

Lipid geochemistry of remote aerosols from the southwestern Pacific Ocean sector

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Abstract

Aerosol samples collected on Ninety Mile Beach on the West coast of the North Island of New Zealand were analyzed for three classes of naturally occurring organic compounds (*n*-alkanes, fatty alcohols and long-chain *n*-aldehydes) which are major constituents of epicuticular waxes of terrestrial plants. In the eight samples analyzed, we identified three distinct regional source signatures for these aerosols depending upon their origin: southwest Pacific Ocean, New Zealand or Australia. Source identifications were entirely consistent with the origin of the aerosols derived by isentropic air mass trajectories. Impactor studies provided additional information as to the source of the aerosols and the mode of introduction of the material into the atmosphere.

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1. Introduction

Many investigations have been carried out on air-borne organic matter, most of them with the aim of measuring organic pollutants in urban, suburban and rural areas. Much fewer studies have focussed on characterizing terrestrial biomarkers in the remote atmosphere to determine the long-range transport of aerosols (Simoneit, 1979, 1986; Gagosian, 1986; Gagosian et al., 1981, 1982; Sicre et al., 1987a,b; Gogou et al., 1996; Conte and Weber, 2002a,b; Kawamura et al., 2003) and the impact of atmospheric inputs to the ocean, far

from the continents (Zafriou et al., 1985; Gagosian and Peltzer, 1986).

The studies undertaken within the Sea Air Exchange Program (SEAREX) represent a significant contribution to the understanding of the long-range transport of aerosols, over distances of several thousand kilometers. The primary objectives of this multi-disciplinary program were to measure various organic and inorganic species in the remote aerosol, thus at extremely low concentration levels, and to investigate the meteorological processes controlling the distributions of these species. For this purpose, a sampling strategy allowing the collection of background marine aerosols was developed to avoid sampling of locally derived material. Stringent anti-contamination protocols were set up for the analysis of trace amounts of organic matter occurring in the remote marine air (Peltzer et al., 1984).

Our general approach in this program was to select a few organic compound classes for their usefulness as tracers of terrigenous material, mostly constituents of epicuticular waxes. The chemical information contained in the homologous series was investigated and

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interpreted in conjunction with meteorological data. Air parcel trajectories were initially used to confirm the source determination obtained from the biomarker approach. However, this approach has evolved to the point that it is possible to exploit the chemical information on a regional scale. In this manuscript, we report on new *n*-aldehyde data from bulk aerosols to test the hypothesis of a regional signature of the vegetation in response to climatic conditions earlier proposed by Gagosian et al. (1987), based on preliminary alcohol data. For this purpose, a 3-month record of aldehyde and alcohol distributions in aerosols was acquired to allow comparison of the molecular compositional features of these two biosynthetically related compound classes over a range of meteorological situations. In this work, we also present a multi-biomarker approach combining aldehydes, alcohols and *n*-alkanes data for diagnosing source inputs and elucidating source regions of aerosols using backward trajectory analyses. The same compound classes were analyzed in size fractionated aerosols, and their occurrence and transport pathways in the atmosphere is discussed.

2. Experimental

Aerosol samples have been collected from the top of a 20 m tower erected on Ninety Mile Beach on the North Island of New Zealand, over 3-months, from 13 June to 25 August, 1983. Wind conditions during the experiment allowed us to sample air masses from a variety of source regions. Sampling techniques and detailed analytical methods are presented in Peltzer et al. (1984) and Peltzer and Gagosian (1987). Collection of atmospheric particles was performed through the use of a high volume air sampler with pre-cleaned glass fiber filters. Size fractionated aerosols were simultaneously collected using a five stage cascade impactor to investigate the particle size distribution of organic compounds. Filters were extracted, fractionated into compound classes by silicagel chromatography and analyzed by gas chromatography as described in detail by Peltzer et al. (1984). Recently, Gogou et al. (1998), Kavouras et al. (1999) and Pio et al. (2001) used a similar procedure. Briefly, filters were extracted four times in an ultrasonic bath in glass distilled methylene chloride and fractionated by silicagel column chromatography. *N*-aldehydes, alcohols and *n*-alkanes thereby isolated from the lipid extract were then analyzed by high-resolution gas chromatography using a DB5 fused silica column mounted in a Carlo Erba 4160 gas chromatograph equipped with an on-column injector and a FID detector. The oven was programmed from 80°C up to 300°C. Hydrogen was used as a carrier gas. Peaks were measured by a Varian Vista CDS 401 integrator to achieve quantitation. Structural identification was verified by high resolution

gas chromatography/mass spectrometry on a Carlo Erba gas chromatograph coupled to a Finnigan 4510 mass spectrometer. Mass spectra were recorded at 50 eV. Data were processed on an INCOS 2300 data system. Prior to extraction, filters were spiked with internal standards. The 3-methyltricosane and heptadecanol were used to correct, respectively, hydrocarbon and alcohol concentrations for recoveries. However, since the standard mixture did not contain *n*-aldehyde, concentrations for this compound class were not corrected for losses occurring during analytical procedure. We estimated (based on the very high recoveries of the other compound classes) that these losses were small.

3. Results and discussion

3.1. Sources

N-aldehydes, fatty alcohols and *n*-alkanes were analyzed to investigate the vegetation signature in airborne particles, after being transported over several thousand kilometers. The *n*-aldehyde series included high molecular weight (HMW) compounds having from 24 to 34 carbon atoms with a strong even to odd predominance, the major homolog being either *n*-C₂₆ or *n*-C₂₈. The occurrence of HMW *n*-aldehydes has rarely been reported in airborne particulate matter. *N*-C₂₆, *n*-C₂₈ and *n*-C₃₀ aldehydes have been documented by Wils et al. (1982) in urban aerosols. HMW aldehydes have also been described in coastal sediments as indicators of higher plant inputs (Cardoso and Chicarelli, 1983; Albaiges et al., 1985; Prah and Pinto, 1987). They have been determined in sugarcane waxes (Lamberton, 1965), in fruit cuticles (Croteau and Fagerson, 1971) and in cuticular waxes from foliage and pollen of deciduous trees (Prah and Pinto, 1987). Fatty alcohols, in these same samples, ranged from *n*-C₁₃ to *n*-C₃₄ displaying bimodal distributions (from *n*-C₁₃ up to *n*-C₂₀ and from *n*-C₂₁ up to *n*-C₃₆) with a strong even/odd predominance in the HMW range, typical of a terrestrial plant wax signal. Like the *n*-aldehydes, the C₂₆ or C₂₈ homolog dominated this series. Aerosols were also analyzed for *n*-alkanes which is one of the most widely distributed class of compounds in the environment. They can either be produced by natural sources, i.e., higher plants or marine organisms, or be released during anthropogenic activities. Terrestrially derived *n*-alkanes are easily recognizable as their distribution displays a characteristic odd to even predominance with high values of the carbon preference index (CPI). However, it is not easy to distinguish between marine and anthropogenic *n*-alkanes as they both lead to a regular distribution with no predominance (CPI = 1). *N*-alkanes in our samples pointed out a major land derived source input, with CPI values ranging from 2.1 up to 8.5. The concentration

Table 1
Concentrations of aldehydes, fatty alcohols and aliphatic hydrocarbons (in pg/m^{-3}) measured in aerosols collected from Ninety Mile Beach New Zealand

Volume (m^3)	4250	4440	3210	1510	3930	3680	3940	4400	3020
Date	13–17 June 1983	17–21 June 1983	22–26 June 1983	29–7 July 1983	11–16 July 1983	16–20 July 1983	29–7 July–Aug 1983	7–13 Aug 1983	16–25 Aug 1983
Sample no	NZAS-1	NZAS-5	NZAS-7.1	NZAS-7.2	NZAS-15	NZAS-16	NZAS-19	NZAS-20	NZAS-22
<i>Aldehydes</i>									
C ₂₄ –C ₃₄	19	14	10	126	16	17	—	49	66
<i>Fatty alcohols</i>									
C ₁₃ –C ₂₀	37	16	33	330	5	10	18	16	14
C ₂₁ –C ₃₆	116	32	41	436	102	76	91	291	474
<i>Aliphatic hydrocarbons</i>									
C ₁₇ –C ₄₀	74	22	58	539	90	61	66	186	270
CPI	2.3	3.5	2.1	2.4	3.3	3.4	5.8	8.5	4.3

record over time for all three compound series followed parallel trends (Table 1). Aerosol NZAS-7.2 exhibited the highest concentrations. Values were lower in NZAS-20 and NZAS-22 and even more moderate in NZAS-1, NZAS-15, NZAS-16 and NZAS-19. The lowest numbers were found in NZAS-5 and NZAS-7.1.

Three-dimensional air mass trajectories were calculated using wind fields on isentropic surfaces (Merrill et al., 1985) in order to identify the source regions of the aerosols and compare this information to the biomarker data. During the sampling period three major meteorological situations were encountered (Fig. 1). Briefly, the trajectory analyses indicated a southwestern ocean origin of aerosol NZAS-1, NZAS-5 and NZAS-7.1 with possible minor continental influence. Although having similar origin, NZAS-7.2 aerosol passed over New Zealand and consequently was influenced by local island sources. Trajectories for NZAS-15 and NZAS-16 showed that these samples are likely to represent a New Zealand type aerosol, whereas NZAS-20 and NZAS-22 reflect terrestrial sources from southern Australia and Tasmania.

Gagosian et al. (1987) earlier hypothesized that the alcohol carbon distribution would reflect a regional signature of the vegetation. Since naturally occurring *n*-aldehydes in plant waxes are intermediates in the biosynthesis of fatty alcohols (Kolattukudy et al., 1976), the distribution patterns of HMW *n*-aldehydes and alcohols for each of the three typical trajectory categories, namely NZAS-1, NZAS-15 and NZAS-20, should reveal similar compositional trends. Examination of homologous distribution plots of both series indicates distinct features in samples of different source regions (Fig. 2). The *n*-C₂₆ aldehyde and fatty alcohol were predominant in aerosols NZAS-1 and NZAS-15 whereas in NZAS-20 the C₂₈ homolog dominated the *n*-aldehyde series and was as abundant as the C₂₆ analog in the alcohol series. A concomitant increase of the relative abundance of the higher molecular weight C₃₀ and C₃₂ in both series was also observed in the latter sample. These results add further evidence to previous interpretations of preliminary alcohol data (Gagosian et al., 1987) that there is a compositional change of epicuticular wax constituents with the source region. Higher amounts of heavy homologs in NZAS-20 would reflect a tropical character of this aerosol, while NZAS-1 and NZAS-15 would be indicative of the more temperate climate region of New Zealand. It has been proposed that the synthesis of longer chain aliphatic compounds in higher plants leads to an increase of the diffusion resistance of the wax to water vapor providing plants growing in tropical regions a way to restrict water loss. Homologous distribution plots of fatty alcohols and aldehydes would thus reflect climatic conditions of the vegetation. If leaf wax composition results from the response of the vegetation to aridity changes, mean

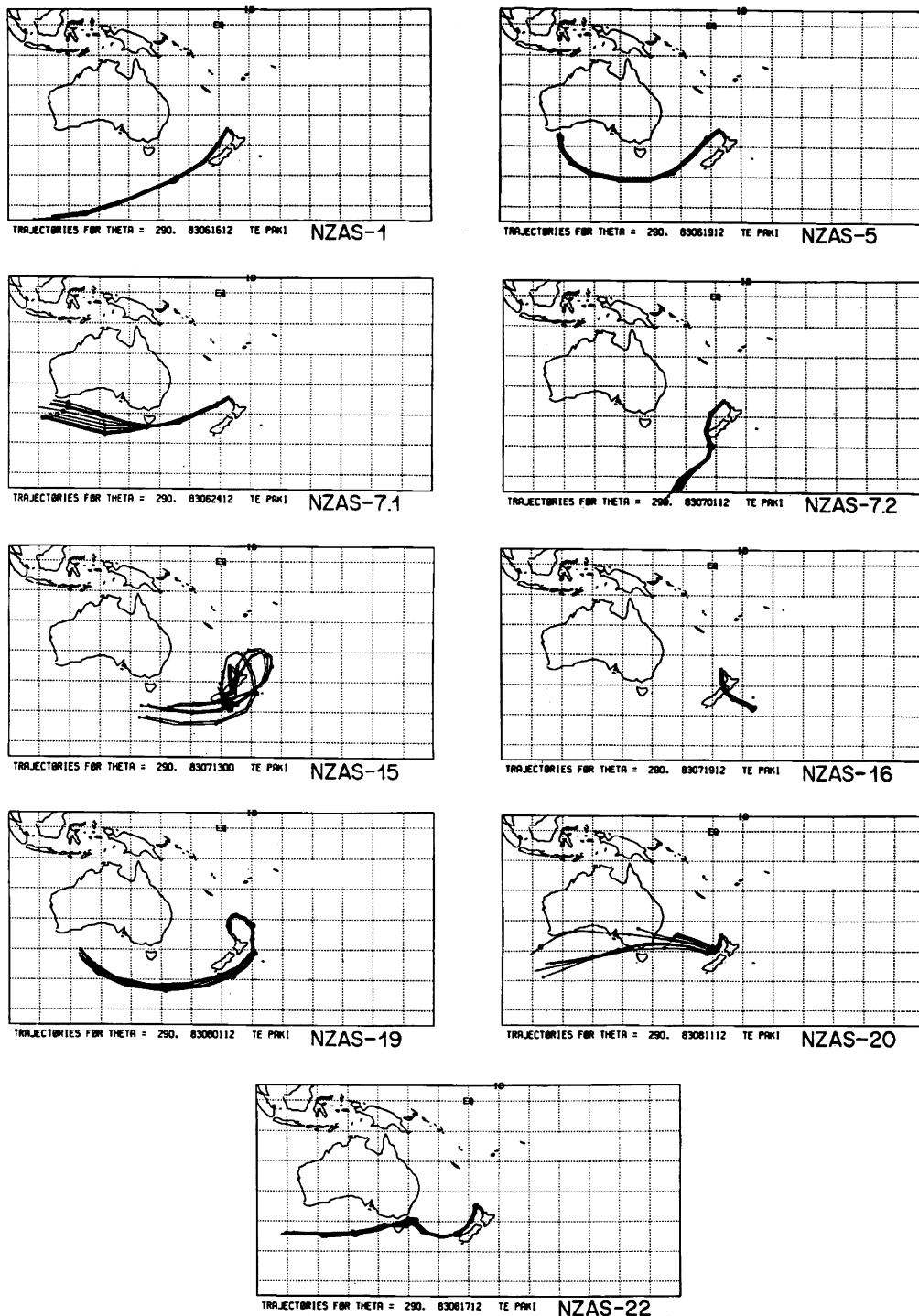


Fig. 1. Three-dimensional air mass backtrajectories of each NZAS. Dots on the trajectories are at 1 day interval.

carbon numbers (MC#) may thus provide a potential index to assess climate changes in the past. Recent paleoclimate studies have shown that terrestrial alcohols

are preserved in marine sediments over hundred thousand years (Ternois et al., 2000; Sicre et al., 2001) and that their mass accumulation rates in the sediment

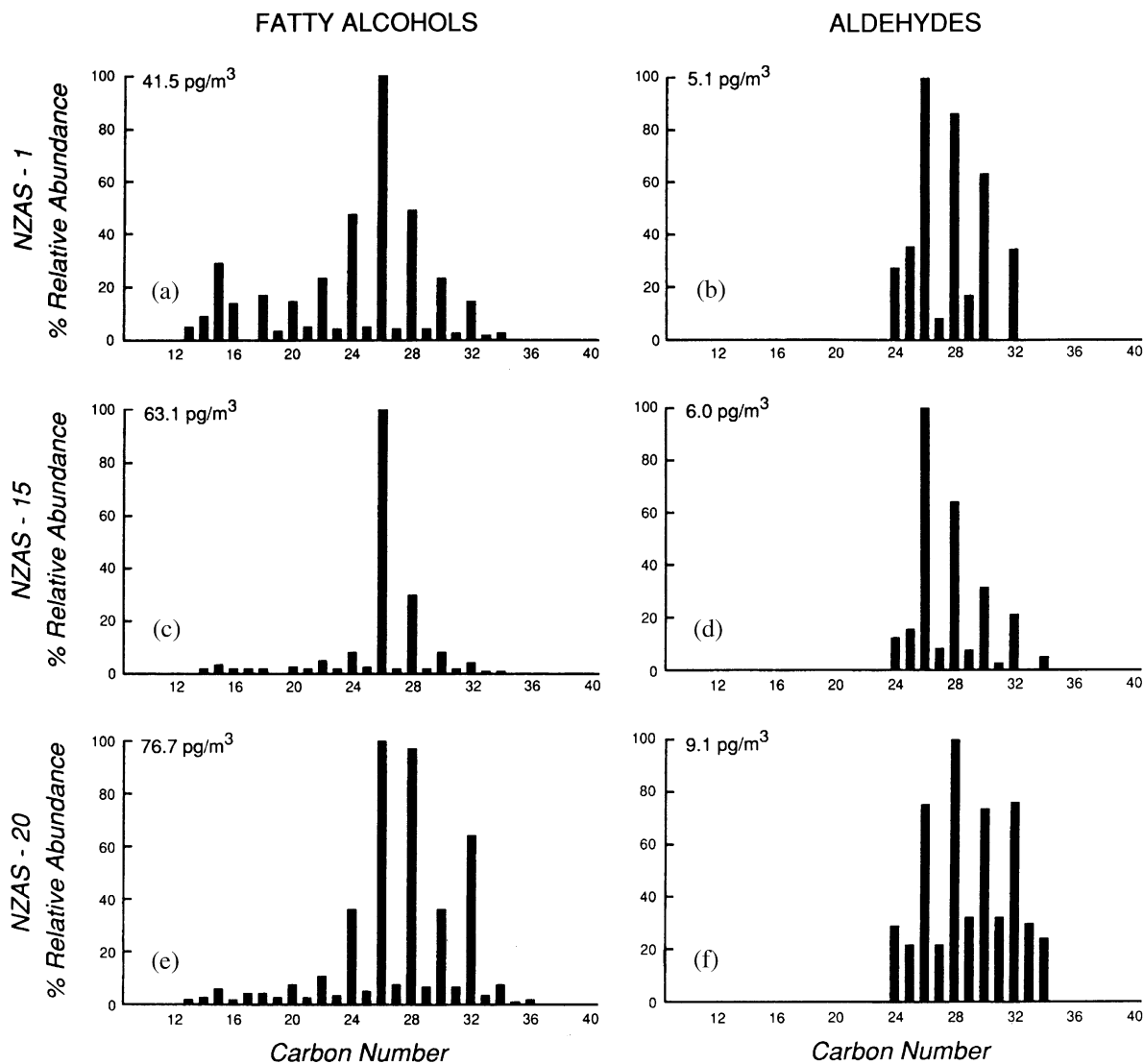


Fig. 2. Homolog distribution plots of fatty alcohols (a, c, e) and *n*-aldehydes (b, d, f) for NZAS-1, NZAS-15 and NZAS-20 representing the three major air mass trajectories: southwest Pacific Ocean air, New Zealand air and Australian air, respectively.

off northwest Africa recorded long-term variations of the northeast trade winds. The molecular distribution of this major lipid compound class could thus be used to evaluate its usefulness for reconstructing aridity changes in past climates. Another notable feature in the alcohol distribution is the relatively large concentration of the low molecular weight (LMW) homologs in NZAS-1 presumably reflecting marine derived inputs (Garrett, 1967). Concentration changes are also consistent with air mass trajectories. They were higher in NZAS-20 than in NZAS-15 and much higher than in NZAS-1 due to the greater distance of the source region and changes in the geographical origin and strength of the terrestrial source. Low concentrations are likely due to the lack or

limited contact with land, while highest concentrations in NZAS-7.2 indicate stronger local terrestrial inputs.

In order to “quantify” the changing distribution patterns over the course of the experiment, the MC#’s were calculated for C₂₁–C₃₆ fatty alcohols, for C₂₅–C₃₄ aldehydes and for C₁₇–C₄₀ alkanes according to Peltzer and Gagosian (1989). This number, representing the average carbon chain length in an homologous series, is more diagnostic of the source than the carbon maximum (C_{max}) and is more appropriate when dealing with broad compound distributions. It is defined as

$$MC\# = \frac{\sum (\text{Conc}(C_i)i)}{\sum \text{Conc}(C_i)},$$

where *i* is the number of carbon atoms in the homologs.

The MC# plotted in Fig. 3 clearly shows the strong compositional similarity between *n*-aldehydes and alcohols confirming similar sources of these compounds and suggesting a good qualitative preservation of the aldehyde to alcohol signal during transport. Aerosols NZAS-1 and NZAS-15 exhibited the lowest MC#, while as expected, NZAS-20 had a high MC#, but surprisingly the MC# of NZAS-5 was very comparable. Although dominating the fatty alcohol distribution in NZAS-5, the C₂₆ homolog was only slightly more abundant than C₂₈. Gagosian et al. (1987) have suggested from the fatty alcohol composition of NZAS-5 that this aerosol was a mixture of several sources including tropical, temperate and marine. The air parcel trajectories confirmed that atmospheric particles being collected from 19 June to 21 June, originated near southern Australia.

While the fatty alcohol and *n*-aldehyde MC#'s tracked each other well, the MC# plot for *n*-alkanes exhibited pronounced differences for samples NZAS-5 and NZAS-16 (Fig. 3). Since HMW fatty alcohols and *n*-aldehydes are exclusively terrestrial, any deviation of the *n*-alkane MC# plot with respect to that of these two compound classes should reveal inputs of a source other than terrigenous. The presence of light *n*-alkanes in NZAS-5 inducing a shift towards a lower MC# is suggestive of an additional component in the LMW range. It is proposed based upon the alcohol fingerprint (presence of LMW alcohols) that this additional

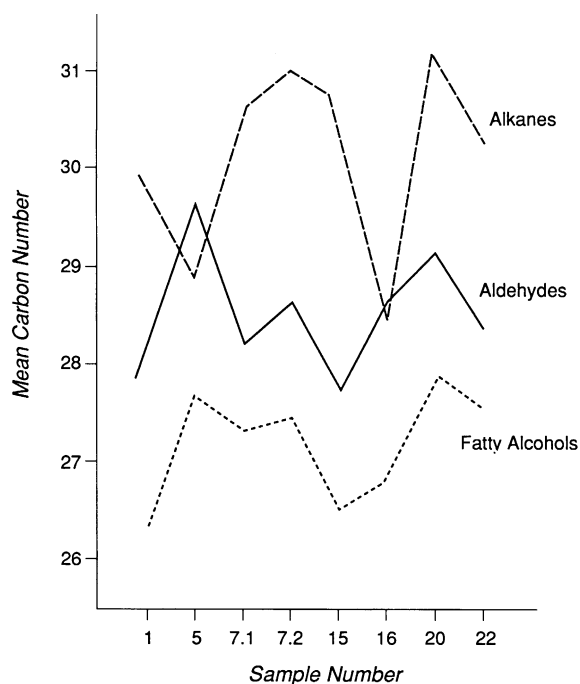


Fig. 3. Mean carbon numbers for the three lipid compound classes: *n*-alkanes, *n*-aldehydes and fatty alcohols, vs. sample number. See text for definition of mean carbon number.

contribution is of marine origin. The low MC# calculated for NZAS-16 requires an alternative explanation. The long-range meteorological data indicates that this aerosol had traveled over urban areas in the south of the North Island and over Christchurch, suggesting that in this case, low alkane MC# may reflect the presence of anthropogenic *n*-alkanes. Besides these two aerosols, temporal trends of the *n*-alkane MC# for the other samples looked similar to those of *n*-aldehyde and alcohol MC#'s indicating major contribution of plant waxes.

3.2. Distributions by particle size

Further investigations were carried out on the same compounds series in the size fractionated aerosol, NZAS-18. Low and HMW fatty alcohol concentrations presented as a function of particle size (Fig. 4) showed that terrestrial alcohols were primarily associated with large particles, while LMW ones showed a bimodal distribution. The major proportion of alcohols were found on particles in the size range above 3.0 μm . They were less abundant in the condensation mode ($d_{\text{eq}} < 3.0 \mu\text{m}$). *N*-aldehydes were essentially detected on the first two stages (dispersion mode), only. Concentrations dropped to almost the detection limit on smaller particles.

Total *n*-alkane distribution (Fig. 5) differed notably from the fatty alcohol one. Concentrations decreased with particle size except on the third stage and backup

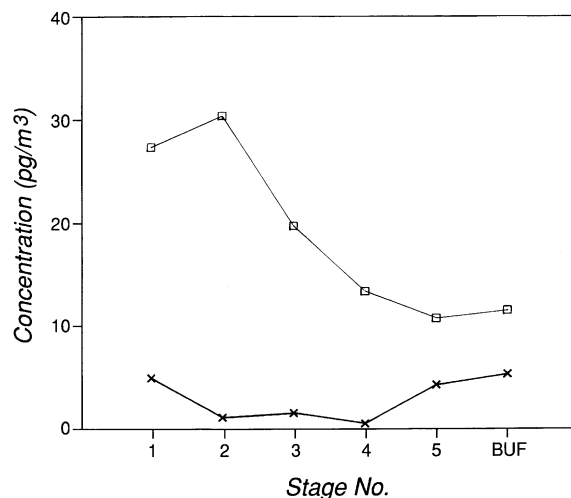


Fig. 4. Particle size distribution of fatty alcohols in a five-stage cascade impactor sample, NZAS-18. (x) C₁₃-C₂₀ marine source fatty alcohols; (\square) C₂₁-C₃₆ terrestrial source fatty alcohols. Aerodynamic cutoff diameters are: (stage 1) $d_{\text{eq}} > 7.2 \mu\text{m}$; (stage 2) $7.2 \mu\text{m} > d_{\text{eq}} > 3 \mu\text{m}$; (stage 3) $3 \mu\text{m} > d_{\text{eq}} > 1.5 \mu\text{m}$; (stage 4) $1.5 \mu\text{m} > d_{\text{eq}} > 1 \mu\text{m}$; (stage 5) $1 \mu\text{m} > d_{\text{eq}} > 0.5 \mu\text{m}$; (backup filter) $d_{\text{eq}} < 0.5 \mu\text{m}$.

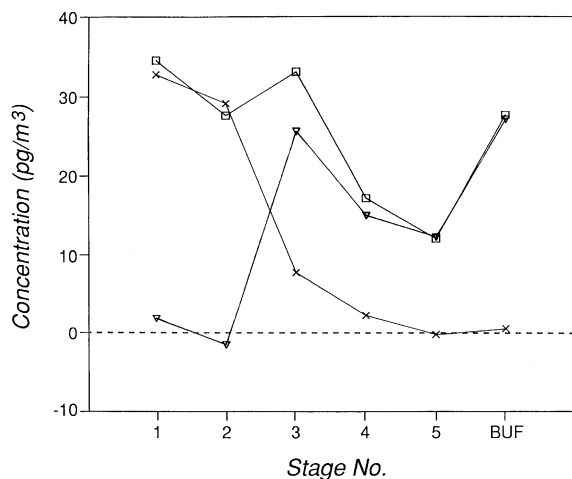


Fig. 5. Results of source model calculation for the C₁₇–C₄₀ *n*-alkanes as a function of particle size in impactor sample NZAS-18. (□) Sum C₁₇–C₄₀ *n*-alkanes; (x) plant wax (CPI = 5) *n*-alkanes; (∇) anthropogenic and marine (CPI = 1) *n*-alkanes. Aerodynamic cutoff diameters are: (stage 1) $d_{eq} > 7.2 \mu\text{m}$; (stage 2) $7.2 \mu\text{m} > d_{eq} > 3 \mu\text{m}$; (stage 3) $3 \mu\text{m} > d_{eq} > 1.5 \mu\text{m}$; (stage 4) $1.5 \mu\text{m} > d_{eq} > 1 \mu\text{m}$; (stage 5) $1 \mu\text{m} > d_{eq} > 0.5 \mu\text{m}$; (backup filter) $d_{eq} < 0.5 \mu\text{m}$.

filter suggesting different origins and/or emission mechanisms of *n*-alkanes over the particle spectrum. Using a simple model based on the CPI values calculated for each stage, the contribution of the main *n*-alkane sources were estimated considering a CPI value of 1 for the anthropogenic and/or marine sources, and a CPI value of 5 for the terrestrial source. The distribution pattern of the plant wax *n*-alkanes (Fig. 5) matched well with the *n*-aldehyde and alcohol ones with concentrations maximizing on stages 1 and 2 and dropping rapidly on the smaller particle sizes, while the CPI = 1 alkanes predominated on the third stage and the backup filter. Similar results concerning terrestrial alkanes have been reported in aerosols collected off the coast of Peru (Schneider et al., 1983) and over the Mediterranean Sea (Sicre et al., 1987a, b). Moreover, Van Vaeck and Van Cauwenberghe (1985) noted the occurrence of plant wax *n*-alkanes in aerosols ($d_{eq} = 3$ to $7 \mu\text{m}$) in suburban areas and on coarser particles ($d_{eq} = 7 \mu\text{m}$) in rural aerosols collected in summer. Although we would expect the distribution size to change with increasing distance from the land, with the preferential loss of the larger size particles, it appears from our results and those found in the literature, that quite similar profiles were observed with aerosols collected over the continent (Van Vaeck and Van Cauwenberghe, 1985), in coastal areas (Schneider et al., 1983) or over the open ocean (Sicre et al., 1987b). These observations suggest that the size spectrum of terrestrially derived compounds remain unchanged during atmospheric transport.

The distribution of individual *n*-alkanes for the different stages were further examined (Fig. 6) to precisely determine the origin and introduction mode of the alkanes present on stage 3 and the backup filter. Only the C₂₅–C₃₆ alkanes were detected on stages 1 and 2 confirming the major contribution of the terrestrial sources in this size range. In contrast, the presence of light hydrocarbons on the third stage, dominated by the C₂₀ and C₂₂ homologs, indicate an additional input source. The *n*-C₂₀ alkane has been reported as the major hydrocarbon accounting for 20–40% of the total aliphatic hydrocarbons in suspended particles collected in the surface waters of Villefranche Bay (Mediterranean Sea) (Goutx and Salot, 1980) and in a wide variety of depositional environments (Dastillung, 1976; Simoneit, 1977; Farrington and Tripp, 1977; Pelet and Debysier, 1977). Nishimura and Baker (1986) discussed the possibility of a marine bacterial origin of the C₂₀ and C₂₂ alkanes. It is therefore probable that these short chain alkanes have a marine origin. Their occurrence in the atmosphere could involve their evaporation or ejection from the surface ocean due to bubbling in response to wind stress. Since these compounds appear in a narrow range of the spectrum size, i.e., from 1.0 to $3.0 \mu\text{m}$ diameter particles, rather than over the entire spectrum, we favor the hypothesis of the ejection of marine particles into the atmosphere. Sicre et al. (1990) have demonstrated the ejection of marine coccolithophorids by the presence of alkenones of stages 1 and 2 of this same aerosol.

LMW alkanes, from C₁₇ to C₂₃, were also found on the backup filter, but in smaller quantities. As opposed to the third stage, there was no predominating homolog but yet a marine origin of these compounds cannot be ruled out. Differences between LMW *n*-alkane distribution on the third stage and final filter may be attributed to a different mode of introduction of these molecules into the atmosphere. We propose evaporation of marine *n*-alkanes or gas stripping during bubbling followed by adsorption onto particles as one possible mechanism. Alternatively, LMW *n*-alkanes could reflect anthropogenic emissions and result from gas condensation on the small particles of the aerosol. Fig. 6 also reveals the presence of HMW hydrocarbons with unusual even/odd predominance. These compounds have been documented in offshore New Zealand sediments (Kennicutt II and Brooks, 1990) but their origin is unknown.

4. Conclusions

Distinct vegetation signatures of plant derived *n*-aldehydes and alcohols were observed with changing source regions as confirmed by the air mass trajectories. Plots of MC# for *n*-aldehydes and alcohols showed similar temporal trends. High MC# in aerosols from

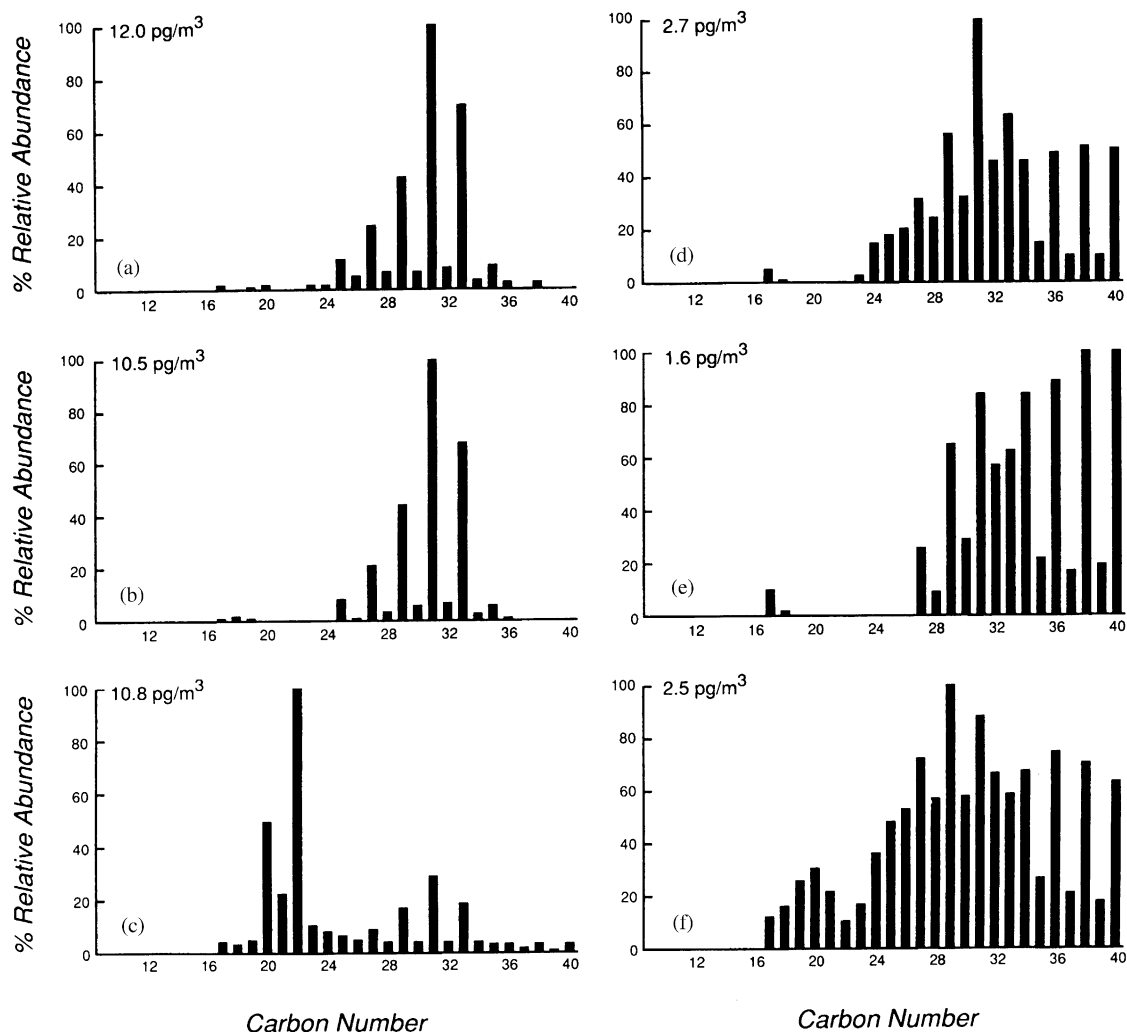


Fig. 6. Homolog distribution plots for the *n*-alkanes as a function of particle size in impactor sample NZAS-18. Aerodynamic cutoff diameters: (a) $d_{eq} > 7.2 \mu\text{m}$; (b) $7.2 \mu\text{m} > d_{eq} > 3 \mu\text{m}$; (c) $3 \mu\text{m} > d_{eq} > 1.5 \mu\text{m}$; (d) $1.5 \mu\text{m} > d_{eq} > 1 \mu\text{m}$; (e) $1 \mu\text{m} > d_{eq} > 0.5 \mu\text{m}$; (backup filter) $d_{eq} < 0.5 \mu\text{m}$.

Australia were attributed to the more tropical nature of these aerosols presumably reflecting an adaptation of the vegetation to climate. Lower values were found in airborne particles coming from more temperate regions.

Deviations of the alkane MC# values with respect to those of *n*-aldehyde and alcohol allowed us to identify source inputs other than terrestrial, i.e. marine and anthropogenic.

The same three homologous series were investigated in a size fractionated aerosol. *N*-aldehyde and fatty alcohols were primarily associated with large particles above $3.0 \mu\text{m}$. Plant wax alkane indicated similar trends as *n*-aldehyde and alcohols, while CPI=1 alkanes dominated on the third and final filters. The predominance of the C_{20} and C_{22} analogs in the 1 and $3 \mu\text{m}$

diameter particles suggested the ejection of marine particles from surface waters, possibly bacteria. HMW even carbon numbered *n*-alkanes were for the first time documented in aerosols, but their origin still needs to be elucidated.

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