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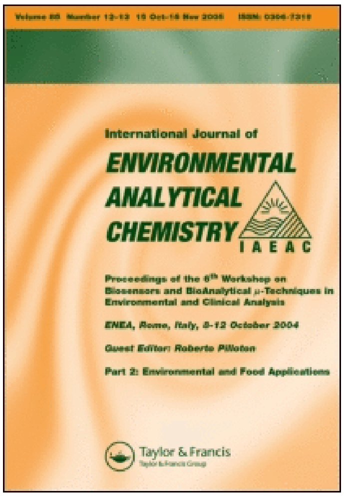

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CHEMICAL COMPOSITION OF PARTICULATE ORGANIC MATTER (POM) COLLECTED AT TERRA NOVA BAY IN ANTARCTICA

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The organic composition of particulate matter collected at Terra Nova Bay during the 1991 Italian Expedition to Antarctica was determined by HRGC-MS. Several biogenic and anthropogenic organic compounds were identified in the liquid chromatographic fractions into which the extract was separated. In addition to n-paraffins, PAH and phtalate esters, alkanoic acid methyl esters, alkyl phospates and arylsulphonamides were identified as major components in the particulate organic matter. The results obtained are highly indicative of the decisive role played by marine aerosols in determining the levels of organic compounds present in suspended particles present at Terra Nova Bay.

KEY WORDS: Particulate organic matter, Antarctica, marine aerosols, air contaminants.

INTRODUCTION

A detailed knowledge of the organic fraction present in suspended particulate matter can be regarded as one of the most effective ways of investigating to what extent anthropogenic pollution affects life on Earth. By studying the composition of organic material adsorbed on particles it is, in fact, possible to distinguish components of man-made origin which, because of their long life-time in the biosphere, are subjected to long range transport from those released into the atmosphere as a consequence of biogenic activities[1,2]. By relating the content of man-made contaminants associated with suspended particles with those existing in sediments, biota and tissues of long living animals at the top of the food chain, accumulation processes can be identified and possible changes occurring in the ecosystem related to the levels of anthropogenic pollution in densely populated areas. Since polar

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regions do not possess significant pollution sources of their own, the evaluation of potentially toxic organic substances in the air can provide a better insight on both the pathways as well as the spatial and temporal scales through which contaminants are spread out over the globe[3].

Within the frame of a National Research Program in Antarctica started by the Italian government in the middle of the 1980's with the establishment of a permanent station in Terra Nova Bay, several monitoring campaigns have been carried out by the Environmental Chemistry Group with the aim of establishing the levels of anthropogenic pollutants in the marine and atmospheric environments[4]. Here, we present the methodology used for the identification and quantification of organic compounds present in particulate matter sampled at the Italian Station in Antarctica from January to the first week of February 1991. The average composition and aerometric concentrations reached by organic compounds of man-made and biogenic origin will be reported. Data will be used to identify the main sources for particulate matter and aerosol present in Terra Nova Bay.

EXPERIMENTAL

Sampling, fractionation and analysis of particulate matter

Suspended particulate matter was collected on quartz fiber filters (20 × 25) prewashed by Soxhlet extraction with CH_2Cl_2 and CH_3OH for 3 hours. Filter samples were collected with a high volume sampling device equipped with a size selective inlet for the collection of particles smaller than 10 um (Sierra Andersen, Atlanta, GA, USA) and a sensor for measuring the flow rate through the filter.

A sampling duration of one week was selected in order to get a large enough amount of matter for GC-MS determinations. Five filters were collected starting from the 2nd of January 1991. The sampler was installed near to Meteo Station, located about 1 Km from the Italian Base. The sampling site was 50 m above sea level, in front of Tethys Bay. Its exact location is shown in Figure 1.

After sampling, the filters were immediately wrapped in aluminum foil and sealed in plastic containers kept at −10°C. When the campaign ended, they were shipped to the laboratory, where they were stored at low temperatures until they were extracted and analyzed.

Particulate organic matter was extracted by maintaining the filters in a Soxhlet apparatus for 8 hours. A mixture of benzene-methanol (4 : 1) was used for liquid extraction. After evaporation to dryness with a flow of N_2 at ambient temperature, the residue was passed over a bed of Erbasil (Carlo Erba Farmitalia, Milan, Italy) to remove particles. Aliquots of the redissolved solution were fractionated on a column (16 × 0.8 cm) packed with deactivated basic alumina (3.5% H_2O w/w, 100–300 mesh) for separating aliphatic compounds from the bulk of polyaromatic hydrocarbons and polar organic compounds. Four fractions were collected during this separation step. Sequential elution was obtained by passing aliquots of *n*-hexane, CH_2Cl_2, CH_3CN and CH_3OH through the column. The CH_2Cl_2 fraction was further submitted to HPLC separation on silica columns for separating PAH (HPLC-1) from

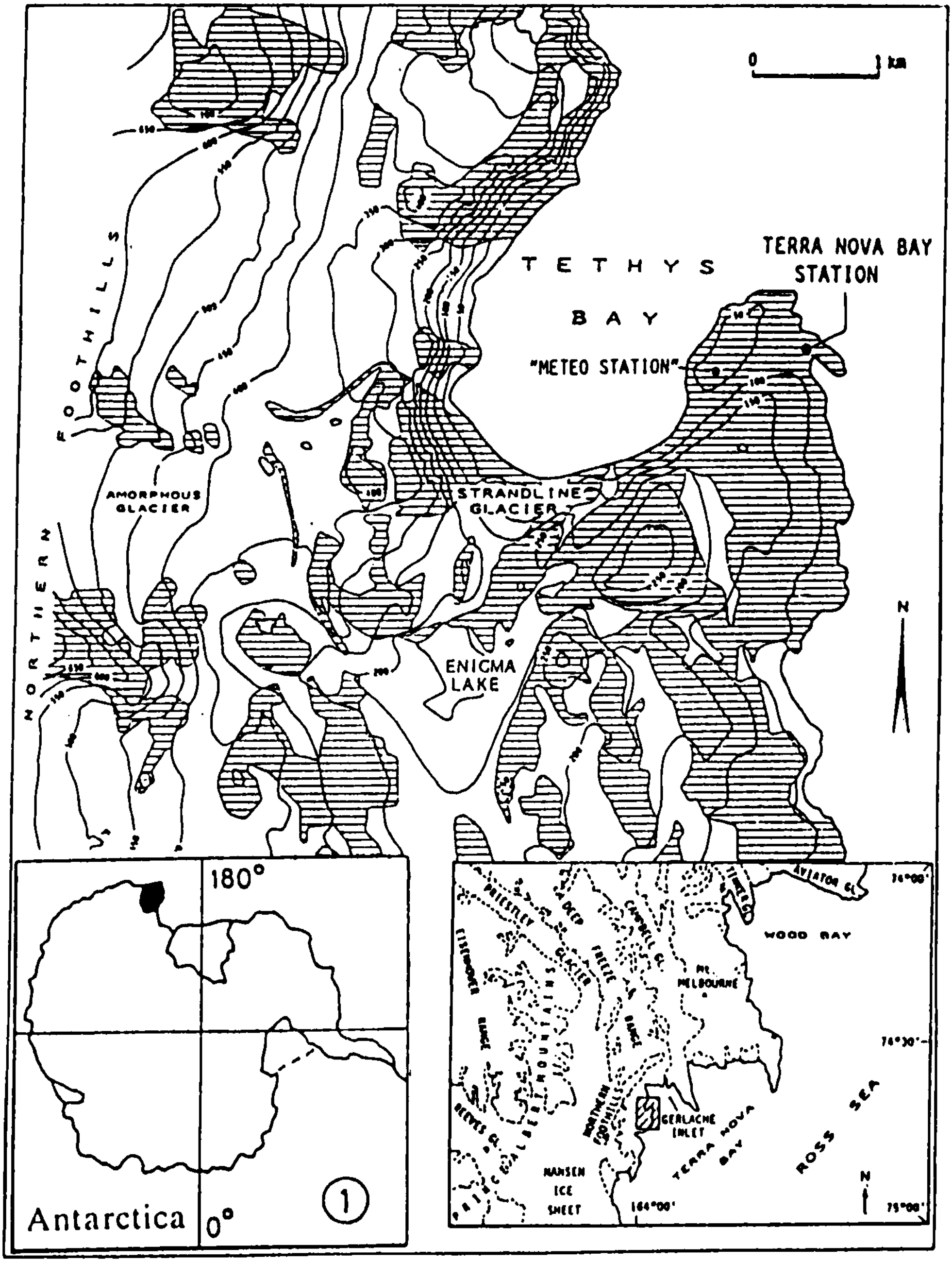

Figure 1 Map showing the exact location of the Italian Base installed at Terra Nova Bay and the position of the Meteo Station where high volume samples of suspended particulate matter were collected.

moderately-polar aromatic compounds (HPLC-2 and 3). A detailed description of the HPLC separation procedure can be found in a previous publication[5].

Although time consuming, this separation scheme was preferred to simpler clean-up procedures because it allowed an accurate evaluating of nitrated (HPLC-2) and oxygenated polyaromatic hydrocarbons (HPLC-3) possibly present in the sample. This was considered an important part of our research, since some nitrated-PAH can be formed by the gas-phase reaction of parent PAH with hydroxyl radicals and NO_2[6]. Since photochemical reactions occur everywhere in the atmospheric boundary layer and the products formed can be subject to long-range transport, the possible presence of nitro-PAH in the particulate matter sampled over Antarctica could not be completely ruled out.

After the liquid chromatographic separation, all fractions were submitted to HRGC-MS determinations by injecting aliquots into a 15 m fused silica-capillary column coated with DB-17 (0.25 mm i.d., 0.5 um film thickness) supplied by J&W Scientific Company (Rancho Cordova, CA, USA). All separations were carried out on a Hewlett-Packard GC model 5890 combined with a quadrupole MSD model 5970B supplied by the same company (Hewlett-Packard, Palo Alto, CA, USA). The GC oven was programmed from 30° to 200°C at a rate of 20 °C/min and then 3 °C/min up to 270°C. This allowed a good separation of the organic components present in the various liquid chromatographic fractions.

RESULTS AND DISCUSSION

Identification of the anthropogenic and biogenic tracers present in the liquid chromatographic fractions extracted from particulate matter

Figure 2 reports a typical profile recorded when the *n*-hexane fraction was submitted to HRGC-MS determination. As can be seen from Figure 2, the aliphatic portion of POM was comprised of *n*-alkanes ranging from 16 to 34 carbon atoms although the most abundant components resulted to be linear olefinic components with 18 and 20 carbon atoms. The molecular fraction above C_{24} did not show any appreciable odd-even distribution. In this range, the carbon preference index (C.P.I.) was close to 1, and the maximum centered around C_{26}. The use of selected ion detection made it possible to detect traces of biological markers (tri-and/or tetracyclic terpanes having a typical fragment at m/z 191 and steranes characterized by a fragment at m/z 217) in the aliphatic fraction (see the detail of Figure 2). Although the occurrence of these markers in particulate matter sampled in urban areas is strongly indicative of combustion sources whenever coupled with a C.P.I. close to 1[1], such close relation is questionable in remote areas. It is, in fact, possible that a similar distribution might arise from natural sources (bituminous shales, coal particles and crude oil) dispersed in the atmosphere in the form of fine particles and aerosols. In this case, the lack of an odd-even distribution can be explained either by strong diagenetic processes to which source rocks or fossil fuels were subjected during their formation, or from oxidation and bacterial degradation of the aliphatic fraction taking place in the environment. This is particularly true if resuspended particles and aerosols previously deposited on watersheds and soil, contribute to air samples.

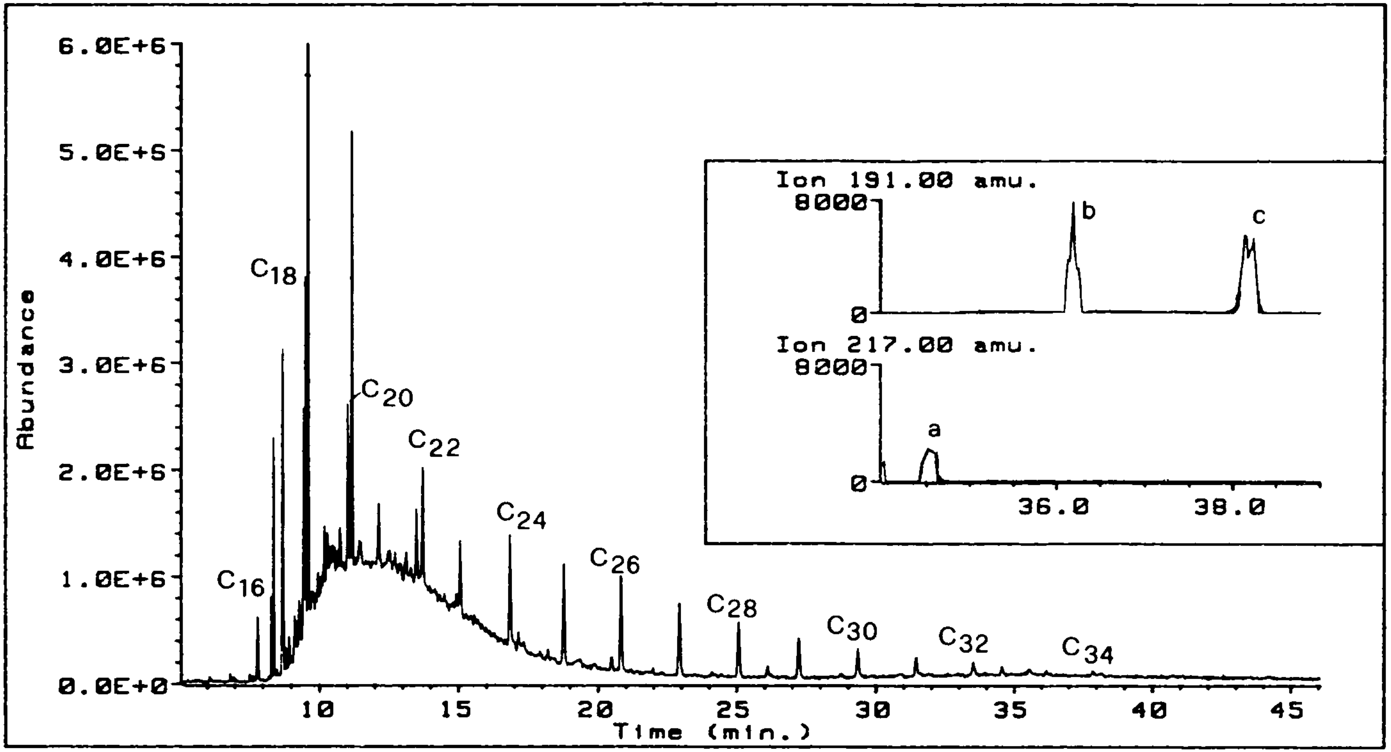

Figure 2 HRGC-MS profile of the n-hexane fraction extracted from particulate organic matter collected at Terra Nova Bay. The selected ion profiles refer to alycyclic terpanes (peak b and c recorded at m/z 191) and a sterane component (peak a at m/z 217).

In the case of Figure 2, the large abundance of unresolved compounds and the lack of pristane and phytane in the chromatogram, seem to be quite suggestive of bacterial degradation of particles coming from natural sources. The even-odd distribution seen in the lower part of the chromatogram, (C.P.I. < 1) where the C_{17} and C_{19} alkanes are negligible when compared to the C_{16}, C_{20} and C_{22} components, leaves little doubt about the biogenic origin

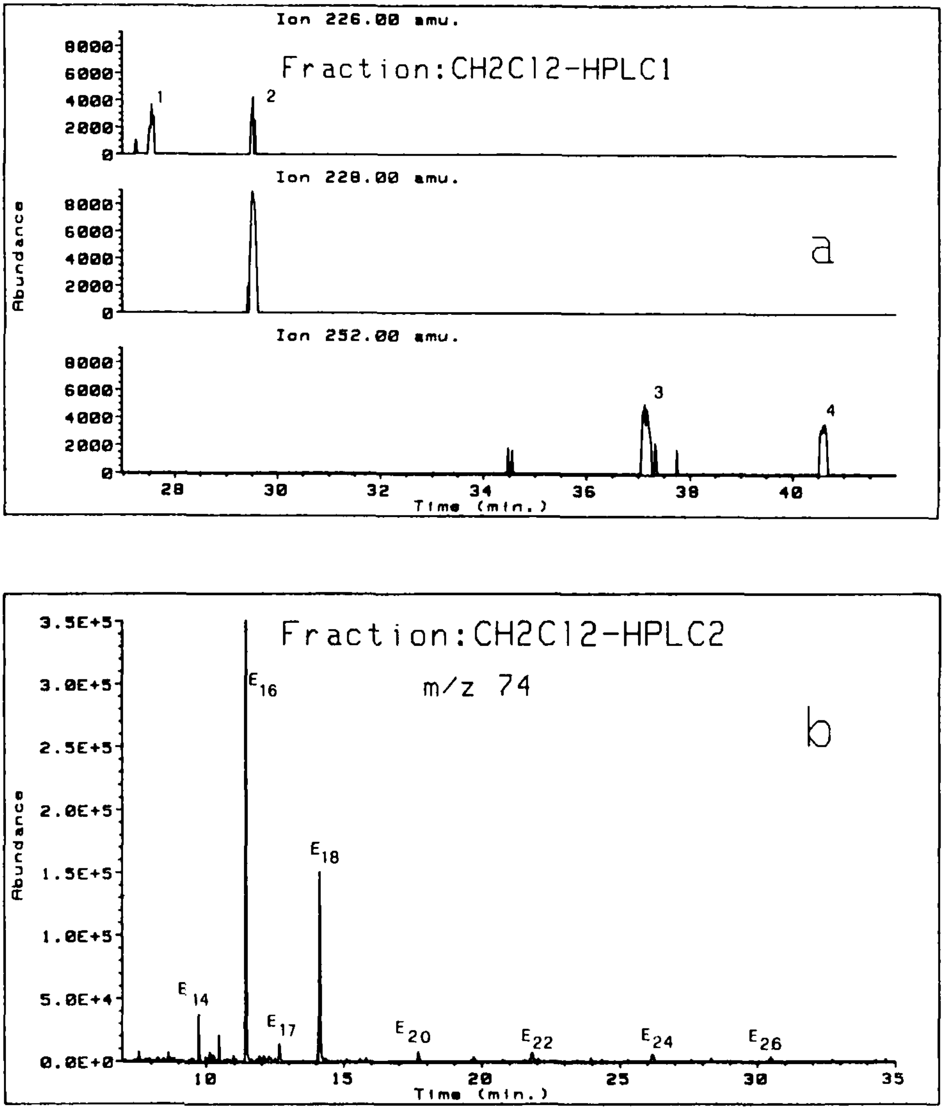

Figure 3 a) Selected ion profiles of selected PAH obtained during the HRGC-MS analysis of HPLC-1 fraction extracted from particulate organic matter sampled at Terra Nova Bay. 1) Benzo(ghi) fluoranthene, 2) Chrysene, 3) Benzo(b) fluoranthene + Benzo(k) fluoranthene, 4) Benzo(e)pyrene.

b) Selected ion profile obtained by submitting the HPLC-2 fraction extracted from particulate organic matter sampled at Terra Nova Bay to HRGC-MS determination. Peaks in the Figure refer to alkanoic acid methyl esters. E16 is used to indicate hexadecanoic acid methyl ester.

of these compounds, since it has already been reported that in the Antarctica region some organisms are actually capable of producing *n*-alkanes with an even number of carbon atoms and they can be found in some biological matrices[7,8].

The observation that C.P.I.'s lower than 1 were recorded in sea water samples[9] can be taken as indicative of the fact that marine aerosol somehow contributes to the aliphatic fraction of particulate organic matter present at Terra Nova Bay. The low input from combustion sources was confirmed by the tiny amounts of PAH found in the CH_2Cl_2 fraction. Unlike urban and suburban samples, PAH originating from combustion were found only in the HPLC-1 fraction whose selected ion profile is partly shown in Figure 3a.

Based on the average composition of PAH reported in Figure 4, it is clear that only PAH known to be highly resistant to degradation processes (either photolytic or bacterial) were present in particulate matter. This seems to indicate that PAH found in the POM were mainly associated with fine carbon particles present in aged air masses reaching Antarctica by long-range transport. Similar profiles have also been found in other long-range transported aerosols and have been attributed to the refractory components from coal combustion emissions[10].

The lack of nitrated and oxygenated PAH in fraction HPLC-2 and 3, respectively, also supports this hypothesis by suggesting that degradation processes of moderately polar PAH were not adequately compensated by their photochemical production, since it usually occurs in strongly photochemical polluted areas[11].

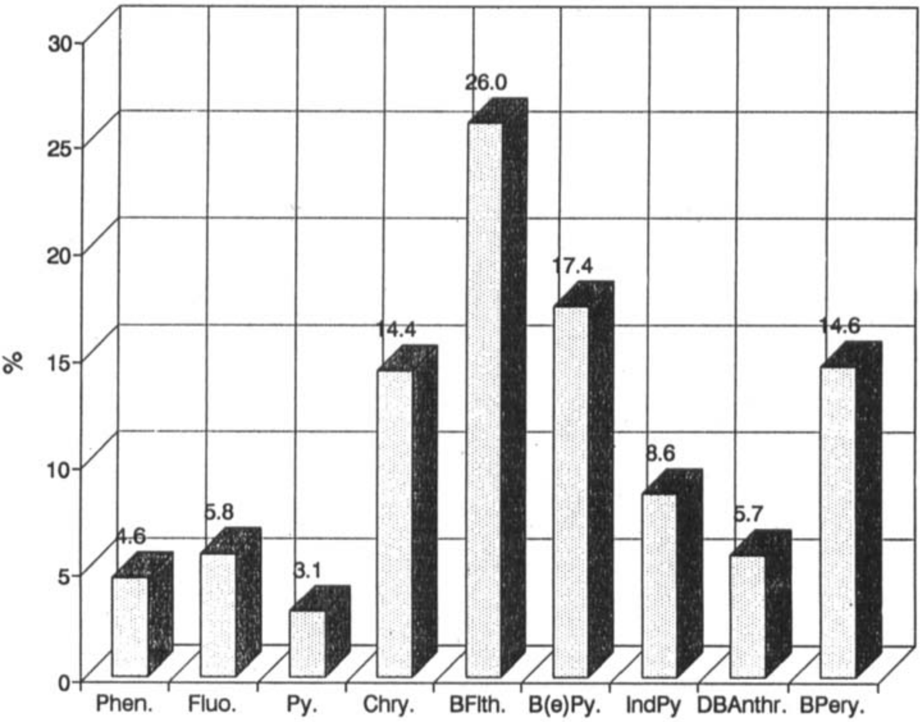

Figure 4 Average percent distribution of PAH in the HPLC-1 fraction of particulate organic matter sampled at Terra Nova Bay.

The chromatogram of Figure 2b which reports the HRGC-MS profile recorded during the analysis of the HPLC-2 fraction, reveals the presence of alkanoic acids methyl esters in the POM. The predominance of methyl esters of alkanoic acids, characterized by an even number of carbon atoms, was indicative of their biogenic origin, possibly arising from the presence of marine aerosols in the air samples.

The GC-MS profiles of Figure 5a, b and c relative to the fraction HPLC-3, CH_3CN and CH_3OH, respectively, provide evidence of the presence of anthropogenic air contaminants in the POM. All of them seem to be related to the manufacturing of plastic materials, and are highly soluble in water. Although phtalates and other benzenedicarboxlic acid esters were found in all the three fractions reported in Figure 5, the bulk of them was concentrated in the HPLC-3 fraction. As can be seen from the Figure, the distribution was dominated by di-(2-ethylhexyl)phtalate, di-*n*-butylphtalate and di-*iso*-butylphtalate, already reported as major constituents in water, pack-ice and sediment samples collected at Terra Nova Bay[9,12,13].

The most abundant species found in the CH_3CN fraction were alkyl phosphates. Until now, the presence of these contaminants in POM has been only reported in samples collected in heavy polluted airsheds[1]. Since alkyl phosphates are widely used as plasticizers, it is reasonable to think that they undergo the same dispersion processes as phtalates and, since they are soluble in water, they are also associated with marine aerosols. The same considerations made for the alkyl phosphates can be extended to 2- and 4-methyl-benzensulphonamides the use of which as antistatic products in the manufacturing of plastic polymers can somehow explain their presence in the chromatogram of Figure 5c.

Relative content of anthropogenic and biogenic tracers in the Particulate Organic Matter

The average percentage of contribution by the main classes of organic compounds to each one of the fractions in which the POM has been separated are displayed in Figure 6a, b, c and d, whereas the percentage of contribution of each fraction to the total content of organic material found in particulate matter is reported in Figure 7.

Data reported in these two Figures well reflect the composition of particulate matter, in that the variations from filter to filter are quite small from the absolute concentrations measured. By combining the information of all Figures, it is evident that the largest portion of particulate organic matter is represented by anthropogenic contaminants associated with production and/or manufacturing of plastic materials, whereas the contribution arising from combustion sources appears to be negligible. The biogenic contribution, which is restricted to part of the aliphatic fraction and to the alkanoic acids methyl esters, accounts only for about 30% of the entire organic material.

Although some differences are noticed with respect to the composition of the water and pack-ice samples determined at Terra Nova Bay, the predominance of phtalates (higher than 40% if we account for the contribution coming from the CH_3CN and CH_3OH fractions) and aliphatic components, coupled with the similarity in the distribution of organic components within these two fractions, leave little doubt that marine aerosols play a major role in determining the content of organic material associated with suspended particulate matter.

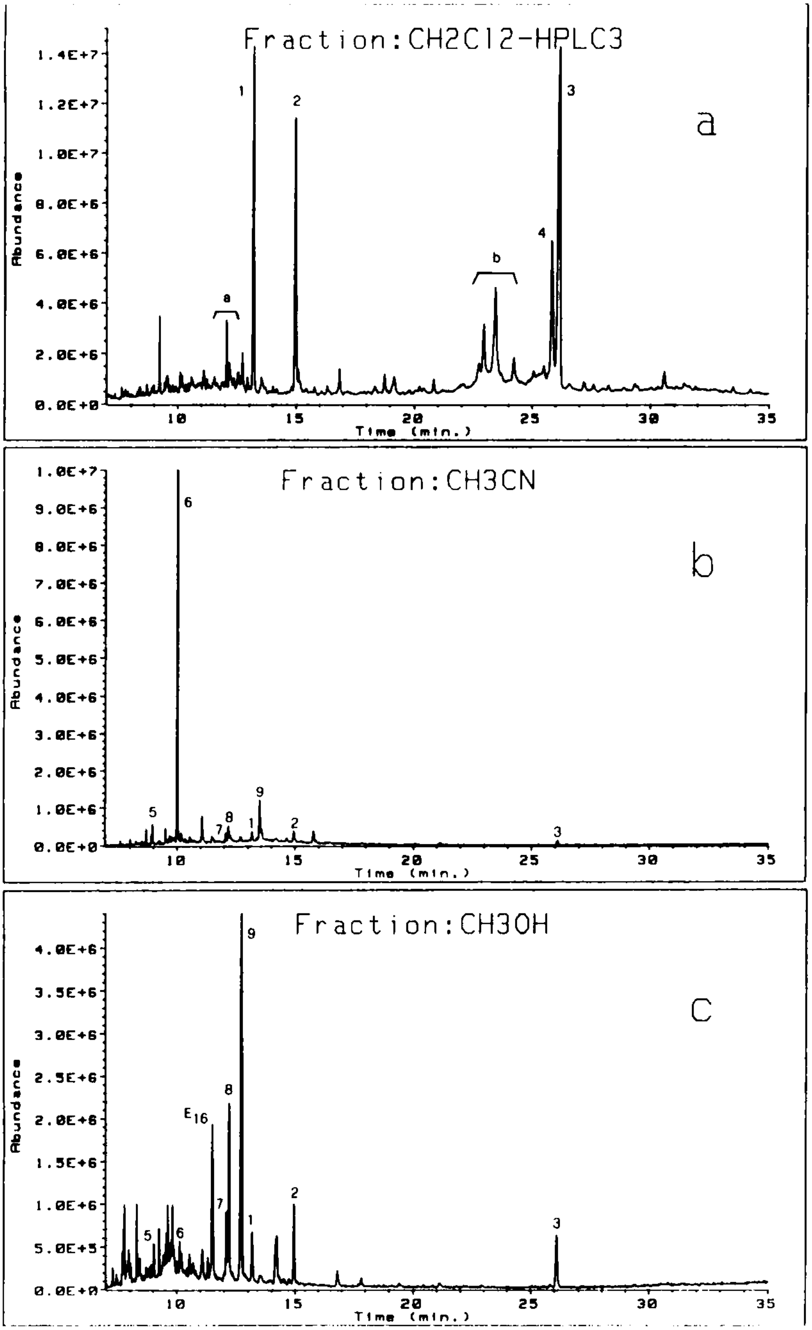

Figure 5 HRGC-MS profiles recorded during the analysis of a) the HPLC-3 fraction, b) the CH3CN fraction and c) the CH3OH fraction extracted from particulate organic matter sampled at Terra Nova Bay.
1) Di-*iso*-butyl phtalate; 2) Di-*n*-butyl phtalate; 3) Di-(2-ethylhexyl) phtalate, a) Dicarboxylic acid alkyl esters, b) Dicarboxylic acid alkyl esters; 4) 2-Ethylhexyl, diphenyl phosphate; 5) Butyl phosphate; 6) Butyl phosphate; 7) Alkyl phosphate; 8) 2-methyl- benzene sulphonamide; 9) 4-methyl-benzene sulphonamide; E16) Hexanoic acid methyl ester.

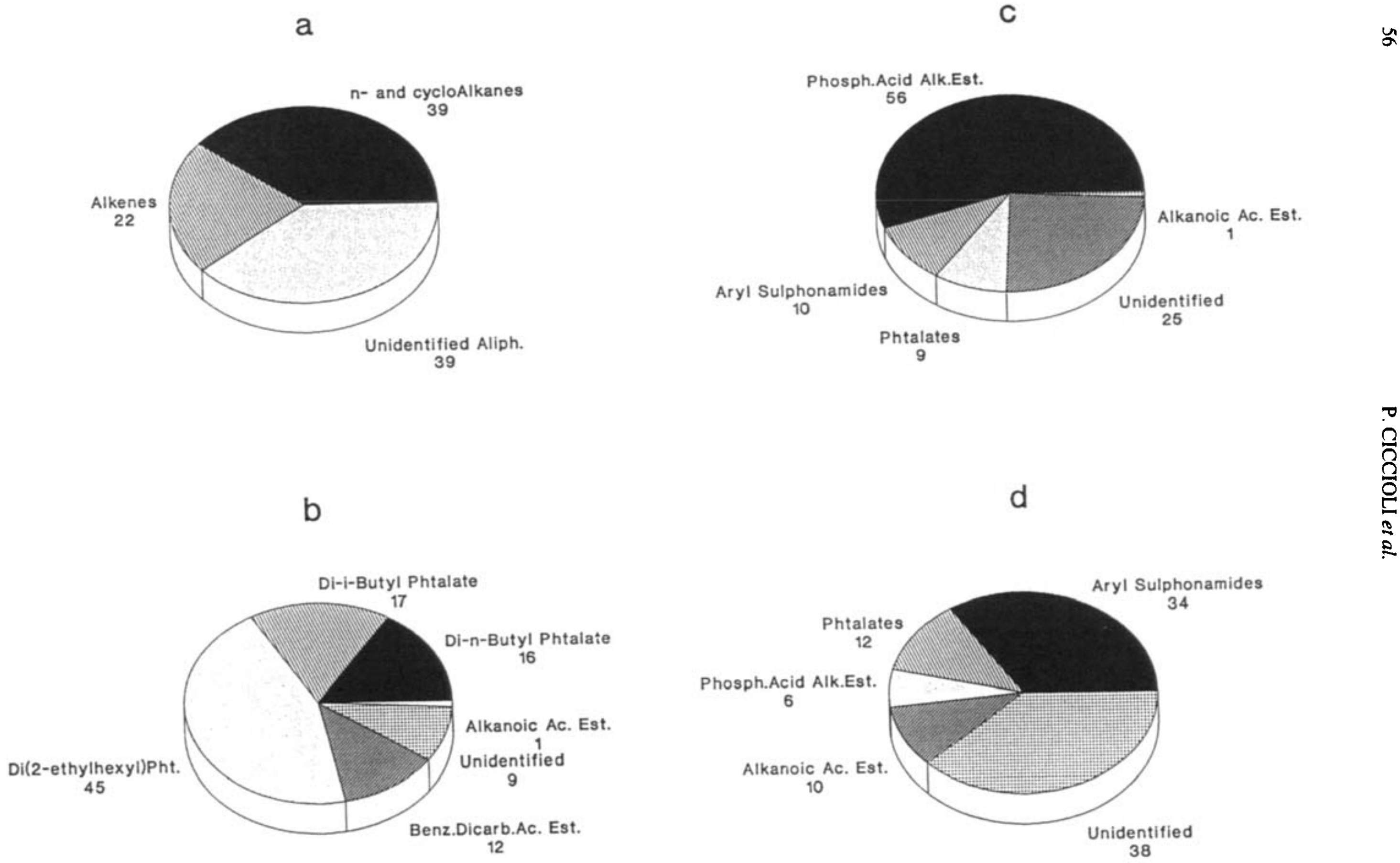

Figure 6 Percent distribution of the organic components in the various fractions extracted from particulate organic matter sampled at Terra Nova Bay: a) *n*-hexane, b) HPLC-3, c) CH3CN and d) CH3OH. For the distribution of PAH in fraction HPLC-1, see Figure 4.

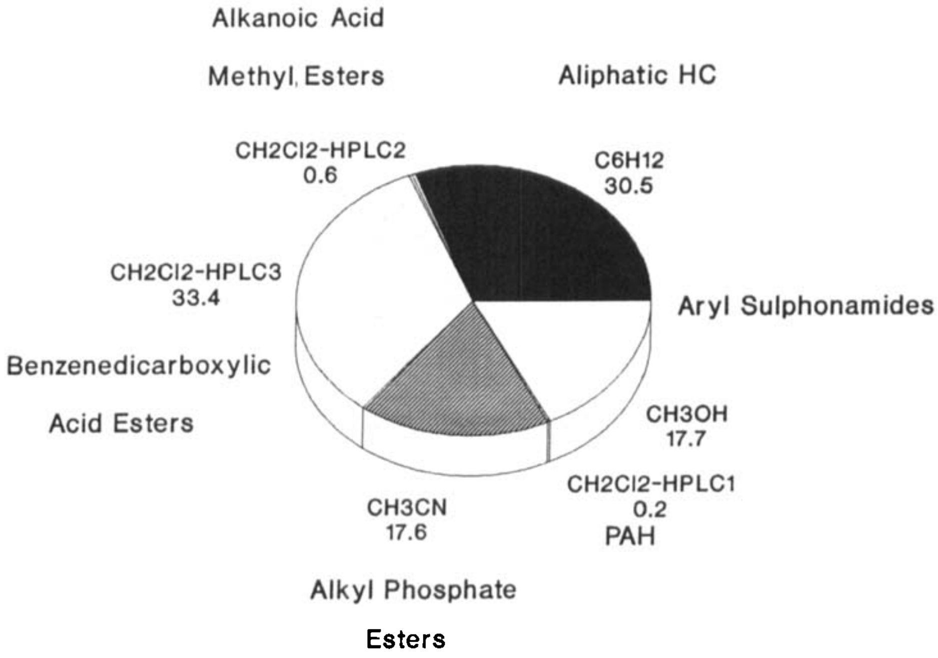

Figure 7 Average percent contribution of the various liquid chromatographic fractions to the total particulate organic matter sampled at Terra Nova Bay in Antarctica.

Since the direct influence of long-range transport of fine carbon particles containing PAH is negligible, it is fair to say that the main pathway through which anthropogenic pollution reaches Terra Nova Bay is through the marine environment.

Content of Particulate Organic Matter in the Terra Nova Bay station

Figure 8 reports the aerometric concentrations for the various classes of organic compounds detected during the monitoring campaign carried out from January to February 1991. As can be seen from the Figure, a similar trend is followed by the components associated with marine aerosols, whereas PAH seem to deviate somehow from this general pattern, showing high levels in the third week monitoring when wind velocities as high as 25 m/sec were blowing over Terra Nova Bay. If we look at the *n*-alkane profile recorded during the same period of time (see Figure 9), we can see that a drastic reduction in the anthropogenic contaminants is concurrent with the disappearance of the even-odd distribution characteristic of low molecular weight *n*-alkanes, whereas a value of the C.P.I. equal to 1 is reached for the components larger than C_{24}. Both effects seem to be consistent with a drastic decrease in the marine contribution, with respect to that associated with long-range transport of carbon particles containing PAH and *n*-alkanes from combustion.

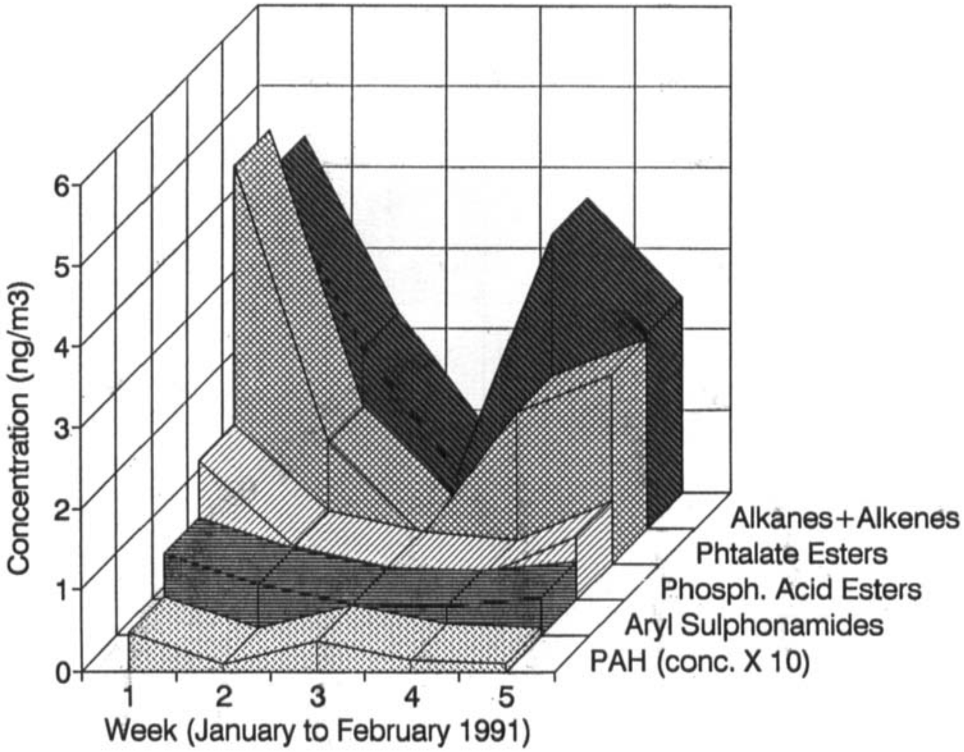

Figure 8 Aerometric concentrations of the main biogenic an anthropogenic indicators present in the particulate organic matter sampled from the first week of January to the first week of February 1991 at Terra Nova Bay.

CONCLUSIONS

From the observations made it appears that the main contribution to the Particulate Organic Matter sampled at Terra Nova Bay from January to February 1991, was derived from organic compounds of both natural and man-made origin associated with marine aerosols. This conclusion mainly relies on the information based on phtalate esters and PAH of man-made origin and *n*-alkanes of biogenic origin. Although such a conclusion is in agreement with what is presently known about the atmospheric aerosol present in Antarctica, more experiments are needed to verify the unexpected presence of alkyl phosphates and arylsulphonamides in particulate organic matter and to relate their presence to the marine aerosols present at Terra Nova Bay.

Acknowledgements

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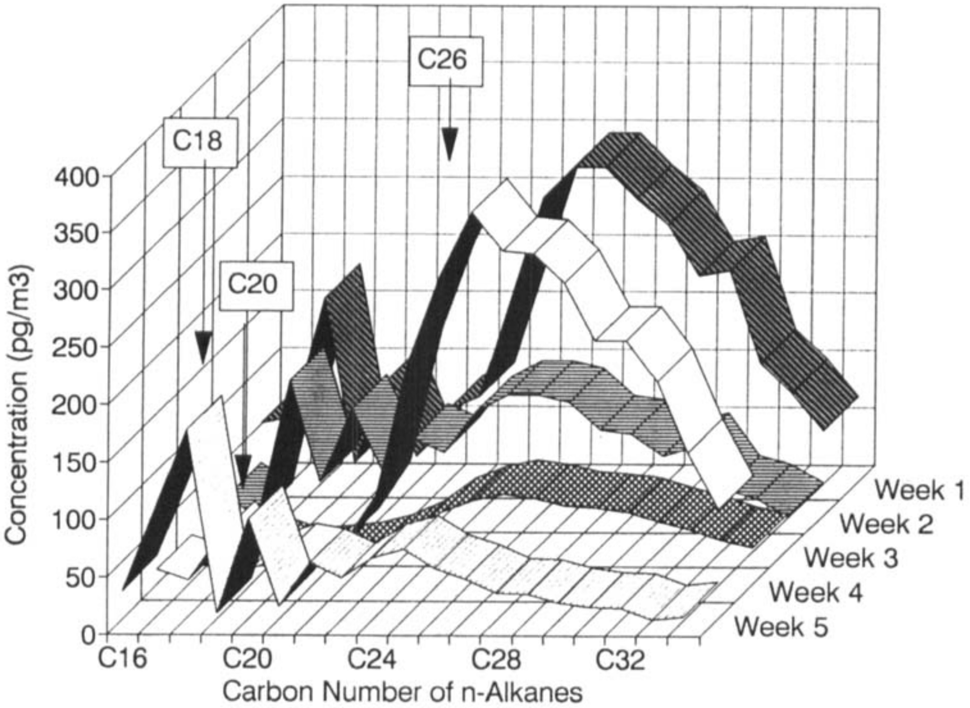

Figure 9 Aerometric concentrations of *n*-paraffins recorded at Terra Nova Bay. The sampling period is the same as that reported in Figure 8.

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