

Organic characterisation of PM₁₀ in Cape Verde under Saharan dust influxes



C. Gonçalves^{a,*}, C. Alves^a, T. Nunes^a, S. Rocha^a, J. Cardoso^{a,b}, M. Cerqueira^a, C. Pio^a, S.M. Almeida^d, R. Hillamo^c, K. Teinilä^c

^a Centre for Environmental and Marine Studies, Department of Environment and Planning, University of Aveiro, 3810-193 Aveiro, Portugal

^b University of Cape Verde, Palmarejo Campus, 279 Praia, Cape Verde

^c Finnish Meteorological Institute, Air Quality Research, Sahaajankatu 20E, FIN-00810 Helsinki, Finland

^d URSN, IST/ITN, Instituto Superior Técnico, Technical University of Lisbon, Sacavém, Portugal

HIGHLIGHTS

- PM₁₀ concentrations were influenced by the Saharan dust influxes.
- Highest PM₁₀ values were registered for the dry months: November to March.
- PM₁₀ concentrations frequently exceeded environmental organisation's limits.
- PM₁₀ carbonaceous content was very low.
- Sahara/Sahel dust influxes transport organic compounds to the Cape Verde islands.

ARTICLE INFO

Article history:

Received 4 December 2013

Accepted 12 February 2014

Keywords:

PM₁₀
Organic compounds
GC–MS
Cape Verde archipelago
Sahara dust

ABSTRACT

The current study presents, for the first time, a long-term organic speciation of aerosol at the Cape Verde archipelago. The Cape Verde location, in the Atlantic Ocean, provides a unique laboratory to study background aerosol, long-range transport, aerosol mixing with mineral dust, biomass burning and sea surface components. In order to contribute to a better understanding of this environment, a one-year long measurement campaign was performed in Praia City, Santiago Island. PM₁₀ concentrations (20.5–370 µg/m³) and the organic composition of PM₁₀ were influenced by the African dust influxes. The carbonaceous content of PM₁₀ was very low, suggesting that most of the mass has mineral origin. The PM₁₀ composition was essentially characterised by a large variety of organic compounds, which can be grouped into general compound classes, such as *n*-alkanes, *n*-alkanols, *n*-acids and sugars. The *n*-alkane total concentrations varied from 3.77 to 53.2 ng/m³. The *n*-alkanols distribution showed a significant biogenic contribution whether from microbial origin or from epicuticular plants during African dust outbreaks. The total concentrations of *n*-alkanoic acids varied from 0.011 to 4.51 ng/m³. The lower *n*-alkenoic acids content, obtained during the periods of long-range transport from Africa, indicated a more aged aerosol. The monosaccharide anhydrides were detected in all samples with a range of concentrations from 2.06 to 12.7 ng/m³.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Atmospheric suspended particulate matter plays an important role on radiative forcing, changing precipitation patterns (serving

as cloud and ice condensation nuclei) (Mahowald et al., 2010), modifying the availability of nutrients in the different biogeochemistry systems (Martin et al., 1991) and affecting human health (Mauderly and Chow, 2008). It is known that c.a. 44% of global emissions of particulate matter have mineral origin (Prospero et al., 2002). Deserts, dry lakebeds and semi-arid surfaces are the main sources of this type of aerosol. The human action on the landscape also leads directly to mineral aerosol formation by removing surface vegetation for agriculture (Gillette et al., 1997) or pasture usage (Neff et al., 2005), or

* Corresponding author. Institute of Geosciences, Department of Geology and Natural Resources, University of Campinas, João Pandiá Calógeras Street, Campinas 13083-870, Brazil.

E-mail addresses: goncalves.catia@gmail.com, catiagoncalves@ua.pt (C. Gonçalves).

through mismanagement of water resources (Reheis, 1997). The largest dust regions of the world are located in the Northern Hemisphere, particularly in North of Africa (the Bodélé Depression at the Sahara Desert and the Sahel region) (Mbourou et al., 1996; Washington et al., 2006; Prospero, 1996), Arabian Peninsula and Oman deserts and the Gobi and Taklamakan in China. In South Hemisphere stands out the Lake Eyre and the Great Artesian Basin in Australia and desert areas in Patagonia and in Western Argentina (Formenti et al., 2011). The Sahara desert, considered one of the largest dust producers of the world (Washington et al., 2003), annually exports an estimated billion tons of mineral dust from the northwest Africa (Ridley et al., 2012) to the Mediterranean towards Europe (Moulin et al., 1998; Müller et al., 2009), western Asia (Ganor et al., 2010), Caribbean region (Swap et al., 1996; Liu et al., 2008) and South America (Prospero et al., 1981; Formenti et al., 2001; Ansmann et al., 2009; Ben-Ami et al., 2010).

This global atmospheric transport of dust predominately carries mineral particulate matter. But primary biogenic aerosol, such as pollen (Cariñanos et al., 2004), spores, microorganisms (Griffin et al., 2001; Kellogg et al., 2004), and particles from fossil fuel and biomass burning (Hand et al., 2010; Kandler et al., 2011) also have an important contribution. The carbonaceous aerosols are a significant fraction of continental aerosols, but some gaps remain on its spatial distribution and physico-chemical characterisation, and consequently on its impact on human health and climatic changes.

The Cape Verde archipelago is in the transport path of the continental aerosols from the African continent to the Atlantic. This particular location in the Atlantic Ocean provides a unique field laboratory to study background aerosol, long-range transport, biomass burning and sea surface components. The identification and characterisation of the highly variable distribution of these types of aerosols is a complex task. In order to contribute for a better understanding of this environment, a one-year long measurement campaign was performed at Santiago Island, one of the ten islands of the Cape Verde archipelago, in the Atlantic Ocean. Although some previous attempts have been made to characterise the organic composition of aerosols over the Atlantic after sampling campaigns on board of research vessels (e.g. Alves et al., 2007; Nemirovskaya, 2006; Schefuß et al., 2003; Simoneit et al., 1991), the information is still very scarce and heavily directed towards the contribution from the surface waters. As far as we know, the current study presents, for the first time, a long-term organic speciation of aerosol transported from the Sahara to the Atlantic.

2. Materials and methods

2.1. Sampling

A monitoring field station was implemented in the surroundings of Praia City (14°55' N, 23°29' W, 98 m above sea level), at Santiago Island, where aerosol sampling, throughout different samplers, was performed. In order to characterise its chemical composition, particulate matter was collected with a high volume sampler (Tisch) with a standard PM₁₀ inlet head, on quartz fibre filters pre-baked at 500 °C for 6 h, to remove organic contamination. Sampling took place between January 2011 and January 2012, totalising 115 filters. Based on the observed low organic carbon (OC) content of collected samples, 3 to 10 consecutive filters were pooled to perform the extractions, resulting in 21 sets of samples (CV1 to CV21). The filters that form these sets were collected consecutively, providing a good characterisation of the different time periods.

2.2. Analytical methods

Gravimetric analysis was performed with a microbalance (Sartorius M5P) after 24 h equilibration in a temperature and humidity controlled room. Filter weights before and after sampling were obtained as the average of three measurements, when observed variations were less than 5%.

The carbonaceous content (organic carbon (OC), elemental carbon (EC)) of particulate matter was measured with a homemade thermal–optical system, based on the thermal desorption/oxidation of particulate carbon to CO₂, which is subsequently analysed by non-dispersive infrared (NDIR) CO₂ analyser. Controlled heating in anoxic conditions was performed to separate OC into two fractions of increasing volatility. The first fraction corresponds to the volatilization at $T < 200$ °C of lower molecular weight organics (OC₁). The second fraction is related to decomposition and oxidation of higher molecular weight species at temperatures ranging from 150 to 600 °C (OC₂). The last fraction of OC is identified by transmittance and corresponds to pyrolysed organic carbon (PC) produced in the previous heating steps. Separation between OC and EC was achieved by initially heating the filter punches under an inert atmosphere to evaporate first the OC fraction. The remaining fraction is sequentially evaporated/burnt under a gas flow containing O₂. This last carbon fraction contains initial EC plus OC that has pyrolysed during heating under an inert atmosphere. The interference between PC and EC can be controlled by continuous evaluation of the blackening of filter using a laser beam and a photodetector measuring the filter light transmittance. The carbonate fraction was determined by sample acidification with phosphoric acid (H₃PO₄). The filter punches were dropped into the concentrated acid and the carrier gas brought the released CO₂ to the carbon analyser (Pio et al., 2011).

The PM₁₀ composite samples were subjected to detailed organic analysis by gas chromatography–mass spectrometry (GC–MS). The combined portions of the filters were consecutively extracted with dichloromethane and methanol (Fisher Scientific) and the total organic extract was separated into five different organic fractions by flash chromatography with silica gel and different solvents of increasing polarity. After elution, the different fractions were vacuum concentrated and evaporated by ultra-pure nitrogen stream. The detailed description of the methodology for the organic compounds extraction can be found in Alves et al. (2011). The fractionated extracts were analysed with a Gas Chromatography model 6890, quadrupole Mass Spectrometry Detector 5973 from Hewlett Packard and with a Gas Chromatography Trace Ultra, quadrupole DSO II from Thermo Scientific. Before injection, the compounds with hydroxylic groups were converted into the corresponding trimethylsilyl derivatives by addition of N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA): trimethylchlorosilane (TMCS) 99:1 (Supelco). Fatty acids were derivatised by methylation/esterification using a BF₃(10%)/methanol complex. The GC–MS calibration was performed with injection of about 110 standards in different concentration ranges and relative response factors calculated for each compound and for each organic class. For those with no authentic standards available, relative response factors were calculated as an average of the relative response factors from the overall homologous series or from compounds of similar chemical structure and retention time. Standards and samples were both co-injected with one internal standard: Tetracosane-d₅₀ (Sigma–Aldrich). Compounds identification was based on comparison of resulting spectra with mass spectra libraries (Wiley 275 and NIST MS Search 2.0), co-injection with authentic standards and analysis of fragmentation patterns. The quantitative analysis was performed by both single ion monitoring (SIM) and total ion chromatogram (TIC) methods, in two separate GC runs. Anhydrosugars (levoglucosan, mannosan and galactosan) were analysed by high performance anion-exchange chromatography (HPAEC) with

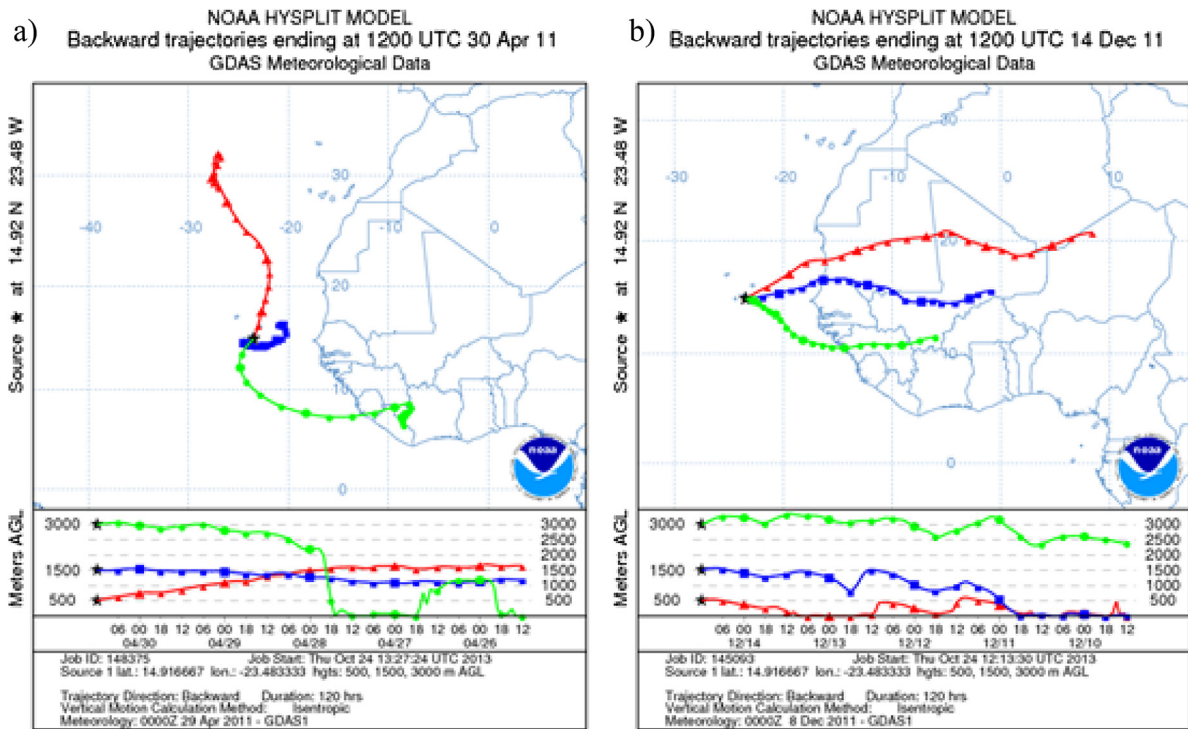


Fig. 1. HYSPLIT model backward trajectories arriving at Praia city area, Santiago Island.

electrospray ionisation–mass spectrometry (ESI–MS) detection. The detailed description of the extraction and analytical procedures can be found elsewhere (Saarnio et al., 2010).

Quantitative data for the identified compounds in the field filter blanks were obtained in the same way as for samples, and blank levels were subtracted from the samples in order to obtain blank-corrected results.

3. Results and discussion

3.1. Climatic conditions and backward trajectory analysis

The Cape Verde archipelago is located in the sub-Saharan region with an arid or semi-arid climate. The temperature is moderated by the ocean action and the trade winds. The temperature, relative humidity and precipitation mean values obtained during the sampling campaign were 24.4 °C, 73.5% and 151 mm, respectively. August (51 mm) and October (82 mm) were the rainiest months. In the dry season, from December to March, the area is subject to northeasterly trade winds, locally called “Harmattan” carrying the Sahara mineral dust to long distances.

The Sahara dust influence can be observed in the backward trajectories calculated using the HYSPLIT transport and dispersion model and READY (Draxler and Rolph, 2013). Fig. 1 shows two different frequent situations. Samples collected between the end of November and the beginning of March were related to air mass outflow from or linked to the African continent, especially through the Saharan and Sahel corridor (Fig. 1b). On the other months, samples were more dominated by Atlantic air conditions, sometimes with regional recirculation (Fig. 1a).

3.2. Aerosol mass and carbonaceous content

The PM₁₀ measured concentrations varied between 20.5 and 370 µg/m³. Higher values (CV2 – 370 µg/m³; CV18 – 261 µg/m³)

correspond to periods of the year with the greatest dust outflow from the Sahara region (Fig. 2). In the remaining months, the average concentration was 42.2 µg/m³. This value can be considered as the local background. In the Eastern Atlantic off West Africa dust concentrations from 2.0 µg/m³ to 60.0 µg/m³ have been described, though in some events airborne dust levels may reach as high as 13,735 µg/m³ (Goudie and Middleton, 2006 and references therein). In Canary Islands, daily PM₁₀ concentrations during Saharan dust events can reach up to 1000 µg/m³, which contrasts with a regional background value of only 19 µg/m³ (Querol et al., 2004). A more recent study made in Canary Islands determined one of the highest peaks of African dust of recent times, 5586 µg/m³ in 2002 (Gelado-Caballero et al., 2012). In the Azorean archipelago PM_{2.5} concentrations ranging from 5 to 86 µg/m³, with an average concentration of 21.4 µg/m³, have been described (Alves et al., 2007). The PM₁₀ average concentration measured during the

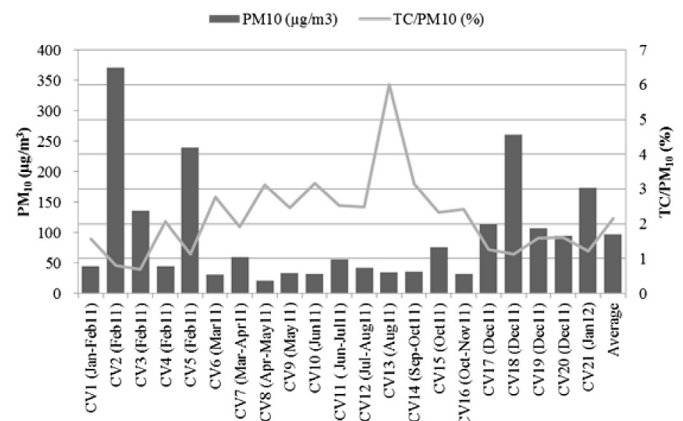


Fig. 2. Variation of aerosol mass and percentage of total carbon in PM₁₀.

sampling period was $97.1 \mu\text{g}/\text{m}^3$. This means that the concentration of particulate matter throughout the year is most often higher than the different limits set by different environmental and health organisations: $20 \mu\text{g}/\text{m}^3$ established by World Health Organization (2000), $40 \mu\text{g}/\text{m}^3$ defined by the European Directive (2008/50/EU) and $50 \mu\text{g}/\text{m}^3$ determined by U.S. Environmental Protection Agency (2008).

The carbonaceous content of PM_{10} was very low. The OC and EC represented, on average, 1.76% and 0.41% of the aerosol mass, respectively, suggesting that most of it is of mineral origin. The OC content varied between 0.50 and $3.0 \mu\text{g}/\text{m}^3$, with an average of $1.29 \mu\text{g}/\text{m}^3$. The OC concentration was higher during the dust episodes (CV2 and CV5; CV17 to CV21) (Fig. 2). The EC content presented values between almost undetectable and $0.74 \mu\text{g}/\text{m}^3$, averaging $0.17 \mu\text{g}/\text{m}^3$. The OC and EC levels are comparable to those obtained by Querol et al. (2013) in Izaña, in the Canary Islands. In this remote site, the OC and EC annual average concentrations ranged from 1.1 to $1.6 \mu\text{g}/\text{m}^3$ and from 0.07 to $0.13 \mu\text{g}/\text{m}^3$, respectively. On the other hand, the carbonaceous content is higher than those registered by Alves et al. (2007) in Terceira Island, North-Eastern Atlantic. The OC and EC average concentrations observed in the Azorean Island were $0.33 \pm 0.26 \mu\text{g}/\text{m}^3$ and $0.043 \pm 0.029 \mu\text{g}/\text{m}^3$, respectively. In general, the total carbon ($\text{TC} = \text{OC} + \text{EC}$) represented 1–3% of the PM_{10} mass, excepting in August 2011, when the percentage reached 6%. This unusual value coincides with the EC content increase ($0.745 \mu\text{g}/\text{m}^3$), which may be related to local traffic emissions (Fig. 2).

3.3. Particulate matter organic speciation

OC encompasses a large variety of organic compounds, which can be grouped into general compound classes, such as *n*-alkanes, *n*-alkanols, fatty acids, sugars, etc. A description of the organic compounds found in this study is presented in the following paragraphs.

Aliphatic compounds comprised the *n*-alkane homologous series from C_{17} to C_{36} , with a clear preference for molecules with an odd number of carbon atoms and maximising for the homologues $\geq \text{C}_{23}$. The higher molecular weights with an odd carbon number represent typical *n*-alkanes attributable to natural plant waxes (Abas and Simoneit, 1996, 1997; Alves, 2008). The *n*-alkane homologues with the highest concentrations (C_{max}) were C_{29} and C_{27} . The ratio between these two homologues remained approximately constant over the observation period (Table 1), suggesting a constancy in the typology of wax *n*-alkane emissions throughout the year. The *n*-alkane total concentrations varied from 3.77 to $53.2 \text{ ng}/\text{m}^3$, with an average of $12.7 \text{ ng}/\text{m}^3$. The carbon preference index (CPI) for the whole range of *n*-alkanes oscillated from 0.93 to 2.07 (Fig. 3). CPI values close to unity denote the input of *n*-alkanes from anthropogenic activities, for example, derived from petroleum

products or from the incomplete combustion of fossil fuels. On the other hand, values greater than 3 indicate that the *n*-alkanes are predominantly from biological materials. An average CPI value of 1.29 clearly reveals that the anthropogenic inputs superimposed the biogenic contributions. The highest CPI value (2.07) was obtained for the CV4 sample set, when the wax contributions were at their maximum and the bacterial/algal inputs were the lowest. The *n*-alkane content was higher than those registered by Alves et al. (2007) in Azores, who presented values from 0.30 to $6.18 \text{ ng}/\text{m}^3$, with an average of $1.11 \text{ ng}/\text{m}^3$, but smaller than the average concentrations determined by Ladji et al. (2010) in Algerian Sahara desert dusts ($66 \pm 32 \text{ ng}/\text{m}^3$). With respect to *n*-alkanes, it was not observed any well-marked seasonality. Two batches of samples are noteworthy for having concentrations substantially higher than the others (CV2 and CV14). These peaks are likely of local anthropogenic origin, since they correspond to the minimum values of the global CPI.

From the analysis of *n*-alkanes in samples collected in a cruise, Schefuß et al. (2003) asserted that the distribution of the CPI values along the African coast indicates a potential explanation for their variations. Lowest CPI values were found off the arid regions, the Sahara and Sahel, and off the coast of Gabon, areas that are sparsely vegetated. Highest CPI values were found off the tropical rainforest regions. According to the authors, this suggests that the *n*-alkane distributions are sensitive to the contribution of fossil fuel- or marine-derived compounds when the fluxes of the plant waxes are low due to a low vegetation density in the source regions.

The *n*-alkanols series ranged mainly from C_{12} to C_{30} , maximising at C_{19} and C_{17} . The distributions are characterised by an odd carbon number predominance. The global CPI for *n*-alkanols ranged from 1.37 to 6.14 (average = 3.46), presenting a distribution that seems directly related to the Saharan dust influxes. In fact, the lowest *n*-alkanols concentrations and the highest CPI values (whole range) were registered in the sets of filters collected during Saharan dust influxes (CV18 to CV21). In the remaining composite samples, collected in periods without dust influxes (except CV2 and CV5), the CPI values were low, ranging from 0.115 to 0.722 , with an average of 0.379 (Fig. 4). This distribution showed a significant biogenic contribution whether from microbial origin or from epicuticular plants during African dust outbreaks. Griffin et al. (2003) and Kellogg et al. (2004) have identified up to 120 bacteria types in African dust, some of which are of direct concern to human health. The total concentrations of *n*-alkanols varied from 1.63 to $138 \text{ ng}/\text{m}^3$, with an average of $18.2 \text{ ng}/\text{m}^3$. Once again, the concentrations obtained in this study are higher than those observed in Terceira Island (0.75 – $18.6 \text{ ng}/\text{m}^3$) (Alves et al., 2007). The ratios of *n*-alkanols $> \text{C}_{20}$ to those $\leq \text{C}_{20}$ and to *n*-alkanes $\geq \text{C}_{25}$ are given in Table 1. The homologues $\leq \text{C}_{20}$ are not found in fresh vascular plant waxes and may have a microbial origin. The homologues $> \text{C}_{20}$ may derive from epicuticular vegetation (Abas and Simoneit, 1996, 1997). During the Saharan dust episodes, an increase in the relative proportions of *n*-alkanols associated with epicuticular plant waxes was observed.

Fatty acids constitute another group of solvent-extractable compounds present in the Cape Verde aerosol samples. The distribution of *n*-fatty acids (C_9 – C_{29}) is characterised by an odd carbon number predominance, carbon maximum at C_{17} and carbon minimum at C_{10} . The CPI (whole range) showed a constant distribution with values always below 1. The total concentrations of *n*-fatty acids varied from 0.011 to $4.51 \text{ ng}/\text{m}^3$, with an average of 0.784 (Fig. 5). As regards to saturated acids, the concentrations obtained in this study are lower than those observed in Terceira Island (0.42 – $86.56 \text{ ng}/\text{m}^3$) (Alves et al., 2007) and in Algerian Sahara desert dusts ($80 \pm 39 \text{ ng}/\text{m}^3$) (Ladji et al., 2010). This group of compounds showed the dominance of *n*-carboxylic acids $< \text{C}_{20}$,

Table 1
Ratios calculated with same homologous compound series.

	Ratios	Range	Average
Without Sahara/Sahel dust influxes	<i>n</i> -alkanes $\text{C}_{29}/(\text{C}_{29} + \text{C}_{27})$	0.454–0.685	0.559
	<i>n</i> -alkanols $> \text{C}_{20}/\leq \text{C}_{20}$	0.120–0.464	0.325
	<i>n</i> -alkanols $\geq \text{C}_{20}/\text{n-alkanes} \geq \text{C}_{25}$	0.010–1.13	0.474
	<i>n</i> -carboxylic acids $> \text{C}_{22}/\leq \text{C}_{20}$	0.041–0.200	0.128
	C18:0/C18:1	0.093–0.395	0.243
	C18:0/C18:2	0.615–0.918	0.724
With Sahara/Sahel dust influxes	<i>n</i> -alkanols $> \text{C}_{20}/\leq \text{C}_{20}$	0.794–1.33	1.03
	<i>n</i> -alkanols $\geq \text{C}_{20}/\text{n-alkanes} \geq \text{C}_{25}$	1.08–1.40	1.27
	<i>n</i> -carboxylic acids $> \text{C}_{22}/\leq \text{C}_{20}$	0.264–0.508	0.333
	C18:0/C18:1	0.302–0.522	0.445
	C18:0/C18:2	0.953–2.24	1.48

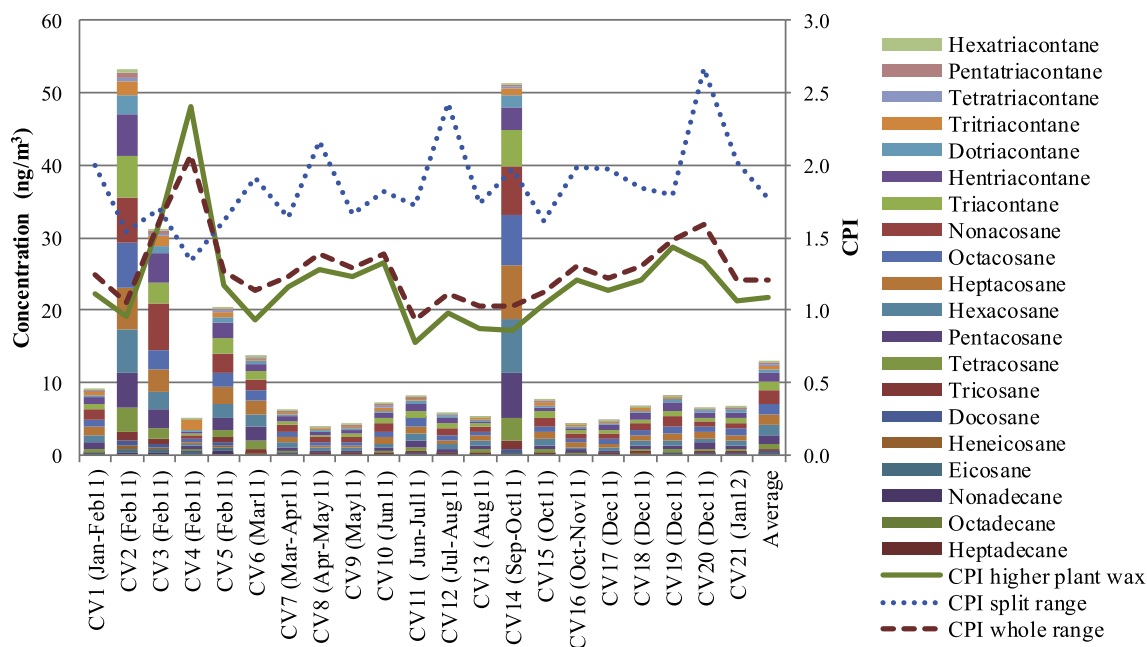


Fig. 3. Temporal variation of concentration of n-alkanes and CPI indexes.

with ratios $>C_{22}/<C_{22}$ under 1 (Table 1). The homologues $<C_{20}$ may represent a microbial component (Alves, 2008) or, taking into account the oceanic characteristics of the sampling site, are more probably derived from marine phytoplankton (Kawamura et al., 2003).

In addition to *n*-alkanoic acids, *n*-alkenoic acids, such as palmitoleic (C16:1), oleic (C18:1) and linoleic (C18:2) acids, were also detected in the aerosol samples. These unsaturated fatty acids are common in phytoplankton and bacteria (Rogge et al., 1993; Simoneit et al., 2004). Due to their nature, these compounds are

rather unstable in the atmosphere and are often used as an indication of the age of aerosols. Their presence in the aerosol suggests recent biogenesis (Abas and Simoneit, 1996). The ratio between the concentration of the saturated C₁₈ alkanolic acid (C18:0) and the unsaturated C₁₈ alkenolic acid (C18:1) is frequently used, since the unsaturated acid breaks down much faster by atmospheric oxidation than the saturated analogue. The ratio C18:0/C18:1 obtained in this study (Table 1) ranged from 0.302 to 0.522, with an average of 0.445, during dust influxes from Sahara. In the remaining sampling periods, values were lower. The C18:0/C18:2 ranged from 0.953 to

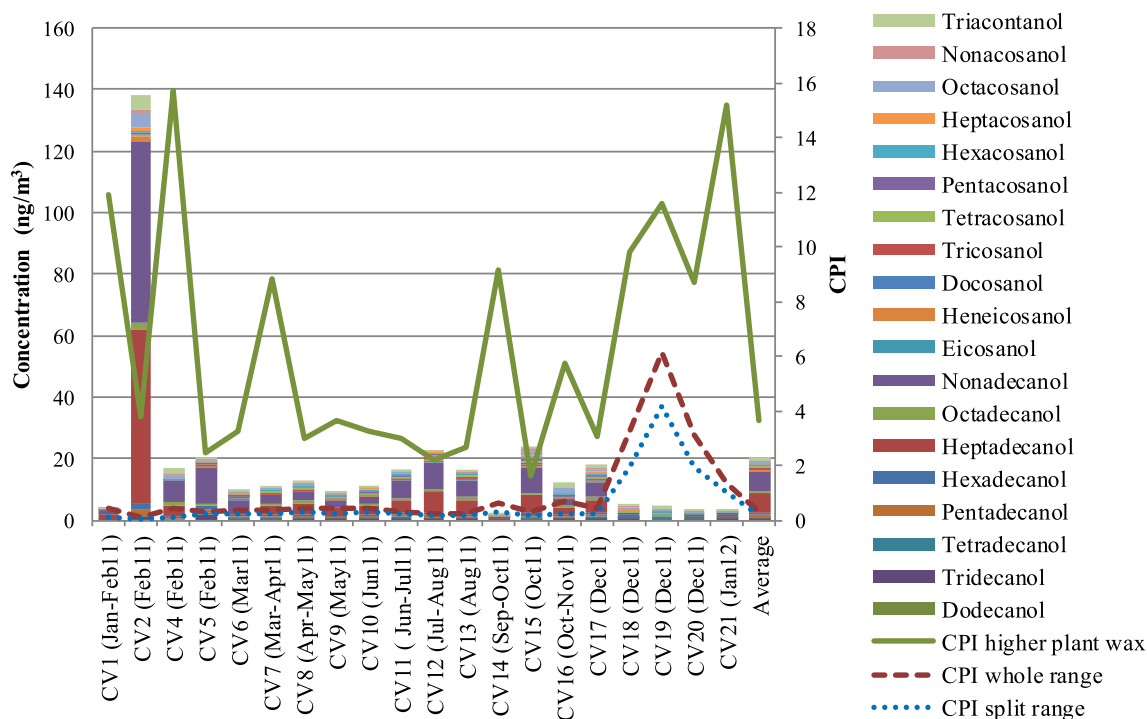


Fig. 4. Temporal variation of concentration of n-alkanols and CPI indexes.

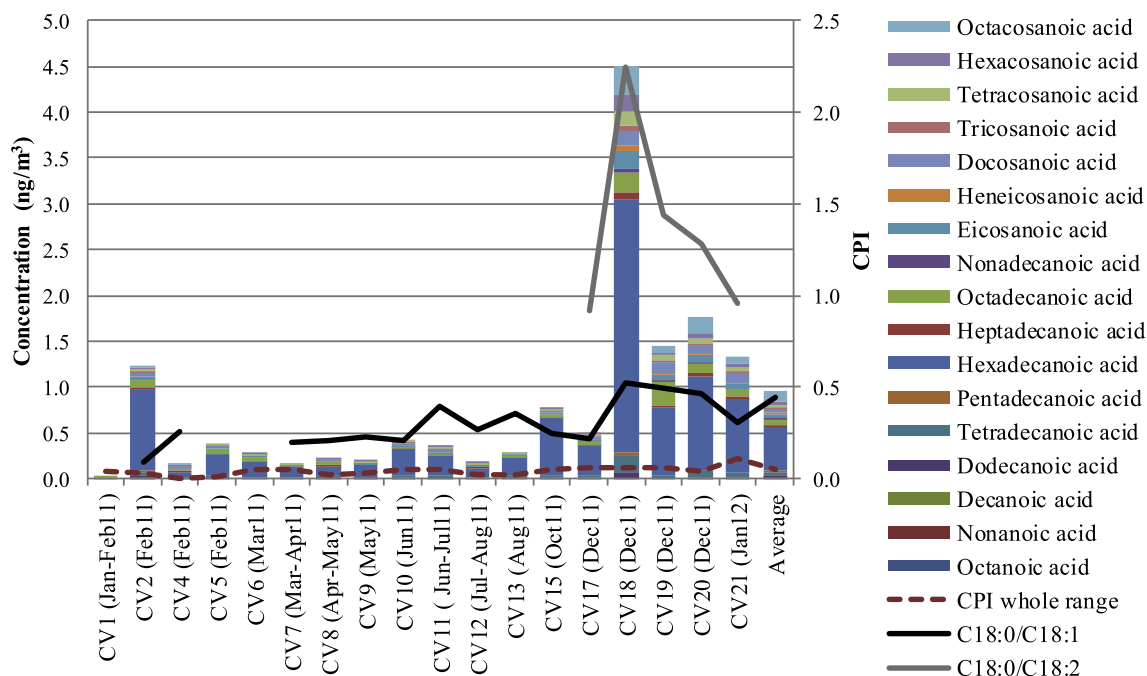


Fig. 5. Temporal variation of concentration of *n*-alkanoic acids and CPI indexes.

2.24, with an average of 1.48 during Sahara dust influxes, showing the same trend of the previous ratio for the remaining periods. The lower content obtained during the periods of long-range transport from Africa indicated a more aged and processed aerosol, in which the unsaturated compounds have suffered oxidative or breakdown reactions.

The *n*-alkanedioic acids are also present in these samples. The series ranged from C₈ to C₁₅, maximising at C₁₁. The total concentration varied from 0.0278 to 0.951 ng/m³, with an average of 0.369 ng/m³. These compounds may have different origins. They could be oxidation products from polypeptides, nucleic acid or

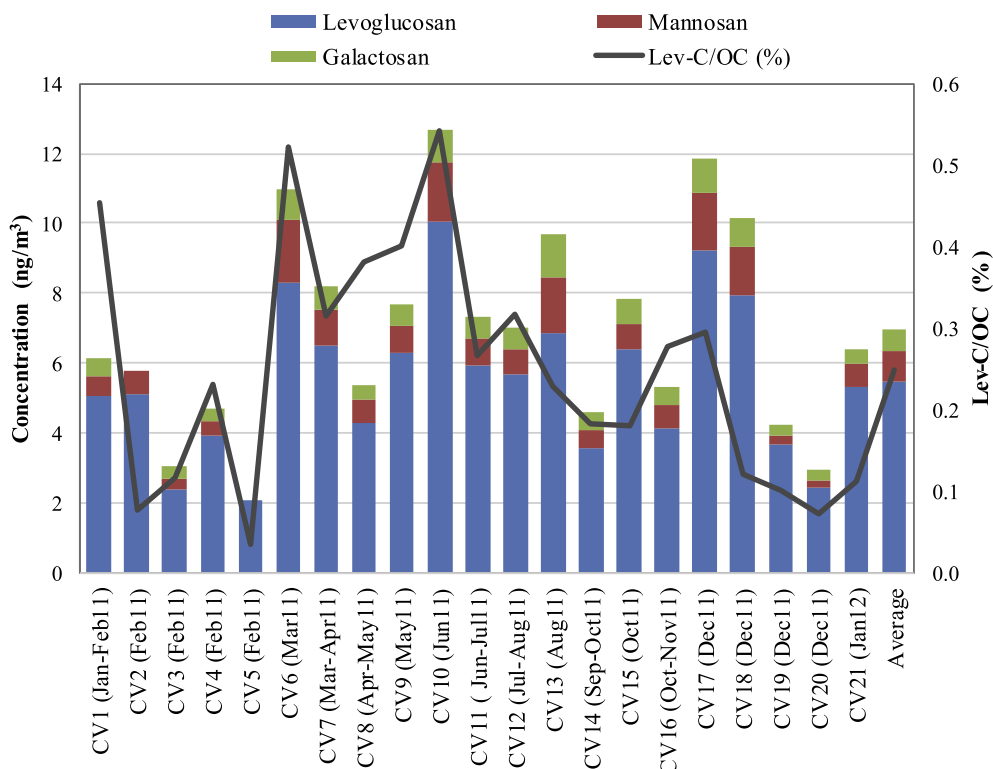


Fig. 6. Temporal variation of concentration of monosaccharide anhydrides and Lev-C/OC (%) ratio. The conversion factor for levoglucosan-C = levoglucosan*0.444.

other lipid components or incomplete combustion products (Alves, 2008).

The monosaccharide anhydrides (MAs) (levoglucosan, mannosan and galactosan) are organic compounds widely used as biomass burning markers (Simoneit et al., 1999). They were detected in all samples at concentrations ranging from 2.06 to 12.7 ng/m³, with an average of 6.86 ng/m³ (Fig. 6). Levoglucosan represented, on average, 81% of the total concentrations of the 3 isomers. The levoglucosan concentration varied from 2.06 to 10.0 ng/m³, averaging of 5.47 ng/m³. Concentrations from around 0.2 to 1.3 ng/m³ and from 0.3 to 19.2 ng/m³ have been observed in North Pacific marine/remote areas (Kesselmeier et al., 2009) and in Azores, Portugal (Puxbaum et al., 2007). In general, the levoglucosan-C (Lev-C = levoglucosan*0.444) represented only 0.1–0.3% of the OC mass, excepting in March (CV6) and June (CV10), when the percentage reached 0.5%. These higher values may be related to biomass burning periods with greater local influence (Fig. 6). According to Puxbaum et al. (2007), the contribution of Lev-C to OC for Azores Islands varied between 0.04% and 3.71% with an average of 0.89%. The levoglucosan-to-mannosan (L/M) ratio has been used to distinguish different biomass burning sources (Schmidl et al., 2008). In this study, the L/M ratio was in the range of 4.27–14.2, averaging 7.56. These values indicate that the burned species belong to the softwood group, which is in agreement with the typical savanna species observed in the Santiago Island.

4. Conclusion

In this study, a long-term organic characterisation of the aerosol off the coast of northwest Africa was performed for the first time. The organic compounds found in particulate matter could be conducive to source apportionment studies and will contribute to the improvement of emission inventories in the Saharan/sub-Saharan region, overcoming the existing lack of information.

An increase in PM₁₀ concentration was observed between the end of November and the beginning of March. This event was related to air mass outflow from or linked to the African continent, especially through the Saharan and Sahel corridor. The particulate matter concentration throughout the year was frequently higher than the limits set by different environmental and health organisations. This raises concerns about the people's health who are constantly exposed to these air conditions.

The PM₁₀ carbonaceous content was very low. Due to local characteristics, most of the aerosol mass had mineral origin. As observed for PM₁₀, the OC concentration was higher during the dust influxes from the African continent. Taking into account the predominant wind direction, the abnormally high value of TC observed in August could be justified with the increase of EC emissions from local traffic.

The organic compounds found in the particulate material can contribute to a better source apportionment. With respect to *n*-alkanes, it was not observed any well-marked seasonality. In general, *n*-alkanes are likely of local anthropogenic origin, as suggested by the low values of CPI. The *n*-alkanol distributions showed a significant biogenic contribution whether from microbial origin or from epicuticular plants during African dust outbreaks. The *n*-alkanoic acids were probably derived from marine phytoplankton. The low content of *n*-alkenoic acids during dust influxes periods was indicative of aging and processing of the aerosol during long-distance transport. The presence of levoglucosan and its isomers denotes some local influence from biomass burning.

Acknowledgements

Cátia Gonçalves acknowledges: the postdoc grant SFRH/BPD/77019/2011; the "Atmospheric aerosol in Cape Verde region:

Seasonal evaluation of composition sources and transport (CV-Dust)" project, PTDC/AAC-CLI/100331/2008, both funded by the Portuguese Science Foundation (FCT) and the PEst-C/MAR/LA0017/2013.

References

- Abas, M.R.B., Simoneit, B.R.T., 1997. Gas chromatographic and gas chromatographic-mass spectrometric characterization of biogenic and petrogenic organic matter in the atmosphere. *The Malaysian Journal of Analytical Sciences* 3, 9–23.
- Abas, M.R.B., Simoneit, B.R.T., 1996. Composition of extractable organic matter of air particles from Malaysia: initial study. *Atmospheric Environment* 15, 2779–2793. [http://dx.doi.org/10.1016/1352-2310\(95\)00336-3](http://dx.doi.org/10.1016/1352-2310(95)00336-3).
- Alves, C.A., Vicente, A., Monteiro, C., Gonçalves, C., Evtugina, M., Pio, C., 2011. Emission of trace gases and organic components in smoke particles from a wildfire in a mixed-evergreen forest in Portugal. *Science of the Total Environment* 409, 1466–1475. <http://dx.doi.org/10.1016/j.scitotenv.2010.12.025>.
- Alves, C.A., 2008. Characterisation of solvent extractable organic constituents in atmospheric particulate matter: an overview. *The Anais da Academia Brasileira de Ciências* 80, 21–82. <http://dx.doi.org/10.1590/S0001-37652008001000003>.
- Alves, C., Oliveira, T., Pio, C., Silvestre, A.J.D., Fialho, P., Barata, F., Legrand, M., 2007. Characterisation of carbonaceous aerosols from the Azorean Island of Terceira. *Atmospheric Environment* 41, 1359–1373. <http://dx.doi.org/10.1016/j.atmosenv.2006.10.022>.
- Ansmann, A., Baars, H., Tesche, M., Müller, D., Althausen, D., Engelmann, R., Pauliquevis, T., Artaxo, P., 2009. Dust and smoke transport from Africa to South America: lidar profiling over Cape Verde and the Amazon rainforest. *Geophysical Research Letters* 36, L11802. <http://dx.doi.org/10.1029/2009GL037923>.
- Ben-Ami, Y., Koren, I., Rudich, Y., Artaxo, P., Martin, S.T., Andreae, M.O., 2010. Transport of North African dust from the Bodélé depression to the Amazon Basin: a case study. *Atmospheric Chemistry and Physics* 10, 7533–7544. <http://dx.doi.org/10.5194/acp-10-7533-2010>.
- Cariñanos, P., Galan, C., Alcazar, P., Dominguez, E., 2004. Analysis of the particles transported with dust-clouds reaching Cordoba, southwestern Spain. *Archives of Environmental Contamination and Toxicology* 46, 141–146. <http://dx.doi.org/10.1007/s00244-003-2273-9>.
- Draxler, R.R., Rolph, G.D., 2013. HYSPLIT (HYbrid Single-particle Lagrangian Integrated Trajectory) Model Access via NOAA ARL READY Website. NOAA Air Resources Laboratory, College Park, MD. <http://www.arl.noaa.gov/HYSPLIT.php>.
- European Parliament and of the Council, 2008. Directive 2008/50/EC on Ambient Air Quality and Cleaner Air for Europe. Available at: <http://eur-lex.europa.eu/>.
- Formenti, P., Schuetz, L., Balkanski, Y., Desboeufs, K., Ebert, M., Kandler, K., Petzold, A., Scheuvs, D., Weinbruch, S., Zhang, D., 2011. Recent progress in understanding physical and chemical properties of mineral dust. *Atmospheric Chemistry and Physics* 11, 8231–8256. http://dx.doi.org/10.1007/978-94-017-3354-0_13.
- Formenti, P., Andreae, M.O., Lange, L., Roberts, G., Cafmeyer, J., Rajta, I., Maenhaut, W., Holben, B.N., Artaxo, P., Lelieveld, J., 2001. Saharan dust in Brazil and Suriname during the Large-Scale Biosphere-Atmosphere Experiment in Amazonia (LBA) – cooperative LBA Regional Experiment (CLAIRE) in March 1998. *Journal of Geophysical Research* 106, 14919–14934. <http://dx.doi.org/10.1029/2000JD900827>.
- Ganor, E., Osetinsky, I., Stupp, A., Alpert, P., 2010. Increasing trend of African dust, over 49 years, in the eastern Mediterranean. *Journal of Geophysical Research* 115, D07201. <http://dx.doi.org/10.1029/2009JD012500>.
- Gelado-Caballero, M., López-García, P., Prieto, S., Patey, M., Collado, C., Hernández-Brito, J., 2012. Long-term aerosol measurements in Grand Canaria, Canary Islands: Particle concentration, sources and elemental composition. *Journal of Geophysical Research* 117, 3304–3319. <http://dx.doi.org/10.1029/2011JD016646>.
- Gillette, D., Hardebeck, E., Parker, J., 1997. Large-scale variability of wind erosion mass flux rates at Owens Lake. 2. Role of roughness change, particle limitation, change of threshold friction velocity, and the Owen effect. *Journal of Geophysical Research* 102, 25989–25998. <http://dx.doi.org/10.1029/97JD00960>.
- Goudie, A., Middleton, N., 2006. *Desert Dust in the Global System*. Springer, Heidelberg, Germany.
- Griffin, D.W., Kellogg, C.A., Garrison, V.H., Lisle, J.T., Borden, T.C., Shinn, E.A., 2003. Atmospheric microbiology in the northern Caribbean during dust events. *Aerobiologia* 19, 143–157. <http://dx.doi.org/10.1023/B:AERO.0000006530.32845.8d>.
- Griffin, D.W., Garrison, V.H., Herman, J.R., Shinn, E.A., 2001. African desert dust in the Caribbean atmosphere: microbiology and public health. *Aerobiologia* 17, 203–213. <http://dx.doi.org/10.1023/A:1011868218901>.
- Hand, V.L., Capes, G., Vaughan, D.J., Formenti, P., Haywood, J.M., Coe, H., 2010. Evidence of internal mixing of African dust and biomass burning particles by individual particle analysis using electron beam techniques. *Journal of Geophysical Research – Atmospheres* 115. <http://dx.doi.org/10.1029/2009jd012938>.
- Kandler, K., Lieke, K., Benker, N., Emmel, C., Küpper, M., Müller-Ebert, D., Ebert, M., Scheuvs, D., Schladitz, A., Schütz, L., Weinbruch, S., 2011. Electron microscopy of particles collected at Praia, Cape Verde, during the Saharan Mineral Dust Experiment: particle chemistry, shape, mixing state and complex refractive index. *Tellus B* 63, 475–496. <http://dx.doi.org/10.1111/j.1600-0889.2011.00550.x>.

- Kawamura, K., Ishimura, Y., Yamazaki, K., 2003. Four years' observations of terrestrial lipid class compounds in marine aerosols from the western North Pacific. *Global Biogeochemical Cycles* 17, 1003. <http://dx.doi.org/10.1029/2001GB001810>.
- Kellogg, C.A., Griffin, D.W., Garrison, V.H., Peak, K.K., Royall, N., Smith, R.R., Shinn, E.A., 2004. Characterization of aerolized bacteria and fungi from desert dust events in Mali, West Africa. *Aerobiology* 20, 99–110. <http://dx.doi.org/10.1023/B:AERO.0000032947.88335.bb>.
- Kesselmeier, J., Guenther, A., Hoffmann, T., Piedade, M.T., Warnke, J., 2009. Natural volatile organic compound emissions from plants and their roles in oxidant balance and particle formation. In: *Amazonia and Global Change*. Geophys. Monogr. Ser., vol. 186. AGU, Washington, D.C., p. 565. <http://dx.doi.org/10.1029/GM186>.
- Ladji, R., Yassaa, N., Balducci, C., Cecinato, A., 2010. Organic components of Algerian desert dusts. *Chemosphere* 81, 925–931. <http://dx.doi.org/10.1016/j.chemosphere.2010.07.059>.
- Liu, Z., Omar, A., Vaughan, M., Hair, J., Kittaka, C., Hu, Y., Powell, K., Trepte, C., Winker, D., Hostetler, C., Ferrare, R., Pierce, R., 2008. CALIPSO lidar observations of the optical properties of Saharan dust: a case study of long-range transport. *Journal of Geophysical Research* 113, D07207. <http://dx.doi.org/10.1029/2007JD008878>.
- Mahowald, N.M., Kloster, S., Engelstaedter, S., Moore, J.K., Mukhopadhyay, S., McConnell, J.R., Albani, S., Doney, S.C., Bhattacharya, A., Curran, M.A.J., Flanner, M.G., Hoffman, F.M., Lawrence, D.M., Lindsay, K., Mayewski, P.A., Neff, J., Rothenberg, D., Thomas, E., Thornton, P.E., Zender, C.S., 2010. Observed 20th century desert dust variability: impact on climate and biogeochemistry. *Atmospheric Chemistry and Physics* 10, 10875–10893. <http://dx.doi.org/10.5194/acp-10-10875-2010>.
- Martin, J., Gordon, R.M., Fitzwater, S.E., 1991. The case for iron. *Limnology and Oceanography* 36, 1793–1802.
- Mauderly, J.L., Chow, J.C., 2008. Health effects of organic aerosols. *Inhalation Toxicology* 20 (3), 257–288. <http://dx.doi.org/10.1080/08958370701866008>.
- Mbourou, G., Bertrand, J., Nicholson, S., 1996. The diurnal and seasonal cycles of wind-borne dust over Africa north of the Equator. *Journal of Applied Meteorology* 36, 868–882. [http://dx.doi.org/10.1175/1520-0450\(1997\)036<0868:TDASCO>2.0.CO;2](http://dx.doi.org/10.1175/1520-0450(1997)036<0868:TDASCO>2.0.CO;2).
- Moulin, C., Lambert, C.E., Dayan, U., Masson, V., Ramonet, M., Bousquet, P., Legrand, M., Balkanski, Y.J., Guelle, W., Marticorena, B., Bergametti, G., Dulac, F., 1998. Satellite climatology of African dust transport in the Mediterranean atmosphere. *Journal of Geophysical Research* 103, 13137–13144. <http://dx.doi.org/10.1029/98JD00171>.
- Müller, D., Heinold, B., Tesche, M., Tegen, I., Althausen, D., Alados Arboledas, L., Amiridis, V., Amodeo, A., Ansmann, A., Balis, D., Comeron, A., D'Amico, G., Gerasopoulos, E., Guerrero-Rascado, J.L., Freudenthaler, V., Giannakaki, E., Heese, B., Iarlori, M., Knippertz, P., Mamouri, R.E., Mona, L., Papayannis, A., Pappalardo, G., Perrone, R.M., Pisani, G., Rizi, V., Sicard, M., Spinelli, N., Tafuro, A., Wiegner, M., 2009. EARLINET observations of the 14–22 May long-range dust transport event during SAMUM 2006: validation of results from dust transport modelling. *Tellus* 61B, 325–339. <http://dx.doi.org/10.1111/j.1600-0889.2008.00400.x>.
- Neff, J., Reynolds, R., Belnap, J., Lamothe, P., 2005. Multi-decadal impacts of grazing on soil physical and biogeochemical properties in southeast Utah. *Ecological Applications* 15, 87–95. <http://dx.doi.org/10.1890/04-0268>.
- Nemirovskaya, I.A., 2006. Organic compounds in the aerosols and surface waters of the East Atlantic. *Oceanology* 46, 348–357. <http://dx.doi.org/10.1134/S0001437006030064>.
- Pio, C., Cerqueira, M., Harrison, R.M., Nunes, T., Mirante, F., Alves, C., Oliveira, C., Campa, A.S.D.L., Artíñano, B., Matos, M., 2011. OC/EC ratio observations in Europe: re-thinking the approach for apportionment between primary and secondary organic carbon. *Atmospheric Environment* 45, 6121–6132. <http://dx.doi.org/10.1016/j.atmosenv.2011.08.045>.
- Prospero, J.M., Ginoux, P., Torres, O., Nicholson, S., 2002. Environmental characterization of global sources of atmospheric soil dust derived from the NIMBUS7 TOMS absorbing aerosol product. *Reviews of Geophysics* 40, 2–1–2–27. <http://dx.doi.org/10.1029/2000RG000095>.
- Prospero, J., 1996. *Saharan Dust Transport over the North Atlantic Ocean and Mediterranean: an Overview*. Kluwer Academic Publishers, The Netherlands, Dordrecht, The Netherlands, pp. 133–151.
- Prospero, J.M., Glaccum, R.A., Nees, R.T., 1981. Atmospheric transport of soil dust from Africa to South America. *Nature* 289, 570–572. <http://dx.doi.org/10.1038/289570a0>.
- Puxbaum, H., Caseiro, A., Sánchez-Ochoa, A., Kasper-Giebl, A., Claeys, M., Gelencsér, A., Legrand, M., Preunkert, S., Pio, C., 2007. Levoglucosan levels at background sites in Europe for assessing the impact of biomass combustion on the European aerosols background. *Journal of Geophysical Research* 112, D23505. <http://dx.doi.org/10.1023/2006JD008114>.
- Querol, X., Alastuey, A., Viana, M., Moreno, T., Reche, C., Minguillón, M.C., Ripoll, A., Pandolfi, M., Amato, F., Karanasiou, A., Pérez, N., Pey, J., Cusack, M., Vázquez, R., Plana, F., Dall'Osto, M., de la Rosa, J., Sánchez de la Campa, A., Fernández-Camacho, R., Rodríguez, S., Pio, C., Alados-Arboledas, L., Titos, G., Artíñano, B., Salvador, P., García Dos Santos, S., Fernández Patier, R., 2013. Variability of carbonaceous aerosols in remote, rural, urban and industrial environments in Spain: implications for air quality policy. *Atmospheric Chemistry and Physics* 13, 6185–6206. <http://dx.doi.org/10.5194/acp-13-6185-2013>.
- Querol, X., Alastuey, A., Rodríguez, S., Viana, M.M., Artíñano, B., Salvador, P., Mantilla, E., García dos Santos, S., Fernández Patier, R., de la Rosa, J., Sanchez de la Campa, A., Menéndez, M., Gil, J.J., 2004. Levels of particulate matter in rural, urban and industrial sites in Spain. *Science of the Total Environment* 334/335, 359–376. <http://dx.doi.org/10.1016/j.scitotenv.2004.04.036>.
- Reheis, M.C., 1997. Dust deposition downwind of Owens (dry) Lake, 1991–1994: preliminary findings. *Journal of Geophysical Research* 102, 25999–26008. <http://dx.doi.org/10.1029/97JD01967>.
- Ridley, D.A., Heald, C.L., Ford, B., 2012. North African dust export and deposition: a satellite and model perspective. *Journal of Geophysical Research Atmospheres* 117, D02202. <http://dx.doi.org/10.1029/2011JD016794>.
- Rogge, W.F., Mazurek, M.A., Hildemann, L.M., Cass, G.R., Simoneit, B.R.T., 1993. Quantification of urban organic aerosols at a molecular level: identification, abundance and seasonal variation. *Atmospheric Environment* 27A, 1309–1330. [http://dx.doi.org/10.1016/0960-1686\(93\)90257-Y](http://dx.doi.org/10.1016/0960-1686(93)90257-Y).
- Saarnio, K., Teinilä, K., Aurela, M., Timonen, H., Hillamo, R., 2010. High-performance anion-exchange chromatography–mass spectrometry method for determination of levoglucosan, mannosan, and galactosan in atmospheric fine particulate matter. *Analytical and Bioanalytical Chemistry* 398 (5), 2253–2264. <http://dx.doi.org/10.1007/s00216-010-4151-4>.
- Schefuß, E., Ratmeyer, V., Stuut, J.B.W., Jansen, J.H.F., Damste, J.S.S., 2003. Carbon isotope analyses of n-alkanes in dust from the lower atmosphere over the central eastern Atlantic. *Geochimica Cosmochimica Acta* 67, 1757. [http://dx.doi.org/10.1016/S0016-7037\(02\)01414-X](http://dx.doi.org/10.1016/S0016-7037(02)01414-X).
- Schmidl, C., Marr, I.L., Caseiro, A., Kotianová, P., Berner, A., Bauer, H., Kasper Giebl, A., Puxbaum, H., 2008. Chemical characterisation of fine particle emissions from wood stove combustion of common woods growing in mid-European Alpine regions. *Atmospheric Environment* 42, 126–141.
- Simoneit, B.R.T., Kobayashi, M., Mochida, M., Kawamura, K., Lee, M., Lim, H.J., Turpin, B.J., Komazaki, Y., 2004. Composition and major sources of organic compounds of aerosols particulate matter sampled during the ACE-Asia campaign. *Journal of Geophysical Research* 109, D19S10. <http://dx.doi.org/10.1029/2004JD004598>.
- Simoneit, B.R.T., Schauer, J.J., Nolte, C.G., Oros, D.R., Elias, V.O., Fraser, M.P., Rogge, W.F., Cass, G.R., 1999. Levoglucosan, a tracer for cellulose in biomass burning and atmospheric particles. *Atmospheric Environment* 33, 173–182. [http://dx.doi.org/10.1016/S1352-2310\(98\)00145-9](http://dx.doi.org/10.1016/S1352-2310(98)00145-9).
- Simoneit, B.R.T., Cardoso, J.N., Robinson, N., 1991. An assessment of terrestrial higher molecular weight compounds in aerosol particulate matter over the South Atlantic from about 30–70°S. *Chemosphere* 23, 447–465.
- Swap, R., Ulanski, S., Cobbett, M., Garstang, M., 1996. Temporal and spatial characteristics of Saharan dust outbreaks. *Journal of Geophysical Research* 101 (D2). <http://dx.doi.org/10.1029/95JD03236>.
- US Environmental Protection Agency, 2008. Clean Air Act. Available at: <https://www.epa.gov>.
- Washington, R., Todd, M., Engelstaedter, S., Mbainayel, S., Mitchell, F., 2006. Dust and the low-level circulation over the Bodélé Depression, Chad: observations from BoDEX 2005. *Journal of Geophysical Research* 111, 1–15. <http://dx.doi.org/10.1029/2005JD006502>.
- Washington, R.M., Todd, C., Middleton, N., Goudie, A.S., 2003. Dust-storm source areas determined by the total ozone monitoring spectrometer and surface observations. *Annals of the Association of American Geographers* 93, 297–313. <http://dx.doi.org/10.1111/1467-8306.9302003>.
- World Health Organization, 2000. *Air Quality Guidelines for Europe*. WHO, Copenhagen. Regional Publications Number 91.