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Carbon isotope analyses of *n*-alkanes in dust from the lower atmosphere over the central eastern Atlantic

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Abstract—Atmospheric dust samples collected along a transect off the West African coast have been investigated for their lipid content and compound-specific stable carbon isotope compositions. The saturated hydrocarbon fractions of the organic solvent extracts consist mainly of long-chain *n*-alkanes derived from epicuticular wax coatings of terrestrial plants. Backward trajectories for each sampling day and location were calculated using a global atmospheric circulation model. The main atmospheric transport took place in the low-level trade-wind layer, except in the southern region, where long-range transport in the mid-troposphere occurred. Changes in the chain length distributions of the *n*-alkane homologous series are probably related to aridity, rather than temperature or vegetation type. The carbon preference of the leaf-wax *n*-alkanes shows significant variation, attributed to a variable contribution of fossil fuel- or marine-derived lipids. The effect of this nonwax contribution on the δ^{13}C values of the two dominant *n*-alkanes in the aerosols, *n*-C_{29} and *n*-C_{31} alkane, is, however, insignificant. Their δ^{13}C values were translated into a percentage of C_4 vs. C_3 plant type contribution, using a two-component mixing equation with isotopic end-member values from the literature. The data indicate that only regions with a predominant C_4 type vegetation, i.e. the Sahara, the Sahel, and Gabon, supply C_4 plant-derived lipids to dust organic matter. The stable carbon isotopic compositions of leaf-wax lipids in aerosols mainly reflect the modern vegetation type along their transport pathway. Wind abrasion of wax particles from leaf surfaces, enhanced by a sandblasting effect, is most probably the dominant process of terrigenous lipid contribution to aerosols. *Copyright © 2003 Elsevier Science Ltd*

1. INTRODUCTION

Atmospheric transport has long been recognized as an important transport mechanism of continental-derived material to the oceans (Darwin, 1846). Observations of dust storms in arid areas of North Africa led to the conclusion that a large portion of marine sediments could be of eolian origin (Radczewski, 1939). Sampling of eolian dust itself has enhanced insight into its characteristics, enabling the assignment of source regions (Chester et al., 1972; Chester and Johnson, 1971).

Organic geochemical analyses of dust led to the recognition of lipids derived from various sources, e.g., terrestrial higher plants, microbial activity, sea spray, vehicle exhaust (Cox et al., 1982; Simoneit, 1977; Simoneit et al., 1977). Homologous series of long-chain *n*-alkanes, *n*-alcohols, and fatty acids are typical lipids found in dust (Cox et al., 1982; Eichmann et al., 1979; Gagosian et al., 1981; Lepple and Brine, 1976; Simoneit et al., 1977) and marine sediments (Bird et al., 1995; Huang et al., 2000; Kuypers et al., 1999; Poynter et al., 1989). These lipids are abundant constituents of terrestrial higher plant epicuticular waxes (Eglinton and Hamilton, 1963), occurring as protective coating on leaves and stems. The wax layer sustains the water balance of the plant under dry conditions (Hall and Jones, 1961). The wax particles are easily sloughed off the surface of the leaves by wind, especially by a sandblasting effect, and can become airborne (Simoneit, 1977). Alternatively, decaying plant organic matter in soils can be lifted during dust storms and transported by wind. Plant-wax lipids are therefore commonly found in dust above remote ocean areas, i.e., the North Pacific (Gagosian and Peltzer, 1986; Gagosian et al., 1981), the South Pacific (Gagosian et al., 1987), the eastern Atlantic (Cox et al., 1982; Lepple and Brine, 1976; Simoneit, 1977; Simoneit et al., 1977; Simoneit et al., 1988), and the western South Atlantic (Simoneit et al., 1991).

The combined occurrence of *n*-alkanes, *n*-alcohols, and fatty acids in aerosol samples is strong evidence for a common terrestrial origin of the leaf-wax compounds (Eglinton and Hamilton, 1963; Kolattukudy, 1980). Occurrence of short-chain fatty acids and *n*-alcohols may indicate an additional marine source, probably introduced to the atmosphere via sea spray (Gagosian et al., 1987; Gagosian et al., 1981; Simoneit, 1977; Simoneit et al., 1991). A major fraction of the fatty acids is present as salts in the aerosol samples (Peltzer and Gagosian, 1987). Oxygenated compounds, like triterpenols and phytosterols, are rapidly altered or degraded during atmospheric transport (Simoneit et al., 1991; Simoneit and Mazurek, 1982). The nonfunctionalized *n*-alkanes, however, are relatively refractory compounds. Therefore, they probably constitute the best biomarkers for terrestrial-derived vegetation waxes in dust. Leaf waxes of terrestrial higher plants contain predominantly odd-numbered *n*-alkanes and even-numbered fatty acids and *n*-alcohols (Eglinton and Hamilton, 1963; Kolattukudy, 1980; Mazurek and Simoneit, 1984; Tulloch, 1976). This is expressed as Carbon Preference Index (CPI, equation given in Table 1; Kolattukudy, 1976). Natural vegetation waxes have high (>5) CPI (Eglinton and Hamilton, 1963; Mazurek and Simoneit,

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Table 1. Locations and distribution parameters of *n*-alkanes of the investigated dust samples.

Sample	Latitude		Longitude		Date	Range[a]	C_{max}[b]	ACL[c]	31/(29 + 31)[d]	CPI[e]
D1	30.44	N	11.72	W	15.2.98	24–35	29	27.6	0.48	2.40
D3	22.89	N	17.44	W	17.2.98	24–35	31	27.6	0.57	2.45
D4	19.74	N	17.91	W	17.2.98	24–35	31	26.9	0.60	2.24
D5	16.00	N	17.93	W	18.2.98	24–35	31	29.2	0.62	3.43
D6	15.29	N	17.92	W	18.2.98	24–35	31	29.3	0.61	4.23
D7	14.70	N	17.92	W	18.2.98	24–35	31	28.8	0.60	3.83
D8	13.93	N	17.92	W	18.2.98	24–33	31	29.1	0.55	4.39
D9	10.44	N	17.19	W	19.2.98	24–35	29	28.7	0.44	3.16
D10	7.26	N	14.19	W	20.2.98	24–33	29	28.8	0.28	5.79
D11	6.29	N	13.09	W	20.2.98	24–35	29	29.2	0.31	7.65
D12	3.71	N	10.23	W	21.2.98	24–33	29	28.8	0.33	5.09
D13	1.30	N	6.94	W	22.2.98	24–35	29	29.0	0.36	4.40
D14	1.32	N	2.86	W	23.2.98	24–31	29	27.0	0.12	3.71
D15	1.52	N	0.60	W	24.2.98	24–35	29	29.2	0.31	5.87
D16	1.76	N	1.64	E	24.2.98	24–35	29	29.2	0.33	5.48
D17	2.61	N	6.54	E	26.2.98	24–35	29	28.8	0.30	4.68
D18	1.68	N	7.97	E	27.2.98	24–33	29	28.4	0.24	6.09
D19	1.74	N	9.14	E	28.2.98	24–35	29	29.1	0.37	4.55
D20	1.65	N	9.11	E	1.3.98	24–33	29	28.7	0.25	5.17
D21	1.38	S	8.54	E	4.3.98	24–35	29	27.7	0.35	2.81
D22	2.91	S	9.21	E	5.3.98	24–31	29	26.0	0.15	3.23
D23	6.18	S	10.05	E	7.3.98	24–35	29	27.5	0.32	3.11
D24	8.00	S	11.86	E	8.3.98	24–35	29	28.8	0.39	4.37
D25	10.69	S	12.50	E	11.3.98	24–35	29	28.5	0.50	3.01

[a] The detected carbon number range of *n*-alkanes

[b] Carbon number of the homologue with highest abundance.

[c] Average chain length = $\Sigma(i{*}X_i)/\Sigma X_i$, where X is abundance and i ranges from 25 to 35.

[d] Ratio of the *n*-C_{31} to the sum of the *n*-C_{29} and *n*-C_{31} alkane.

[e] $\mathrm{CPI}=\frac{1}{2}{*}\Sigma(X_i+X_{i+2}+..+X_n)/\Sigma(X_{i-1}+X_{i+1}+..+X_{n-1})+0.5{*}\Sigma(X_i+X_{i+2}+..+X_n)/\Sigma(X_{i+1}+X_{i+3}+..+X_{n+1})$, with i = 25 and n = 33.

1984), whereas petroleum–derived *n*-alkanes $>C_{23}$, on the other hand, have a lower odd-over-even carbon number predominance (Simoneit, 1984). The distribution of the *n*-alkanes, therefore, enables the recognition of fossil fuel- or marine-derived contributions to the aerosol lipids (Simoneit, 1977). However, no diagnostic features in the terrigenous lipid distributions, thus far, enable the separation of contributions by different plant types (Collister et al., 1994; Eglinton and Hamilton, 1963). The chain-length distribution of *n*-alkanes is thought to be influenced by conditions other than vegetation type, like aridity or growing season-temperature (Cranwell, 1973; Gagosian and Peltzer, 1986; Poynter et al., 1989).

Compound-specific carbon isotope analyses of leaf-wax lipids provide information on the carbon fixation pathway utilized during photosynthesis. *n*-Alkanes from plants using the Calvin-Benson cycle (C_3 plants) have *n*-alkane δ^{13}C-values around –36‰ (−31 to –39‰ vs. Pee Dee belemnite), whereas plants utilizing the Hatch-Slack (or dicarboxylic acid) cycle (C_4 plants) have *n*-alkane δ^{13}C-values around –21.5‰ (−18 to –25‰). The third type, CAM (Crassulacean Acid Metabolism) plants, can use both carbon fixation pathways, so their δ^{13}C-values are intermediate (−25 to –27‰; Collister et al., 1994; O'Leary, 1981; Rieley et al., 1993). Virtually all trees, most shrubs, and cool-season grasses and sedges use the C_3 pathway, whereas C_4 photosynthesis is found in warm-season grasses and sedges. CAM plants include many succulents, such as cacti (Cerling et al., 1993; Spicer, 1989). C_4 plants are thus predominantly found in tropical savannas, temperate grasslands, and semideserts (Cerling et al., 1993). Most African grasslands, like the Sahel and the grass savannas, are presently dominated by C_4 plant vegetation (Collatz et al., 1998). CAM plants do not form a significant part of the West African vegetation (Winter and Smith, 1996). The stable carbon isotope compositions of *n*-alkanes in marine sediments have been used to determine contributions by C_3/C_4 plant type organic material to marine sediments off NW Africa (Bird et al., 1995; Huang et al., 2000; Kuypers et al., 1999). To date, no survey of their distribution and stable carbon isotope composition in dust has been conducted.

Here we present data on lipid distributions and compound-specific stable carbon isotope compositions of 24 aerosol samples collected on a transect from 30°N to 10°S (D1 to D25) along the African west coast in February and March 1998 (Fig. 1). The variations in carbon isotope compositions of the *n*-alkanes are ascribed to varying relative amounts of C_4 plant-derived material in the dust particulate organic matter and are discussed relative to the vegetation zones and climatic conditions on the adjacent continent. These data provide insight into the sources and transport pathways of terrigenous lipid material in dust and the vegetation signal carried out to the ocean.

2. REGIONAL SETTING

The phytogeographical zonation in West Africa shows essentially latitudinal extending belts of vegetation (Fig. 1; White, 1983). In the north, at the Mediterranean Sea, the Mediterranean forest (Med) is dominated by C_3 plants. The transition to the Sahara desert, the Mediterranean–Saharan transitional steppe (MST), is vegetated by a mixed C_3/C_4 plant vegetation. The Sahara desert is sparsely vegetated, and is

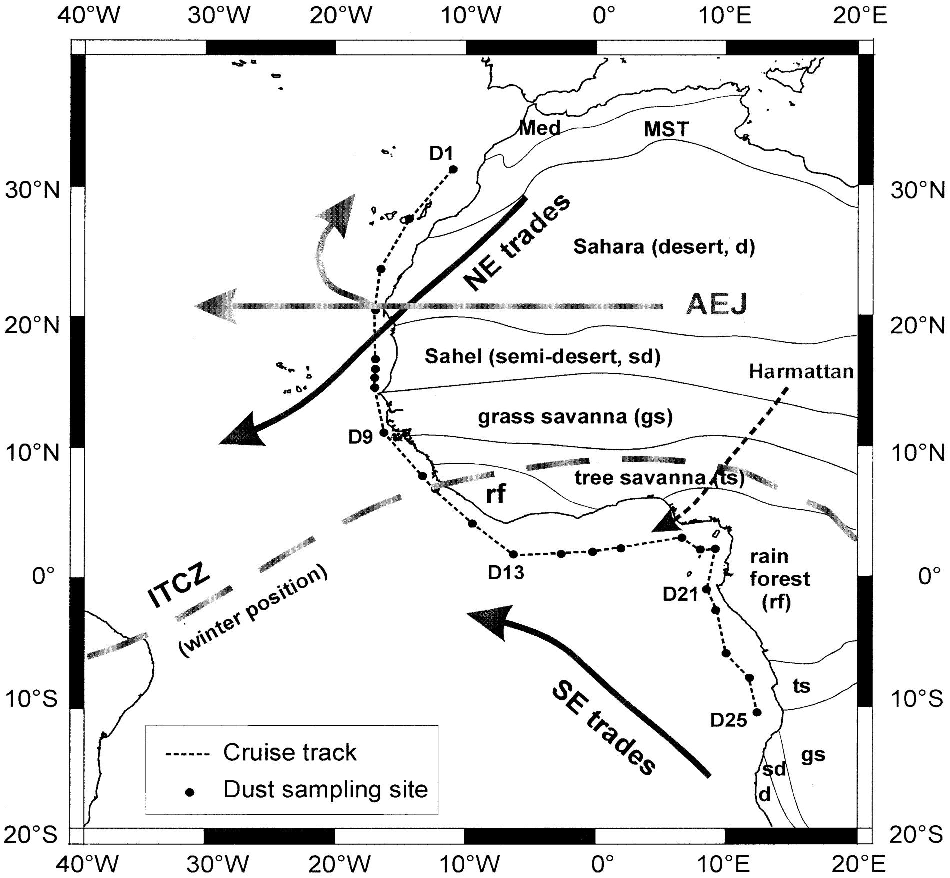

Fig. 1. Ship track and dust sampling sites of *RV Meteor* cruise M41/1 along the West African margin. Phytogeographical zonation of Africa is taken from White (1983): Med = Mediterranean vegetation; MST = Mediterranean–Saharan transition; d = desert; sd = semidesert; gs = grass savanna; ts = tree savanna; rf = rain forest. Major wind systems are drawn after Kalu (1979), Tetzlaff and Wolter (1980), and Sarnthein et al. (1981). Note that samples D19 and D20 were taken at almost the same location.

supplying vast amounts of lithogenic dust to the atmosphere (Chester et al., 1972; Chester and Johnson, 1971; Sarnthein et al., 1981). The satellite picture from the sampling time clearly shows the intense dust outbreaks from the Sahara and Sahel zone and into the Gulf of Guinea during February/March 1998 (Fig. 2). Main dust source areas are dried lake deposits and deflations basins (Gasse et al., 1989). The sparse vegetation is mainly of C_4 plant type. Southwards, the Sahel zone is a semidesert, mainly vegetated by grasses. A main dust source area is the alluvial plain of the Faya Largeau in Chad (Kalu, 1979; Petit-Marie, 1991). Its vegetation consists mainly of C_4 plants. Further south, vegetation belts are formed of grass savanna and tree savanna, containing a mixture of grasslands and semideciduous woodlands. Here, mixed C_3/C_4 plant vegetation occurs. In equatorial Africa, between 10°N and 5°S, tropical rain forest is the dominant vegetation type. It is dominantly of C_3 plant type. South of the tropical rain forest this series of vegetation belts essentially is reversed (White, 1983). From 8°S to 20°S the vegetation consists of transitional dry forest and woodland, intercalated with grass savanna. It is of mixed C_3/C_4 plant type. Along the Atlantic coast to the south stretches a zone of grass-dominated semidesert, which is succeeded by the coastal Namib Desert further southwards. Both desert types are, if at all, vegetated by C_4 plants.

Generally, the Sahara and the Sahel region are the main source regions of eolian transported material over the Atlantic Ocean (Schütz, 1980). During northern hemisphere summer, the main axis of the Saharan dust plume is directed westward at ~20°N, while during winter, associated with the southward migration of the Intertropical Convergence Zone (ITCZ), the main plume axis is located at ~5°N, directed southwards across the equatorial Atlantic (Figs. 1 and 2) (Kalu, 1979; Pye, 1987; Schütz, 1980). Three distinct wind systems are transporting dust from West Africa to the adjacent eastern Atlantic. The shallow (500 to 1500 m) trade wind layer transports dust from the northwestern Sahara in southwestern direction parallel to the coast to the Canary and Cape Verde Islands (Sarnthein et al., 1981). The mid–tropospheric (at ca. 3 km) African Easterly Jet (AEJ) transports dust-laden Saharan air above the trade wind layer across the Atlantic (Prospero and Carlson, 1972). Part of the AEJ is deflected off the African coast to the northwest and then also transports dust to the Canary Islands (Tetzlaff and Wolter, 1980). During winter, when the ITCZ is in its southernmost position, southeasterly cold dry surface

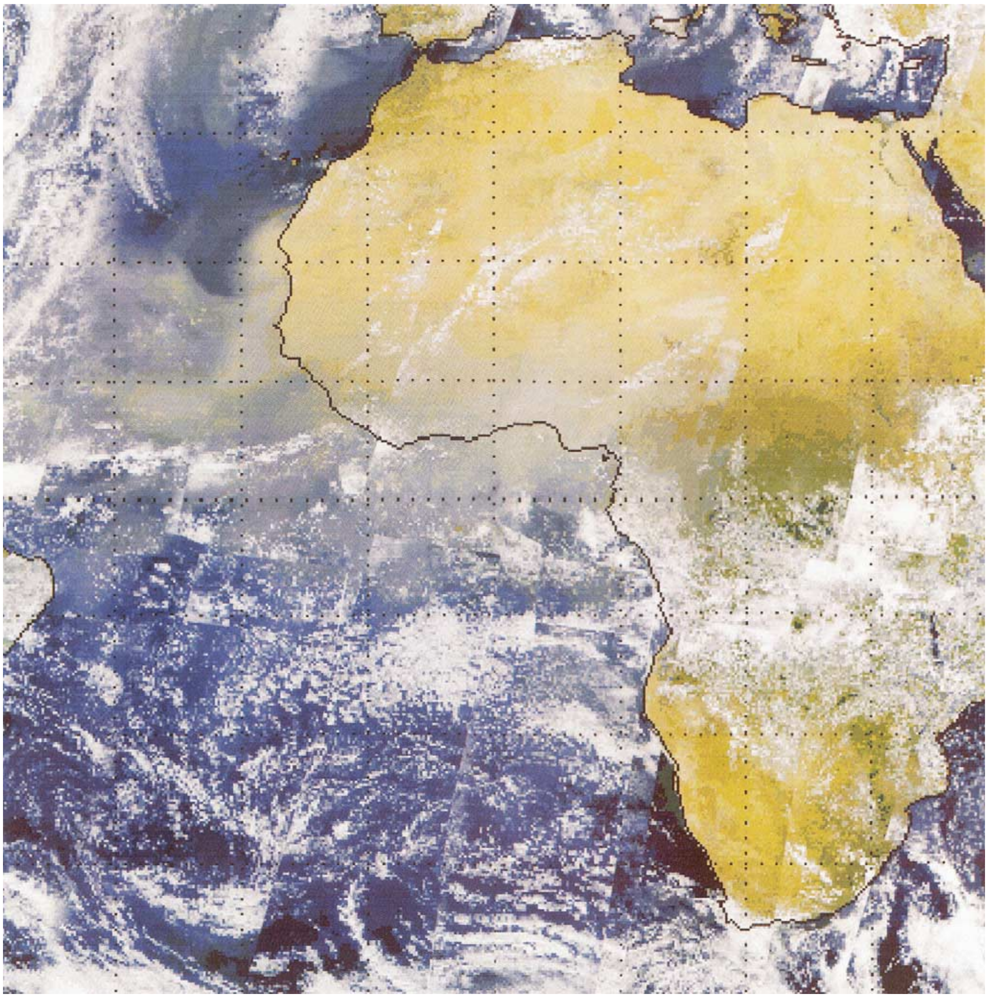

Fig. 2. Quasi-true color satellite composite picture for the sampling period (February–March 1998). Processed by Peer Helmke (University of Bremen).

winds (the Harmattan) transport dust from the Faya Largeau area of Chad southwards into the Gulf of Guinea (Kalu, 1979). Southern Hemisphere trade winds south of the ITCZ blow from southern Africa in northwesterly direction to the equatorial Atlantic (Biscaye et al., 1974; Jansen et al., 1989). Distinct dust outbreaks can be seen in the satellite picture from the sampling time (Fig. 2) off the Sahara and Sahel in NW Africa and in the Gulf of Guinea, there transported by the Harmattan.

3. EXPERIMENTAL

3.1. Samples

Twenty-four eolian dust samples were collected during the *R/V Meteor* cruise M41/1 in February and March 1998 (Schulz et al., 1998). The cruise track stretched from 30°N to 10°S along the African coast (see Fig. 1 for sampling locations). Sampling was conducted with Andersen high-volume particulate matter dust samplers installed on the ship's tower. To avoid contamination of the samples by pollution from the ship's chimney, samples were only collected when the ship was moving and the wind direction was not deviating more than 50° from the direction of the ship's heading. Dust samples for organic analyses were collected on precombusted glass-fiber filters. The filters collect particles >10 μm. After sampling, the filters were wrapped in aluminum foil and stored at –20°C. Procedural blanks have been carried as unopened filters onboard the ship and were analyzed along with the samples. Due to the breakdown of the flow measurement onboard, absolute compound quantifications (in μg m^{-3} air) were not possible.

3.2. Sample Extraction and Compound Isolation

Dust filters were extracted using an ultrasonication disruptor probe and successively less polar solvent mixtures (CH_3OH, CH_3OH/CH_2Cl_2 1:1, CH_2Cl_2), each for 5 min. The extracts were combined, the solvents were removed by rotary evaporation to near dryness at 30°C, and the extracts taken up in CH_2Cl_2 and dried over anhydrous Na_2SO_4. A known amount of standard, perdeutero-*n*-C_{24} alkane, was added and used as reference for quantification of each compound per filter. Saturated hydrocarbon fractions were obtained by column chromatography (activated Al_2O_3) using four column volumes of hexane.

3.3. Gas Chromatography (GC) and GC–Mass Spectrometry (GC-MS)

Analyses were performed on a Hewlett Packard 5890 series II gas chromatograph equipped with an on-column injector and fitted with a fused-silica capillary column (25 m $\times$ 0.32 mm) coated with CP Sil 5 (film thickness 0.12 μm). Helium was used as carrier gas. The GC oven was heated from 70°C to 130°C at 20°C/min, followed by 4°C/min to 320°C (10 min holding time). Effluents were detected using flame ionization (FID). GC–mass spectrometry (GC-MS) was performed using the same type of gas chromatograph and conditions to check compound identifications in selected samples. The chromatographic column was directly inserted into the electron impact ion source of a VG Autospec Ultima mass spectrometer operated with an ionization energy of 70 eV, scanning over a mass range of *m/z* 50 to 800 with a cycle time of 1.8 s. Compound identifications are based on comparison of relative GC retention times and mass spectra published in the literature. Quantification of compounds was performed by peak area integration in FID chromatograms. Data were acquired and integrated using ATLAS analytical software.

3.4. GC–Isotope Ratio Monitoring–MS (GC-irm-MS)

GC–isotope ratio monitoring–MS has been used to measure the carbon isotopic composition of the individual compounds and was described by Hayes et al. (1990). The Hewlett Packard 5890 Series II GC was equipped with a fused silica capillary column (25 m × 0.32 mm) coated with CP-Sil 5 (film thickness 0.12 mm). The carrier gas was helium, and on column injection was applied. The oven-heating program was the same as for GC analyses, except for a longer (30 min) isothermal holding time. CO_2 gas with precalibrated isotopic composition was used as standard. The GC was connected via a combustion interface to a Finnigan Delta C mass-spectrometer. The isotopic compositions of individual compounds were calculated by integration of the mass 44, 45, and 46 ion currents (Merrit et al., 1994). Analyses were done in duplicate or triplicate with standard deviations ($\pm 1\ \sigma$) better than 0.5‰. $\delta^{13}C$ values are expressed vs. Vienna Pee Dee belemnite.

3.5. Trajectory Computations

Four-day backward trajectories were calculated for each sampling location for the specific dates at 850 and 500 hPa barometric levels with a global two-dimensional isobaric model at the Department of Geosciences of Bremen University, based on a model developed at the Norwegian Meteorological Institute (Eliassen, 1976). The wind fields used for trajectory calculation were generated with the ECHAM 3 atmospheric circulation model (Lorenz et al., 1996). The model computes trajectories from zonal and meridional wind components (Petterssen, 1956). Wind data were obtained from the European Center for Medium Range Weather Forecast (ECMWF).

4. RESULTS

4.1. Saturated Hydrocarbon Lipids in Dust Samples

Lipids in the saturated hydrocarbon fractions of the organic solvent extracts of the dust samples are dominated by homologous series of *n*-alkanes (Fig. 3). The *n*-alkanes range in carbon number from *n*-C_{24} to *n*-C_{35} with a predominance of the odd over the even-carbon-numbered homologues. A significant change in the carbon number of the most abundant homologue could be detected. Northern samples, D3 to D8, have the *n*-C_{31} alkane as most abundant homologue, whereas distributions in all other samples are dominated by the *n*-C_{29} alkane. This change is well reflected in the ratio of the *n*-C_{31} to the *n*-C_{29} alkane [31/(29 + 31)], which has maximum values in samples off Senegal around 15°N (Table 1; Fig. 4a). The average chain-length (ACL) does not show a related shift. Significant variation was detected in the carbon preference index (CPI) of the *n*-alkanes series, ranging from 2.40 to 7.65 (Table 1; Fig. 4b). The highest CPI is found in a sample off Liberia (D11), whereas lowest values were detected in samples collected off Morocco (D1 to D4), Senegal (D9), and Gabon (D21 to D23, D25). Distribution parameters of the *n*-alkanes in the investigated dust samples are summarized in Table 1. Additionally, small amounts of $17\alpha,21\beta$(H)-hopanes were detected in all samples. 18(α)-oleanane is present in some samples. In the analytical blanks some minor contaminants were detected, identified as phthalate esters. No *n*-alkanes were detected.

4.2. Stable Carbon Isotopic Compositions of *n*-Alkanes

The stable carbon isotopic compositions of all detected *n*-alkanes (*n*-C_{24} to *n*-C_{35}) in the aerosol samples fall in the range between –25 to –33‰ (Table 2). The odd-numbered *n*-alkanes are relatively more depleted in ^{13}C with increasing chain-length. In general, the *n*-C_{29} or *n*-C_{31} alkanes are the most ^{13}C-depleted compounds in each sample. The longer-chain odd-numbered compounds, *n*-C_{33} and *n*-C_{35}, if present, are isotopically enriched relative to *n*-C_{29} or *n*-C_{31}. The even-numbered *n*-alkanes generally fall into this trend, but show an irregular scatter, which could indicate their higher sensitivity to contamination, due to their low abundance in plant waxes (Eglinton and Hamilton, 1963). The insets in Figure 3 show examples of the stable carbon isotope compositions of *n*-alkanes vs. carbon number.

4.3. Four-day Backward Trajectories

Atmospheric dust transport is known to occur either in the Saharan Air Layer (the African Easterly Jet, Fig. 1) above the trade wind inversion (at pressure levels around 500 hPa), or in the trade wind layer (the NE and SW trades and the Harmattan, at ~850 hPa) below 2 km altitude (Carlson and Prospero, 1972). Recent studies point to the significance of low-level dust transport, particularly for locations of less than 1500 km off the coast (Chiapello et al., 1997), with a direct impact on the Al-, mineral, and grain size distribution of the deep-sea particle inventory and the underlying sediment (Ratmeyer et al., 1999). From the computed backward trajectories (Fig. 5), the dust samples can generally be subdivided into three distinctive groups. Dust material collected in samples D1 to D13, collected off Morocco to the Ivory Coast, was most likely transported in the low-level trade wind layer. Backward trajectories of the midtropospheric 500 hPa level are starting far out over the Atlantic Ocean and are thus not likely to be transport pathways of continental-derived dust. For the dust samples collected in the Gulf of Guinea, D14 to D20, backward trajectories in both pressure levels direct approximately to the same continental source area, the Faya Largeau region in Chad. The southernmost dust sampling sites, D21 to D25, have only short backward trajectories in the trade wind layer, which originate offshore. Only the trajectories in the higher 500 hPa level originate in southern equatorial Africa.

5. DISCUSSION

5.1. Distributions of Plant-wax *n*-Alkanes

It has often been suggested that distributions of vascular plant-wax lipids may potentially be useful for taxonomic purposes. However, despite striking similarities in the *n*-alkane distributions of certain *Crassulaceae* species (Eglinton et al., 1962), such a conclusion is not supported by botanical investigations of plant lipids. Plants of widely divergent families have cuticle waxes of almost the same composition (Eglinton and Hamilton, 1963), whereas plants of the same species show strong variations in their leaf-wax lipid distributions (Borges

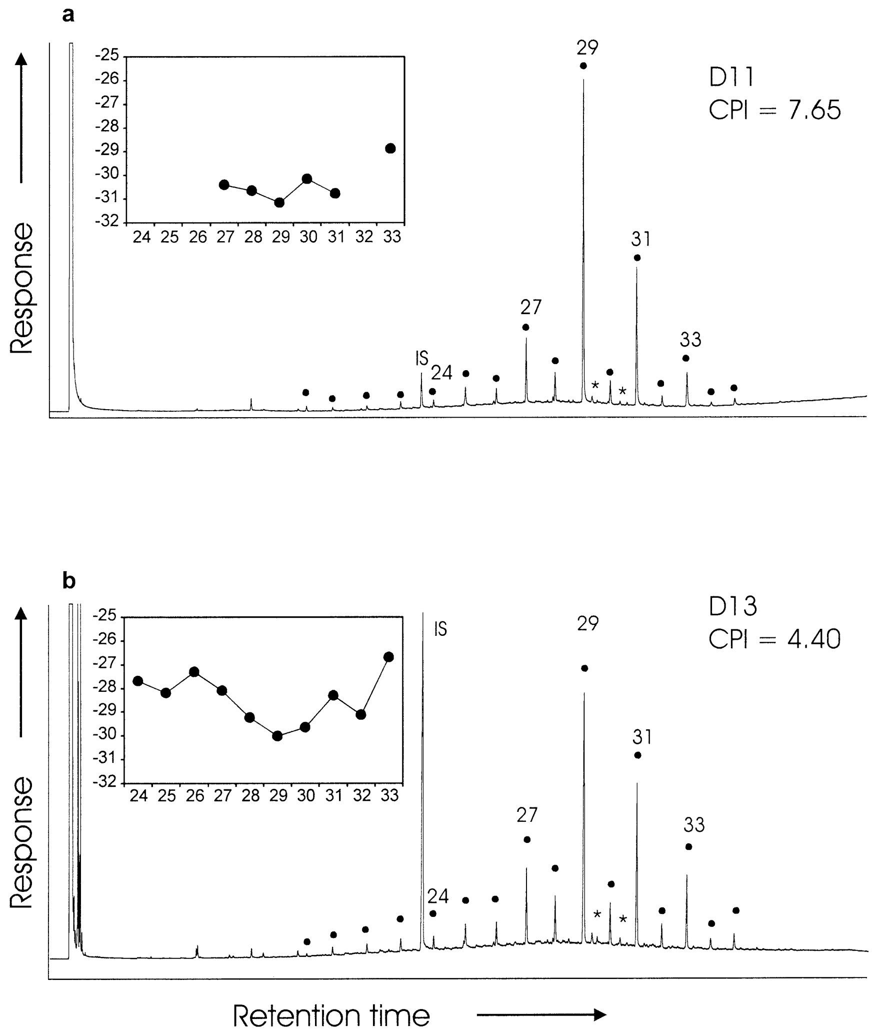

Fig. 3. Gas chromatographic traces of saturated hydrocarbon fractions of organic solvent extracts of aerosol samples with (a) a high and (b) a low CPI (above: D11, CPI = 7.65; below: D13, CPI = 4.40). Dots indicate *n*-alkanes, stars indicate 17α,21β(H)-hopanes. Insets show stable carbon isotopic compositions (in ‰) vs. chain-length of *n*-alkanes.

Del Castillo et al., 1967; Eglinton and Hamilton, 1963). It has been inferred that the *n*-alkane distributions in plant waxes are not sufficiently diagnostic as taxonomic indicators (Borges Del Castillo et al., 1967). Alternatively, the composition of leaf-wax lipids may be strongly dependent on environmental factors due to their biologic functionality to control the water balance of the plant (Hall and Jones, 1961). This may explain the corresponding plant lipid distributions of the *Crassulaceae* species (Eglinton et al., 1962). These species are all adapted to warm and extremely dry climate conditions and all possess substantial amounts of wax coating. All of those investigated species show a strong predominance of the *n*-C_{31} and *n*-C_{33} alkanes with almost negligible amounts of other homologues (Eglinton and Hamilton, 1963).

The *n*-alkanes extracted from the dust samples depict a clear shift in their distribution, with the *n*-C_{31} dominating over the *n*-C_{29} in the northern samples, D3 to D8 (Table 1, Fig. 4a). Changes in the modal chain-length of *n*-alkane distributions in dust samples (Gagosian and Peltzer, 1986; Simoneit et al., 1991; Simoneit et al., 1988) and in sediments (Poynter et al., 1989) have as yet mainly been explained by differences in growing-season temperature of the source regions. It has been assumed that in warmer tropical climates longer-chain compounds are biosynthesized as wax lipids, whereas in cooler temperate regions predominantly shorter chain compounds are produced (Gagosian and Peltzer, 1986). Our data partly contradict this hypothesis. The shift to more *n*-C_{29} dominated *n*-alkanes in dust samples collected off the rain forest areas of equatorial Africa (Fig. 4a) cannot be explained by a decrease in growing-season temperature. However, this region is strongly influenced by a vast moisture influx from the equatorial Atlantic with the monsoon (Leemans and Cramer, 1991). We thus suggest a large influence of the regional precipitation regime on the chain-length distribution of leaf-wax lipids, in accordance with their biologic functionality as regulators of the plant's moisture balance. The chain-length distribution of *n*-alkanes in dust could thus reflect more an aridity—than a temperature—signal.

The CPI of the *n*-alkanes in the dust samples shows a significant variation from 7.65 to 2.40 (Table 1, Fig. 4b).

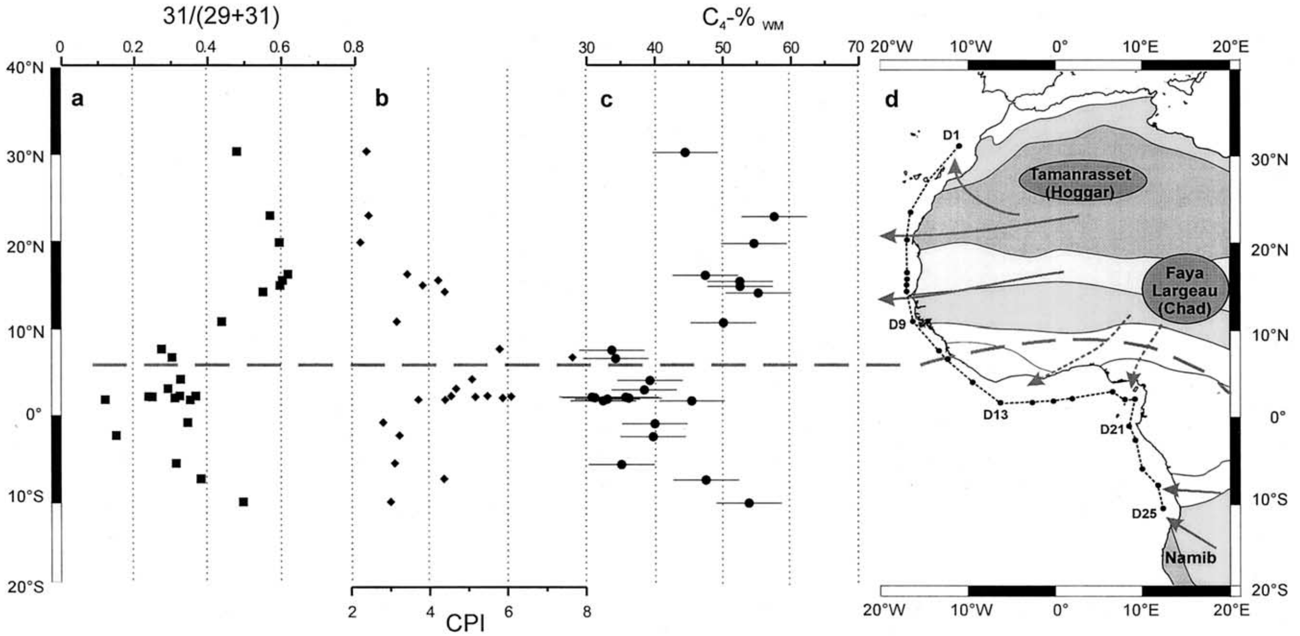

Fig. 4. (a) The variation in the ratio of the two dominant *n*-alkane homologues *n*-C_{31}/(*n*-C_{29} + *n*-C_{31}), (b) the CPI, and (c) the percentage of C_4 plant-derived *n*-alkanes in the aerosol samples vs. latitude. Ship track and sampling sites are shown. Note that sample D2 is missing. (d) Vegetation zones on the continent with mixed C_3/C_4 plant vegetation are light shaded, the Sahara and Namib desert with sparse but predominant C_4 plant vegetation are dark shaded. Major dust source regions and schematic transport pathways are indicated. The gray stippled line indicates the position of the ITCZ.

Contributions of homologous series of *n*-alkanes with a low CPI to the dust in addition to plant waxes with a high (>5) CPI would lower the CPI. The sources of such *n*-alkanes could be vehicle exhaust (Simoneit, 1984), fuel or wood burning (Standley and Simoneit, 1987), or even marine sources (Lichtfouse et al., 1994). Lower temperature fires (e.g., brush fires) essentially steam-distill the vascular plant lipids into the smoke (Simoneit, 1985), while high-temperature fires can result in decrease of the CPI (Standley and Simoneit, 1987). Marine-derived *n*-alkanes can enter the lower atmosphere via sea spray.

The distribution of the CPI values along the coast (Fig. 4b) 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 which are sparsely vegetated. Highest CPI values were found off the tropical rainforest regions. 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. Unfortunately, we cannot support this suggestion with actual flux data due to breakdown of the flux measurement onboard. When, on the other hand, atmospheric transport of plant waxes is presumably high, as in the rainforest regions, the CPI of the *n*-alkanes in the dust remains high.

The contribution of petroleum-derived compounds is confirmed by the presence, albeit in small amounts, of a series of $17\alpha,21\beta$(H)-hopanes in the saturated hydrocarbon fractions (Fig. 3). These compounds are geologically mature compounds and unambiguous fossil biomarkers for petroleum (Ensminger et al., 1974). The same triterpenoids have been previously identified in Harmattan aerosols from Nigeria and urban aerosols from Los Angeles and attributed to the contribution of petroleum residues (Simoneit, 1984; Simoneit et al., 1988). Their occurrence in aerosols was inferred to indicate the adsorption of lubricating oils to dust particulates, as these higher-molecular weight compounds are not constituents of refined gasoline or diesel (Simoneit, 1984). Interestingly, 18(α)-oleanane, identified in some of the investigated dust samples, has earlier been identified as indicator for Nigerian crude oil products in Harmattan aerosols (Simoneit et al., 1988). The petroleum-derived compounds in aerosols could either be derived from the ship itself via contamination of the samples by chimney smoke or derived from fuel-burning processes in urbanized areas along the coast, possibly related to oil production activities. Contamination by the ship itself cannot completely be ruled out, but seems unlikely due to the installed shut-down system of the dust samplers, stopping sampling of aerosols when the ship was not moving or the wind direction was deviating more than 50° from the ship's heading.

5.2. C_4 Plant-derived Wax Lipids in Dust

The detected range of stable carbon isotopic compositions of *n*-alkanes in the aerosol samples ($\delta^{13}C$ = –25 to –33‰) indicates that all the dust lipids consist of varying relative amounts of C_3 and C_4 plant-derived leaf-wax lipids. However, a significant contribution of fossil fuel/marine derived *n*-alkanes might potentially alter the stable carbon isotope compositions of the plant-wax-derived lipids. To estimate whether a potential fossil fuel/marine contribution of *n*-alkanes, detected as a decrease in the CPI, has a significant effect on the stable carbon isotope composition of the dominant *n*-alkane homologues, *n*-C_{29} and

Table 2. Stable carbon isotopic analyses of *n*-alkanes and the calculated C_4 plant-derived percentages in the dust samples.

Sample	$\delta^{13}C_{24}$	$\delta^{13}C_{25}$	$\delta^{13}C_{26}$	$\delta^{13}C_{27}$	$\delta^{13}C_{28}$	$\delta^{13}C_{29}$	$\delta^{13}C_{30}$	$\delta^{13}C_{31}$	$\delta^{13}C_{32}$	$\delta^{13}C_{33}$	$\delta^{13}C_{WM}$[a]	C_4-%[b]	$\delta^{13}C_{29}$ corr.[c]	$\delta^{13}C_{31}$ corr.[c]	$\delta^{13}C_{WM}$ corr.[a]	C_4-% corr.[b]	ΔC_4-%
D1	n.d.	n.d.	n.d.	−28.8	n.d.	−30.1	n.d.	−28.9	n.d.	n.d.	−29.6	44	−30.1	−28.9	−29.5	44	0
D3	n.d.	−27.5	n.d.	−28.1	n.d.	−28.1	n.d.	−27.3	n.d.	−32.4	−27.7	58	−28.1	−27.3	−27.7	58	0
D4	−28.3	−27.2	−27.4	−26.9	−27.7	−28.7	−28.6	−27.7	−28.9	−29.3	−28.1	55	−29.1	−27.5	−28.1	54	1
D5	−27.9	n.d.	−26.9	−27.6	−28.9	−30.1	−28.9	−28.5	−30.7	−27.4	−29.1	47	−30.5	−28.5	−29.3	47	0
D6	−26.8	−32.6	−27.3	−27.4	−28.0	−29.3	−27.4	−27.8	−29.9	−26.0	−28.4	52	−29.6	−27.8	−28.5	51	1
D7	n.d.	−27.1	n.d.	−28.1	n.d.	−29.2	n.d.	−27.9	n.d.	n.d.	−28.4	53	−29.2	−27.9	−28.4	53	0
D8	n.d.	n.d.	−25.2	−27.4	−27.1	−29.1	−27.9	−27.1	n.d.	n.d.	−28.0	55	−29.1	−27.1	−28.0	55	0
D9	n.d.	−29.3	−26.7	−27.7	−29.1	−29.3	n.d.	−28.1	n.d.	−26.6	−28.7	50	−29.3	−28.1	−28.7	50	0
D10	−26.6	n.d.	−28.2	−29.6	−29.8	−31.2	−30.0	−31.0	n.d.	−29.5	−31.1	34	−31.2	−31.5	−31.3	33	1
D11	n.d.	n.d.	n.d.	−30.4	−30.6	−31.2	−30.2	−30.8	n.d.	−28.9	−31.0	34	−31.2	−30.8	−31.0	34	0
D12	−28.6	−28.7	−28.1	−27.6	−28.8	−30.4	−29.0	−30.2	−29.5	−28.8	−30.3	39	−30.4	−30.4	−30.4	39	0
D13	−27.7	−28.2	−27.3	−28.1	−29.3	−30.0	−29.7	−28.3	−29.1	−26.7	−29.4	45	−30.0	−28.4	−29.4	45	0
D14	−26.8	−30.3	−28.6	−29.5	−30.1	−31.5	−28.9	−30.2	n.d.	n.d.	−31.3	32	−31.5	−33.3	−31.7	30	2
D15	−29.3	−29.0	−29.4	−28.9	−29.9	−31.3	−31.2	−31.1	−31.3	−28.7	−31.2	33	−31.3	−31.2	−31.3	33	0
D16	−28.8	n.d.	−28.4	−29.0	−30.3	−31.5	−31.3	−31.7	−31.1	−30.0	−31.5	31	−31.5	−32.0	−31.6	30	1
D17	−27.3	−28.6	−27.4	−28.4	−29.3	−30.4	−29.7	−30.4	n.d.	−29.1	−30.4	38	−30.4	−30.9	−30.6	37	1
D18	−28.1	n.d.	−28.8	−29.0	−29.5	−31.4	−29.0	−31.6	n.d.	−29.5	−31.5	31	−31.4	−32.1	−31.6	30	1
D19	n.d.	n.d.	n.d.	−28.9	−29.8	−31.2	−32.2	−30.2	n.d.	−27.3	−30.8	36	−31.2	−30.2	−30.8	36	0
D20	−28.4	−29.2	−28.3	−28.5	−29.1	−30.9	−28.9	−30.4	−29.9	−27.3	−30.8	36	−30.9	−30.8	−30.9	36	0
D21	n.d.	−27.9	n.d.	−29.7	−32.5	−30.4	n.d.	−29.9	n.d.	−28.2	−30.2	40	−30.4	−29.9	−30.2	40	0
D22	−28.6	−27.6	−30.0	−28.9	−29.7	−30.2	n.d.	n.d.	n.d.	n.d.	−30.2	40	−30.2	n.d.	−30.2	40	0
D23	−27.1	n.d.	−28.9	−29.4	−31.1	−30.9	n.d.	−30.9	n.d.	−29.9	−30.9	35	−31.0	−31.7	−31.2	33	2
D24	−27.4	−28.3	−27.6	−27.9	−28.3	−29.8	−27.8	−28.0	−27.9	−28.9	−29.1	48	−29.8	−28.1	−29.2	47	1
D25	n.d.	n.d.	n.d.	−28.1	−27.5	−29.2	n.d.	−27.2	n.d.	−28.6	−28.2	54	−29.2	−27.2	−28.2	54	0

n.d. = not determined; stable carbon isotope values for *n*-C_{34} and *n*-C_{35} alkanes could only be detected in very few samples, therefore, they have been omitted.

[a] Weighted-mean of the $\delta^{13}C$ values of the *n*-C_{29} and *n*-C_{31} alkane.

[b] Percentage of C_4 plant *n*-alkanes in aerosols, calculated with $\delta^{13}C_{WM}$ and end-member values from the literature (Collister et al., 1994; Rieley et al., 1993).

[c] $\delta^{13}C$ of respective *n*-alkane corrected for fossil fuel-/marine contribution.

n-C_{31} alkane, we applied a mass-balance approach, as described by Huang et al. (2000). We assume that the $\delta^{13}C$ value of the fossil fuel/marine contribution to equal the $\delta^{13}C$ value of the *n*-C_{24} alkane in each sample (Table 2). *n*-C_{24} alkane occurs in most saturated hydrocarbon fractions from the dust samples but is generally absent in plant waxes (Eglinton et al., 1962; Eglinton and Hamilton, 1963; Eglinton and Hamilton, 1967; Tulloch, 1976; Tulloch, 1984). For that purpose, we thus assume that *n*-C_{24} alkane originates from fossil fuel/marine sources in the dust samples. Furthermore we assume for this calculation, that the CPI of fossil fuel/marine-derived *n*-alkanes is 1 and that the CPI of plant waxes, uncontaminated by fossil fuel/marine sources is 7.65, the highest CPI detected in the dust *n*-alkanes (sample D11, Table 1). Both values are assumptions and we are aware that CPI of natural vegetation as well as that of fossil fuel/marine-derived *n*-alkanes can vary significantly in nature. The calculated correction for fossil fuel/marine influence on the $\delta^{13}C$ values is small, $\leq 0.8‰$, with only one exception (3.1‰ for *n*-C_{31} alkane in sample D14; Table 2) due to its relatively low concentration in this sample. If the weighted-average $\delta^{13}C$ value of the *n*-C_{29} alkane and *n*-C_{31} alkane for each sample is calculated and compared with the uncorrected value, only a minor deviation of $\leq 0.4‰$ (Table 2) is detected. The correction of the stable carbon isotope compositions of the dominant plant-wax *n*-alkanes via the CPI is, thus, insignificant and, therefore, not required. This indicates that fossil fuel/marine-derived *n*-alkanes only significantly influence the CPI but not the $\delta^{13}C$ values of the dominant plant-wax compounds.

The weighted-mean uncorrected $\delta^{13}C$ values of the *n*-C_{29}

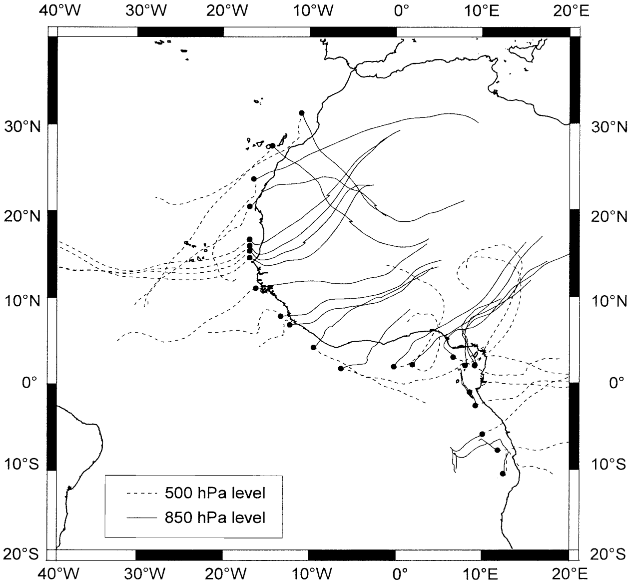

Fig. 5. Four-day atmospheric backward trajectories computed for each sample, for the respective location and time of sampling. Calculated with a global two-dimensional isobaric model at the Department of Geosciences of Bremen University. Shown are trajectories for the 850 hPa (solid lines) and 500 hPa (stippled lines) barometric levels. Wind data were obtained from the European Center for Medium Range Weather Forecast (ECMWF).

alkane and *n*-C_{31} alkane (Table 2) are used to estimate the contribution of *n*-alkanes by C_4 plants using a two-component mixing equation. The end-member values for the mixing equation were taken from stable carbon isotope values of plant lipids reported in the literature: C_4 plant *n*-alkanes = −21.5‰ and C_3 plant *n*-alkanes = −36.0‰ (Collister et al., 1994; Rieley et al., 1993). This results in estimates of C_4 plant contribution varying from 31% to 58% (Table 2, Fig. 4c). A significantly elevated input of C_4 plant-derived wax *n*-alkanes is only found in dust samples collected off the Sahara and the Sahel (samples D3 to D9), as well as off Gabon (samples D24 and D25). Slightly higher input of *n*-alkanes with a C_4 plant-wax signature is found off Morocco and off the Ivory Coast, and to a lesser extent, in the Gulf of Guinea.

Only few compound-specific isotope analyses of leaf-wax lipids in aerosol samples have yet been reported (Huang et al., 2000; Simoneit, 1997). Mean stable carbon isotopic compositions of *n*-alkanes in lipids from Harmattan aerosols from Nigeria vary from –27.7 to –30.9‰, in accordance with a vegetation composite ($\delta^{13}C = -28.9$‰; Simoneit, 1997). This agrees quite well with the $\delta^{13}C$ of the weighted-mean of the *n*-C_{29} and *n*-C_{31} alkanes collected in the dust samples D17 to D20 off Nigeria. *n*-Alkanes in an aerosol sample collected in the eastern equatorial Atlantic (Simoneit, 1977) show an enriched mean stable carbon isotopic composition ($\delta^{13}C = -26.9$‰; Simoneit, 1997), in accordance with their inferred transport via the SW trade winds from SW African grasslands (Simoneit, 1977; Simoneit, 1997). This sample would thus likely be more comparable to the southernmost sample (D25) of our transect ($\delta^{13}C_{wm} = -28.2$‰), which has an inferred origin in the SW African savannas, dominated by C_4 plant vegetation.

There is only a moderate correlation between the weighted-mean $\delta^{13}C$ of the two dominant homologues (*n*-C_{29} and *n*-C_{31} alkane) and the ratio of those compounds [*n*-C_{31}/(*n*-C_{29} + *n*-C_{31})], ($r^2 = 0.69$). This indicates the influence of other factors than photosynthesis type on the chain-length distribution of leaf-wax lipids (see section 5.1). Interestingly, it can be seen from our data that the $\delta^{13}C$ of the *n*-C_{31} alkane is increasingly more depleted than the *n*-C_{29} alkane when the $\delta^{13}C$ of the weighted mean decreases (Table 2). The *n*-alkane isotopic values of C_3 plants usually become depleted with increasing carbon number, whereas C_4 plants produce *n*-alkanes of nearly constant isotopic composition with increasing chain length (Collister et al., 1994; Kuypers et al., 1999). The observed large isotopic difference between the *n*-C_{29} and *n*-C_{31} alkanes in samples D10–D23, thus also indicates a higher contribution of C_3 plant *n*-alkanes to the dust.

5.3. Transport Trajectories and Vegetation Sources

The ITCZ is the thermal equator of the Earth and moves seasonally with the latitudinal insolation shift. The trade winds generally blow in the direction of the ITCZ, either from the north in the Northern Hemisphere or from the south in the Southern Hemisphere. At the ITCZ, large-scale uplift of the converging air masses occurs, associated with a prominent precipitation maximum (Riehl, 1979). The wind field distribution is rather symmetrical around the ITCZ, similar to the climatologic zones and vegetation belts. On their path towards the ITCZ, the low-altitude winds pick up organic material beside the inorganic dust components. The vegetation signal which is measured in the dust organic matter will therefore depend on the kind of vegetation present in that area and how rapidly this signal is overprinted on the existing signal, which was taken up during the previous flow path. It will also reflect the relative importance of the modern vegetation signal vs. the signal of older organic material in soils or dried lakes, reflecting a “fossil” vegetation.

When the relative amounts of C_4 plant-derived *n*-alkanes in dust (Fig. 4c) are compared with the vegetation zonation on the continent (Fig. 1), it is rather obvious that a large C_4 plant-derived fraction of the leaf lipids could only be detected when there is a C_4 plant-dominated vegetation present on the adjacent continent (Fig. 4d). This suggests that wind abrasion of leaf lipids and entrainment en route, possibly by a sandblasting effect, have a stronger effect than the lifting of sedimentary leaf waxes with desiccated soil material or from dried-up lake beds. However, this can only be confirmed when the isotopic signature of “old” leaf lipids in soil or lake bed material is significantly different from the recent vegetation. Soil organic matter should be quite subrecent and thus not carry a significantly different isotopic signature than the recent vegetation. Lakes, however, were present in North Africa as far as 27°N and grasslands as far as 23°N during the African Humid period (14.8 to 5.5 cal. ka BP) (DeMenocal et al., 2000), whereas desert plants were restricted to the area north of 20°N (Jousaume, 1999). It has been suggested that these extensively vegetated areas were largely covered with C_4 plant-dominated vegetation (Petit-Marie, 1991). If that was the case, transport of lake bed–derived material from the Faya Largeau region in Chad, which is transported to the Gulf of Guinea (Figs. 2 and 5), should result in a C_4 plant isotopic signature of the dust lipids collected there. No significant ^{13}C-enriched leaf-wax lipids have been detected in those samples. Therefore, we suggest that leaf-wax lipids in aerosols largely reflect the contemporary vegetation along the transport pathways over the continent. Most probably, the isotopic signature of “old” leaf lipids from soils or lake beds gets rapidly overprinted by abrasion and entrainment of lipids from living plant leaves. The same conclusion has been drawn from a comparison of lipid contents of urban aerosol samples and that of samples downwind of the urban area, indicating a rapid dilution of the anthropogenic components (Simoneit et al., 1988). This interpretation fits with our data to the extent that as we have inferred predominant low-level transport of dust for all collected samples collected north of the equator (see section 4.3). Thus, there is no need to invoke an additional source of ancient lipid material to explain the observed vegetation signal in dust, which leads us to suggest that in our sample set the recent vegetation is the main source.

An unambiguous separation between modern and ancient sources of leaf-wax components can only be obtained by compound-specific ^{14}C-dating of leaf lipids in aerosols (Eglinton et al., 1997). The southernmost dust samples (D21 to D25) were probably transported in higher-altitude air layers (Fig. 5), and they exhibit an isotopically enriched leaf-wax signature, which does not reflect the contemporary vegetation on the adjacent continent (rain forest and woodland) (Fig. 4c). For those samples, we infer a longer-range transport of dust material and a source region that is probably located further south in the grass savannas, steppes, or desert of SW Africa (Kalahari or Namib desert). Based on these findings, we infer that low-level transport of plant-wax lipids mainly reflects the modern vegetation at the last part of the transport trajectory, a signal which is rapidly overprinted onto an existing vegetation signal or that of ancient lipid material from soils or dried lakes.

The investigated aerosol samples reflect only the situation at the sampling time, during the winter season, when the ITCZ and the North African dust plume are in their southernmost position. However, the results are in good agreement with a study of $\delta^{13}C$ of *n*-alkanes in surface sediments off NW Africa by Huang et al. (2000). These authors reported isotopically enriched leaf lipids only in sediments off the coast of the Sahara and Sahel, where they determined a C_4 plant-wax contribution of ~50%, highly consistent with our data. It was concluded that the major contribution of leaf lipids was most probably derived from contemporary vegetation sources on the continent (Huang et al., 2000), which is now supported by our data.

6. CONCLUSIONS

Aerosols sampled along a transect off the African West Coast from 30°N to 10°S were investigated for their lipid content and compound-specific stable carbon isotope compositions.

Saturated hydrocarbon fractions contain predominantly long-chain *n*-alkanes with a strong dominance of odd-carbon-numbered compounds. These lipids are derived from epicuticular waxes of terrestrial plants and indicate the importance of vegetation sources for organic matter in dust.

Backward trajectories confirm that atmospheric transport mainly took place in the low-level trade wind layer (below 2 km), except for the southernmost samples, which are influenced by long-range transport from the SW African steppe and savannas.

The chain length distribution of the *n*-alkanes is most likely a function of the aridity of the source region, in accordance with their biologic functionality to regulate the moisture balance of the plant.

The carbon preference of the *n*-alkanes, indicating the contribution of plant waxes, is higher in dusts from densely vegetated source areas than from arid regions. This is attributed to a higher sensitivity of aerosols from dry areas with a lower leaf-wax content to fossil fuel or marine lipid contributions.

A significant contribution of C_4 plant-derived wax lipids is detected only off regions with predominant C_4 plant type vegetation, the Sahara and Sahel in NW Africa and Gabon in South Africa. Contributions of fossil fuel- or marine-derived lipids have no significant effect on the stable carbon isotope composition of the dominant plant-wax lipids.

The leaf-wax lipids were mainly derived from the contemporary vegetation or subrecent soil organic matter presumably via wind abrasion or sandblasting of leaf surfaces. Input of ancient lipid material, i.e., from dried-up lakes, cannot be confirmed and is apparently rapidly overprinted by the isotopic signature of the modern vegetation.

The findings are highly consistent with studies of *n*-alkanes in surface sediments off NW Africa (Huang et al., 2000) and provide a basis for the reconstruction of vegetation sources by distribution parameters and compound-specific isotope analyses of leaf-wax lipids.

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