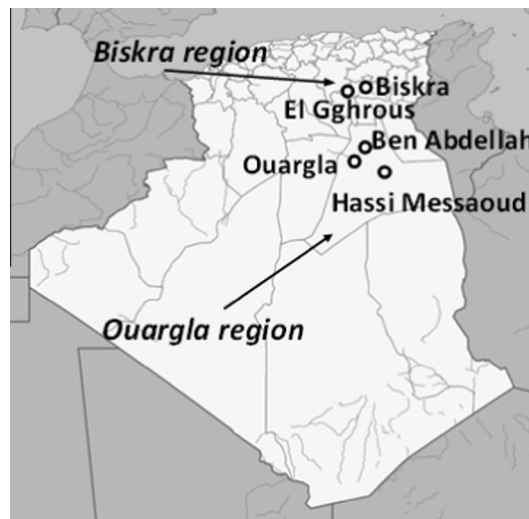

Fig. 1. Map of Algeria with regions where samples were collected. The detailed localization of five sampling sites is also reported.

The localities were representative of industrial and agricultural activities, as well as of pollution sources associated with human presence. Biskra city, the capital of homonymous region, was the most populated locality investigated, reaching ≈300 000 inhabitants. The El Ghrous economy was based on agriculture and the village hosted an important market of agricultural products. Production of vegetables, especially dates, was the most important resource there and in the other three localities of the region. As for the Ouargla Region, Hassi Messaoud oasis was known for the very important petrol extraction fields and refineries; Hassi Ben Abdellah, Aïn Beïda, Sidi Khouiled and Rouissat were oases in the surroundings of Ouargla city. Aïn Beïda hosted the principal airport of the region.

The sand samples were collected and stored according to procedure described elsewhere (Ladji et al., 2010). Briefly, sands were kept up to 2 cm below the ground, outside the inhabited area (ca. 200 m away) and at locations preserved from close emission sources; the soil surface at the collection point was fairly homogenous. The samples, conveniently enveloped and sealed, were stored in freezer until treated for chemical analysis.

2.2. Sample treatment

The analytical methods adopted for *n*-alkanes, acids, PAHs and caffeine were derived from protocols used to explore the airborne particulate composition (Alves et al., 2007; Ladji et al., 2010; Balducci and Cecinato, 2010; Cecinato et al., 2012). Before analysis, the sand samples were homogenized by mechanical stirring, then 50 g aliquots were spiked with perdeuterated internal standards. $C_{14}d_{30}$, $C_{16}d_{34}$, $C_{20}d_{42}$, $C_{24}d_{50}$ and $C_{30}d_{62}$ were used for the *n*-alkanes determination, whilst perdeuterated dodecanoic, tetradecanoic, hexadecanoic, octadecanoic and docosanoic acids were used for the analysis of *n*-alkanoic and *n*-alkanedioc acids, *n*-alkanols, cholesterol and stigmasterol. In order to quantify polycyclic aromatic hydrocarbons (PAHs) and polar components, perdeuterated PAHs, nicotine-d_4 and caffeine-$(C_{13})_3$ were added. Samples were extracted in soxhlet by using a dichloromethane:acetone mixture (4:1 in volume, 16 h, 5 cycles per hour). The extract was reduced to ⩽0.5 mL through Kuderna–Danish distillation followed by ultra-pure nitrogen flushing, and the residue was divided into three aliquots:

Table 1
Geographical coordinates of the sites investigated.

Region	Site		Latitude	Longitude
Biskra	Biskra	BK	34°49′36 N	5°44′48 E
	El Gghrous	EG	34°44′24 N	5°12′19 E
	Tolga	TO	34°44′54 N	5°26′43 E
	Bir Naam	BN	34°45′28 N	5° 7′6 E
	Oumache	OU	34°41′57 N	5°42′50 E
Ouargla	Hassi Messaoud	HM	31°45′18 N	6° 1′11 E
	Hassi Ben Abdellah	HB	32° 0′34 N	5°30′57 E
	Ain Beida	AB	31°55′40 N	5°25′29 E
	Sidi Khouiled	SK	31°59′37 N	5°24′43 E
	Rouissat	RO	31°55′2 N	5°21′4 E

– The first aliquot (50%) was purified and fractionated into three classes of polarity by means of column chromatography on neutral alumina. The extracts were eluted in sequence with isooctane, isooctane/dichloromethane (iso/DCM, 60:40 in volume), and acetone. The isooctane eluate (1st Fraction) comprised non polar n-alkanes, whereas low-polar PAHs and polar components were eluted with iso/DCM and acetone, respectively.

– Further 25% of the crude extract was processed for n-alkanoic and n-alkanedioic acids determination, by converting them into the corresponding esters with BF_3 in excess of isopropanol. Reaction was carried out at 70 °C for 60 min. After cooling, the solution was eluted through a new alumina column with isooctane and dichloromethane, in sequence; isopropanol esters were collected in the second fraction.

– The remaining 25% aliquot of the extract was treated in order to determine alcohols and sterols. For this purpose, 200 μL of BSTFA + 1% TMCS were added to form the corresponding trimethylsilyl ether derivatives. The reaction was carried out at 70 °C for 1 h (Wang et al., 2009). After cooling, silyl derivatives were dried under a gentle nitrogen flow, re-dissolved in toluene and submitted to GC–MS analysis.

All solvents were from ROMIL, of residue-grade purity, and purchased from Delchimica Scientific Glassware (Naples, Italy), while alumina and derivatizing agents were from Aldrich Chimica (Milan, Italy). Glassware was from Marbaglass (Rome, Italy). Chemical standards were provided by Chemical Research 2000 (Rome, Italy), at the maximum purity available (⩾98%). The analytical procedure allowed to evaluate n-alkanes homologues within the C_{14}–C_{37} interval (where the C subscript indicates the carbon number), n-alkanoic acids in the range C_{12}–C_{30} (reported in the text as A_{12}–A_{30}), n-alkanedioic acids with carbons numbers comprised between 6 and 20 (D_6–D_{20}), and C_{14}–C_{30} n-alcohols (L_{14}–L_{30}). Fifteen PAH compounds were investigated, namely phenanthrene, anthracene, fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(j)fluoranthene, benzo(k)fluoranthene, benzo(e)pyrene, benzo(a)pyrene, perylene, indeno(1,2,3-c,d)pyrene, dibenzo(ah)anthracene and benzo(ghi)perylene.

2.3. Instrumental analysis and method effectiveness

The instrumental analysis system consisted of a Trace GC Ultra gas chromatograph equipped with an AS-8000 auto-sampler and Trace DSQ quadrupole mass spectrometer; all of them were purchased from Thermo, Rodano MI, Italy. Chemical determinations were performed by using a DB5-MS column (L = 30 m, i.d. = 250 μm, film thickness = 0.25 μm; from CPS Analytica, Milan, Italy), operating in temperature program (T = 90 °C, 1.5 min; then +15 °C min up to 170 °C, 2 min; then +4 °C min up to 290 °C, 15 min). Carrier gas was helium (1 mL/min). Injection was made in split-less mode (280 °C, 1 min). Signals were generated through electron impact (70 eV) and acquired in scan mode, except for PAHs and polar components (selected-ion monitoring). Target compounds were identified by comparing retention times and mass spectra of GC peaks with those of authentic standards, and using NIST and home-made spectrum libraries. Each analyte was referred to its perdeuterated homologue, when present, or to the closest internal reference compound in the chromatogram. Compounds were quantified by comparing the peak areas with those of the co-injected standards.

Standards of acid isopropyl esters and alcohol/sterol trimethyl-silyl ethers were synthesized "in situ" to check the reliability of the analytical procedure and the detector system performances. According to method protocol, the limits of quantification (LOQs) (signal-to-noise ratios equal to ten and twice the respective limits of detection) of alkanes, alkanoic acids, and dicarboxylic acids were in the ranges $0.1 \div 0.5$ ng g^{-1}, $0.2 \div 3.0$ ng g^{-1} and $0.4 \div 1.5$ ng g^{-1}, respectively. The highest LOQs in each group were associated to long-chain homologues, e.g. that of benzo(ghi)perylene was equal to 0.01 ng g^{-1}. All n-alkanol LOQs were <2 ng g^{-1}, similarly to cholesterol and stigmasterol. Total recoveries lied in the range 92 ± 12% with the worst results associated to alcohols. Analytical interferences were found in the correspondence of palmitic (A_{16}) and stearic (A_{18}) acids and of light n-alkanes (C_{14}–C_{18}); nevertheless, positive identification and quantitative determination could be made by subtracting blanks.

3. Results and discussion

3.1. n-Alkanes

Fig. 2 reports the selected-ion-chromatograms (m/z = 85) of n-alkane fractions recorded respectively at EG, characterized by intense agricultural activity, and HM, affected by petrogenic pollution sources. The two sands showed n-alkane distributions characteristic of patterns observed in this study. In the EG sample the high odd-to-even homologue concentration ratio, together with the predominance of $\geqslant C_{25}$ n-alkanes, depicts the heavy contribution coming from vegetation, especially high plants (biogenic); by contrast, in the HM chromatogram the lack of any odd-to-even prevalence and the maximums shifted to shorter chain homologues suggest that emissions associated to petrogenic sources were predominant (Simoneit, 1989; Rogge et al., 1993; Alves et al., 2007; Wang et al., 2009). In the HM sand the total ion chromatogram profile (not reported here) presented a huge unresolved complex mixture (UCM) of branched and cyclic hydrocarbons, predominating over the n-alkane fingerprint. In this case, the extract was indicative of lubricating oils or bio-degradated petroleum contribution to the total hydrocarbons (Simoneit, 1989; Wang and Fingas, 2003; Wang et al., 2009).
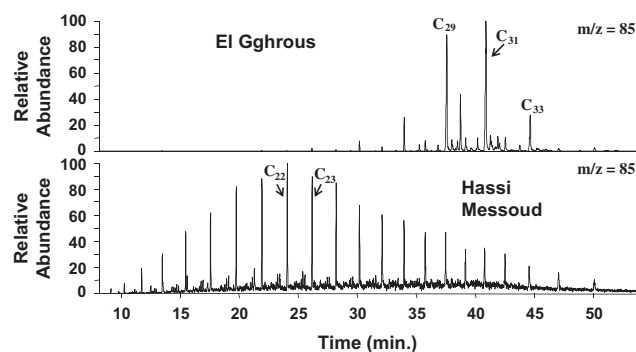

Fig. 2. Selected ion chromatogram (m/z = 85) of n-alkanes detected in El Gghrous and Hassi Messaoud.

According to technical literature, the Carbon Preference Index (CPI) allows to distinguish the input of biogenic n-alkanes from that of petrogenic origin (Simoneit, 1989; Rogge et al., 1993). In fact, CPI values close to 1 are typical of petrol products, whilst biogenic emissions are characterized by CPI values >>2. The CPI values observed at EG and HM were respectively the maximum (8.3) and the minimum (1.1) at our sites (see Table 2); thus, biogenic sources were more important in Biskra than in Ouargla. In fact, in the former region the lowest CPI (2.4), was found in the capital, whilst in the latter the maximum (2.3) was recorded at HB. Moreover, comparing total light-medium alkanes vs. medium-heavy homologues (i.e., C_{14}–C_{24} vs. C_{25}–C_{37}), the ratios were as low as 0.25 ± 0.15 in Biskra and reached 2.07 ± 0.95 in Ouargla. Finally, n-alkanes peaked (C_{max}) in correspondence of C_{31} in Biskra and C_{17}–C_{20} in Ouargla, where the long-chain homologues were often below the respective LOQs, except for HB. Indeed, Ouargla hosted the biggest oil and gas extraction fields in Africa (Yassaa et al., 2001, 2011; Yassaa and Cecinato, 2005); HB was the sole site in the region, where intense agricultural activities were performed. On the other hand, Biskra was famous for the palm tree crops and the quality of date fruits. All these indicators confirm that EG experienced the highest impact of biogenic sources, and HM was the site most affected by anthropogenic sources. It is worth to remark that neat concentrations of biogenic n-alkanes in the EG sands exceeded those of petrogenic hydrocarbons at HM.

3.2. n-Alkanoic acids (fatty acids), n-alkanols

n-Alkanoic acids (fatty acids), and n-alkanols (fatty alcohol) are important markers of biogenic and anthropogenic sources, depending on their percent profiles. The two groups are constituents of biota chemistry, for instance as external lipids in the cuticular waxes of terrestrial plants or internal energy reserves of organisms. In particular, higher plant leaves are coated by a waxy deposit preserving the water balance. This deposit is a complex mixture of long chain alkanes, alcohols, ketones, aldehydes, acetals, esters and acids (Mudge and Norris, 1997). Short fatty acids ($\leqslant A_{20}$) are ubiquitous, released by petrogenic sources and associated to microbial activities. Homologues $\geqslant A_{22}$ show a more pronounced plant origin (Simoneit, 1989; Fine et al., 2001; Wang et al., 2009). With regards to fatty alcohols, biotic sources are usually predominant; microbial sources yield $\leqslant A_{20}$ homologues, whilst vegetation produces the long chain ones (Simoneit, 1989; Rogge et al., 1993; Mudge and Norris, 1997). Also in the case of n-alkanoic acids and n-alkanols the percent distribution profile allows to draw information about the nature of source. Unlike alkanes, the two groups usually display the even-to-odd carbon number predominance, with high values of CPI (Simoneit, 1989). For instance, n-alkanoic acids released by vehicle exhausts show CPI values of $2 \div 4$, whilst CPIs associated to vascular plants range from 7 to 20.

Table 2 reports total fatty acids (A_{TOT}) detected in all samples. They ranged from 814 ng g^{-1} (TO), to 95.1 μg g^{-1} (EG). The CPI rates varied broadly but always exceeded 5.9, in accordance to biogenic nature of monocarboxylic acids. The relative impact of microbial and petrogenic sources vs. that of high plants is depicted in Table 2 through the ratio between the sub-totals of n-alkanoic acids in the $A_{14} \div A_{20}$ and $A_{22} \div A_{30}$ ranges; according to them, vegetation accounted for most of total acids over all Biskra region except for TO. In the Ouargla region the minimum ($A_{14} \div A_{20}$)/($A_{22} \div A_{30}$) ratio (1.1) was recorded at HM and the prevalence of microbial and petrogenic sources was detected at all sites.

Total n-alkanols (Table 2) ranged from a minimum of 280 ng g^{-1} up to ≈20 μg g^{-1}, respectively measured at TO and EG. The alcohol molecular fingerprints showed the regular even-to-odd prevalence with CPIs ranging from 3.7 (BK) to over 30 (AB), with the only exception of HM (CPI = 1.2). The maximums

were in the correspondence of L_{18} at all sites except for EG, where it was at L_{30}. Apart from EG and HM, two behaviors characterized the two regions. In Ouargla L_{18}, L_{20} and L_{22} were predominant and cumulatively accounted for $74\% \pm 8\%$ of the total alcohols; by contrast in Biskra the three homologues accounted for only $31\% \pm 14\%$. At HM the n-alkanol profiles did not display any prevalence along the whole chain length range; at EG L_{26}, L_{28} and L_{30} were predominant, accounting for ca. 76% of the total. The n-alkanols signatures were in contrast with those commonly identified in soils, which peak in the correspondence of L_{26} (Mudge and Norris, 1997), but in accordance with those of Saudi Arabia sands, where L_{18} and L_{30} were the most abundant homologues (Al Mutlaq et al., 2002).

3.3. n-Alkanedioic acids and sterols

Sands were characterized for n-alkanedioic acids (α,ω-dicarboxylic acids, D) belonging to the D_6–D_{20} range (adipic to eicosanoic). Short-chain dicarboxylic acids ($\leqslant D_{10}$) are produced by degradation of fatty acids, or by combustion of biomass and petrogenic products. Long-chain homologues are known to exist in terrestrial higher plants; there they show the typical predominance of D_{16}–D_{22} homologues, depending on the vegetation type (Kawamura and Kaplan, 1987; Kawamura and Gagosian, 1990; Stephanou, 1992; Fine et al., 2001; Al Mutlaq et al., 2002).

In sands total α,ω-dicarboxylic acids ranged from 39 to 1393 ng g^{-1}, with the minimum and the maximum recorded at TO and EG, respectively. The most abundant compounds lied in the $D_6 \div D_{10}$ range and peaked usually in correspondence of the azelaic acid (D_9); the only exception was AB, where adipic acid was predominant. D_9 is produced by oxidation of biogenic unsaturated fatty acids (e.g. oleic) containing double bonds at C_9 position (Stephanou, 1992). $D_6 \div D_{10}$ homologues accounted for ≈55% of the total in Biskra, and over 80% in Ouargla, confirming the importance of petrogenic sources in this region.

Sterols can be used as tracers of input from various species of vegetation and animals. They are structural components of organisms, capable of persisting in the environment more than other biological products (Simoneit, 1989; Wang et al., 2009). Stigmasterol (STI) and cholesterol (CHO), two of the most important sterols, were investigated as representative of the whole group. STI is among the main components of vascular plants. CHO has both vegetal and animal origin; it is produced through food cooking and occurs in domestic sewage. CHO was found in all samples and peaked in EG (550 ng g^{-1}). On the average, higher burdens of CHO were associated to Biskra sands. Low STI contents were observed compared to CHO. That could depend on the respective amounts and strength of sources; anyway, according to Simoneit (1989) either CHO or STI could prevail in rural areas; in particular, CHO predominated in warm climatic regions, maybe due to climatological adaptation of specific plant communities.

3.4. PAHs, nicotine and caffeine

PAHs are extensively investigated as environmental toxicants, due to their carcinogenic properties (Ravindra et al., 2006). They are introduced into soil from atmospheric deposition after local or long-range transport. In the sands investigated total PAHs never exceeded 18.4 ng g^{-1}, while benzo(a)pyrene ranged from 0.02 to 0.64 ng g^{-1}; the maximum was recorded at RO, in the surroundings of Ouargla city. PAHs were, on the average, more abundant in Ouargla (∼5–18 ng g^{-1}) than in Biskra (∼0.4–3.4 ng g^{-1}). To draw further information from organic profiles, the linear correlation among PAH signatures was investigated. In Ouargla the PAH fingerprint was quite similar at all sites (R^2 ranging from 0.71 to 0.92, average = 0.85); by contrast in Biskra (R^2 ranging from 0.27 to 0.83, average = 0.50) a mix of sources occurred. Besides, the

Table 2

Total amount of n-alkanes (in the range C_{14}–C_{37}), n-alkanoic acids (C_{12}–C_{30}), n-alkanedioic acids (C_6–C_{20}), n-alkanols (C_{14}–C_{30}), sterols, PAHs (phenanthrene, anthracene, fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(j)fluoranthene, benzo(k)fluoranthene, benzo(e)pyrene, benzo(a)pyrene, perylene, indeno(1,2,3-c,d)pyrene, dibenzo(ah)anthracene, benzo(ghi)perylene), caffeine and respective chemical indexes.

Sites	Biskra					Ouargla				
	El Ghrous	Biskra	Tolga	Bir Naam	Oumache	Hassi Messaoud	Hassi Ben Abdellah	Rouissat	Sidi Khouiled	Aïn Beïda
	EG	BK	TO	BN	OU	HM	HB	RO	SK	AB
n-Alkanes										
C_{TOT} (ng g^{-1})	3323 ± 186	275 ± 16	214 ± 19	300 ± 24	989 ± 72	1525 ± 167	834 ± 78	837 ± 34	454 ± 28	857 ± 43
CPI	8.3 ± 0.3	2.4 ± 0.1	2.7 ± 0.1	3.50±	7.9 ± 0.4	1.1 ± 0.1	2.3 ± 0.2	1.2 ± 0.1	1.7 ± 0.1	1.4 ± 0.1
$C_{14} \div C_{24}/C_{25} \div C_{37}$	0.06 ± 0.01	0.35 ± 0.01	0.42 ± 0.06	0.33 ± 0.09	0.12 ± 0.05	2.67 ± 0.09	0.90 ± 0.03	2.52 ± 0.07	1.29 ± 0.03	2.99 ± 0.15
C_{max}	C_{31}	C_{31}	C_{31}	C_{31}	C_{31}	C_{18}	C_{31}	C_{20}	C_{17}	C_{18}
n-Alkanoic acids										
A_{TOT} (ng g^{-1})	95 135 ± 869	1232 ± 28	814 ± 17	847 ± 20	2986 ± 51	2823 ± 40	1299 ± 42	7146 ± 77	1958 ± 17	1140 ± 27
CPI	12.3 ± 0.1	6.8 ± 0.2	7.5 ± 0.3	8.3 ± 0.1	8.3 ± 0.1	7.4 ± 0.1	6.8 ± 0.4	9.6 ± 0.1	8.8 ± 0.2	5.9 ± 0.1
$A_{14} \div A_{20}/A_{22 \div 30}$	0.2 ± 0.01	0.8 ± 0.03	1.5 ± 0.04	0.6 ± 0.01	0.2 ± 0.02	1.1 ± 0.1	2.4 ± 0.4	1.6 ± 0.01	6.9 ± 0.2	5.5 ± 0.1
C_{max}	A_{30}	A_{16}	A_{16}	A_{30}	A_{30}	A_{16}	A_{16}	A_{16}	A_{16}	A_{16}
n-Alkanols										
L_{TOT} (ng g^{-1})	20 008 ± 193	428 ± 35	280 ± 13	503 ± 12	2406 ± 30	518 ± 18	5760 ± 83	2811 ± 49	3838 ± 46	7215 ± 125
CPI	16.7 ± 0.2	3.7 ± 0.1	6.6 ± 1.7	5.2 ± 0.1	8.7 ± 0.3	1.2 ± 0.04	16.3 ± 0.2	9.8 ± 0.1	14.6 ± 0.7	33.4 ± 8.3
L_{18}, L_{20}, L_{22} (%)	7.9 ± 0.5	33.8 ± 0.3	28.7 ± 1.4	37.9 ± 1.8	45.7 ± 1.9	25.5 ± 0.3	74.5 ± 0.6	64.0 ± 0.5	75.9 ± 1.1	83.0 ± 1.0
L_{26}, L_{28}, L_{30} (%)	76.7 ± 0.2	16.9 ± 0.1	25.3 ± 0.9	22.2 ± 6.5	26.4 ± 1.4	6.2 ± 1.6	6.4 ± 0.2	14.9 ± 0.3	1.9 ± 0.1	1.4 ± 0.1
C_{max}	L30	L18	L18	L18	L18	L18	L18	L18	L18	L18
n-Alkanedioic acids										
D_{TOT} (ng g^{-1})	1394 ± 47	86 ± 8	39 ± 2	45 ± 3	103 ± 7	189 ± 3	73 ± 4	558 ± 18	186 ± 8	110 ± 4
CPI	1.9 ± 0.05	1.6 ± 0.07	1.3 ± 0.3	1.8 ± 0.05	1.3 ± 0.1	0.6 ± 0.02	0.8 ± 0.06	0.5 ± 0.06	0.7 ± 0.03	0.6 ± 0.04
$D_6 \div D_{10}$ (%)	45.5 ± 0.3	52.5 ± 0.4	65.6 ± 0.6	57.2 ± 0.4	52.3 ± 0.5	83.1 ± 0.3	79.9 ± 0.3	87.4 ± 0.4	78.3 ± 0.6	93.6 ± 0.4
C_{max}	D_9	D_9	D_9	D_9	D_9	D_9	D_9	D_9	D_9	D_6
Stigmasterol (ng g^{-1})	91 ± 37	2.7 ± 0.2	2.4±0.1	<2	7.0 ± 0.4	<2	<2	2.3 ± 0.1	2.3 ± 0.2	<2
Cholesterol (ng g^{-1})	550 ± 29	35 ± 1	11 ± 1	150 ± 8	43 ± 3	16 ± 1	33 ± 2	20 ± 3	32 ± 2	47 ± 3
Total PAHs (ng g^{-1})	3.7 ± 0.3	3.6 ± 0.4	0.41 ± 0.03	0.58 ± 0.09	1.2 ± 0.1	11.9 ± 1.4	8.7 ± 0.9	18.4 ± 1.4	7.7 ± 0.5	5.3 ± 0.6
Benzo(a)pyrene (ng g^{-1})	0.21 ± 0.01	0.25 ± 0.03	0.035 ± 0.002	0.029 ± 0.003	0.054 ± 0.004	0.29 ± 0.03	0.27 ± 0.02	0.64 ± 0.06	0.18 ± 0.01	0.12 ± 0.01
Caffeine (ng g^{-1})	7.6 ± 0.5	1.2 ± 0.1	0.9 ± 0.1	0.8 ± 0.1	1.8 ± 0.2	7.4 ± 0.6	16 ± 1.2	8.1 ± 0.7	1.9 ± 0.1	n.d.

Table 3
values of R^2 calculated for the total burden of each classes in the areas investigated (L = n-alkanols; C = n-alkanes; D = n-alkanedioic acids; A = n-alkanoic acids; PAH = polycyclic aromatic hydrocarbon; Caf. = caffeine).

Biskra							Ouargla					
	L	C	D	A	PAH	Caf.		L	C	D	A	PAH	Caf.
L	1.000						L	1.000					
C	0.999	1.000					C	0.258	1.000				
D	0.541	0.522	1.000				D	0.201	0.001	1.000			
A	0.952	0.944	0.749	1.000			A	0.273	0.008	0.967	1.000		
PAH	0.014	0.017	0.311	0.010	1.000		PAH	0.241	0.221	0.597	0.747	1.000	
Caf.	0.838	0.844	0.682	0.904	0.040	1.000	Caf.	0.245	0.045	0.078	0.023	0.082	1.000

concentration ratios typically adopted for apportioning sources (e.g., phenanthrene/anthracene, fluoranthene/pyrene, benz[a]anthracene/chrysene, chrysene/benzo[a]pyrene, indenopyrene/benzo[ghi]perylene; see; Manoli et al., 2004; Wang et al., 2007; Ravindra et al., 2008) were more spread in Biskra than in Ouargla. Comparing PAH signatures of the two regions, meaningful differences were recorded; in particular, the phenanthrene/anthracene ratio (phe/ant) reached on the average 4.3 ± 2.7 in Biskra and 9.9 ± 2.7 in Ouargla; this finding, together with the lower load of five rings PAHs in the second region ($18.7\% \pm 3.3$ vs. 32.9 ± 4.6 in Biskra), confirms the expected higher contribution of petrogenic sources in this area (Yunker et al., 2002).

Two psychotropic substances, namely nicotine and caffeine, were investigated in the sands, since both compounds were found at high concentrations in atmospheric particulates of Algeria (Moussaoui et al., 2013). Nicotine was present in sands, but important analytical interferences prevented its determination. Algerian people are big coffee consumers and roasting coffee plants are widespread; however, caffeine did not show a clear trend in any of the two regions. Its occurrence was not related either to population amount or to prevalent activity of the area. Caffeine was not detected in AB (Ouargla); nevertheless, at regional scale it was less in Biskra (range 0.8–1.8 ng g^{-1}), apart from EG where its sand load was comparable to that of HM and RO; the caffeine peak was found at Hassi Ben Abdellah (16.6 ng g^{-1}).

3.5. Study of molecular signatures and comparison with previous investigations

By applying the linear correlation modeling to total contents of the four groups investigated and caffeine, the distinct behaviors of the two regions were confirmed (Table 3). In order to avoid misinterpretation of results, the EG series was cut off since its values were very high. In Biskra alcohols, alkanes and monocarboxylic acids correlated almost perfectly ($R^2 > 0.95$), caffeine ($R^2 \sim 0.8$) and dicarboxylic acids ($R^2 \sim 0.63$) less, and PAHs did not. This is in accordance with the different nature of sources, i.e. biogenic for the first three groups, primary and in part secondary for dicarboxylic acids, and anthropogenic for PAHs. In Ouargla the only significant correlations were those of mono- vs. dicarboxylic acids ($R^2 = 0.97$), and PAHs vs. monocarboxylic acids ($R^2 = 0.75$); caffeine did not correlate with any of other series. Thus, the composition of Saharan sands depended overall on biological sources in Biskra and had mixed origin in Ouargla and as total, the contribution of natural sources to the organic fraction of sands exceeded that of the anthropogenic ones.

Sands collected in HM were analyzed also in 2006, together with those coming from other oases of Algerian Sahara (Ladji et al., 2010). Comparing old archives with new data, n-alkanes (550 ng g^{-1} vs. 1525 ng g^{-1}, respectively) and n-alkanoic acids (1040 ng g^{-1} vs. 2820 ng g^{-1}) changed as total loads detected but preserved the respective molecular signatures. Indeed, in 2006 both n-alkane and n-alkanoic acid profiles were in agreement with

the petrogenic origin of compounds; n-alkanes had a low CPI (1.8), the maximum in correspondence of C$_{17}$ and the prevalence of ⩽C$_{20}$ homologues; besides, n-alkanoic acids ⩽A$_{20}$ were predominant and homologues ⩾A$_{26}$ were not detected. The recent increase of the two groups total loads could depend on the year time of sampling or on global emission strength. Interestingly, the PAHs burdens calculated at Hassi Messaoud in the two campaigns were similar, suggesting that the anthropic impact over the region was fairly unaltered. The fact that PAHs in sands were in general lower than those observed previously in other localities of Algeria ($4.9 \div 22$ ng g^{-1}) (Ladji et al., 2010) could depend on the sites typology. In fact, the campaign conducted in 2009 was made at well inhabited oases (>60 000 people each).

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