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### Marine Contribution to the Chemical Composition of Coastal and Inland Antarctic Snow

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## MARINE CONTRIBUTION TO THE CHEMICAL COMPOSITION OF COASTAL AND INLAND ANTARCTIC SNOW

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Biogenic and anthropogenic compounds such as n-alkanes, alcohols, aldehydes, alkylbenzenes and phthalates were measured in "fresh" snow and surface snow taken at different altitudes from Mt. Melbourne (near the coast of Terra Nova Bay, Antarctica) and Rennick Glacier (inland zone) during the 1995/96, 1996/97 and 1998/99 Italian Antarctic expeditions. Among n-alkanes, C<sub>16</sub>, C<sub>24</sub> and C<sub>28</sub> were identified in all samples as "markers" of Baia Terra Nova marine environment, evidencing the important contribution of marine aerosol to the chemical composition of snow even if collected in the inland zones of the continent. More interestingly, the enrichment ratios (Er) of organic compounds with respect to sodium ion concentration, confirmed that fine and hyperfine particles of the aerosol were rich in phthalates and non-volatile n-alkanes, trapped by natural surfactant matter, and were able to reach high altitudes and long distances from the coast according to the spray drop adsorption model (SDAM).

**Keywords:** Antarctica; snow; organic compounds; marine aerosol

### INTRODUCTION

The Antarctic region is remote from major sources of pollution and it is characterised by a very small human activity; this suggested that the type and level of chemical compounds found in Antarctic atmosphere could be an interesting tool for evaluating their origin and transport mechanism<sup>[1-5]</sup>. Recent studies pointed

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out the importance of the chemical composition of snow precipitation events in order to obtain a more detailed knowledge of Antarctic atmosphere composition<sup>[6–8]</sup>. Some researches<sup>[9]</sup>, although limited to surface and deep snow collected near the coast at different altitudes (Mt. Melbourne) during the 1993/94 expedition, evidenced the contribution of marine aerosol to snow content. As regards the inland zones, there are no data correlating the chemical composition of snow falls to sea spray.

In order to evaluate the role of air-sea exchange in the transport of biogenic and anthropogenic substances even at long distances, this investigation was extended to inland zones collecting snow samples at considerable distance from the coast. In addition “fresh” snow, that is collected as soon as possible after deposition or before environmental events that could alter its composition, was taken to find out any eventual relationship between snow and atmosphere composition. To this aim, during the 1995/96, 1996/97 and 1998/99 Italian Antarctic expeditions, a large number of snow samples were collected from the coastal zone (Mt. Melbourne) and from two inner zones (Rennick Glacier) and analysed.

## **EXPERIMENTAL**

### **Sampling sites**

The sampling stations for “fresh” snow and surface snow at different altitudes are indicated in Figure 1 and Table I.

The snow samples were collected after eliminating the top layer (about 5 cm) to avoid contamination of the sample. An aluminum scoop was used to collect a layer of snow approximately 5 cm thick. A total volume of about 40 liters for each sample was obtained.

### **Reagents and materials**

20 Liter stainless steel reservoirs (Inox Sabat, Bologna, Italy) were used for storage of snow samples. Two reservoirs were used for each sample.

Solvents (n-hexane, toluene, ethyl acetate, acetone, methylene chloride) were all “organic residue analysis” grade purchased from Baker (Holland) and distilled three times before use.

Standard organic compounds are commercially available from Supelco (Bellefonte, U.S.A.) and Alltech (Deerfield, U.S.A.).

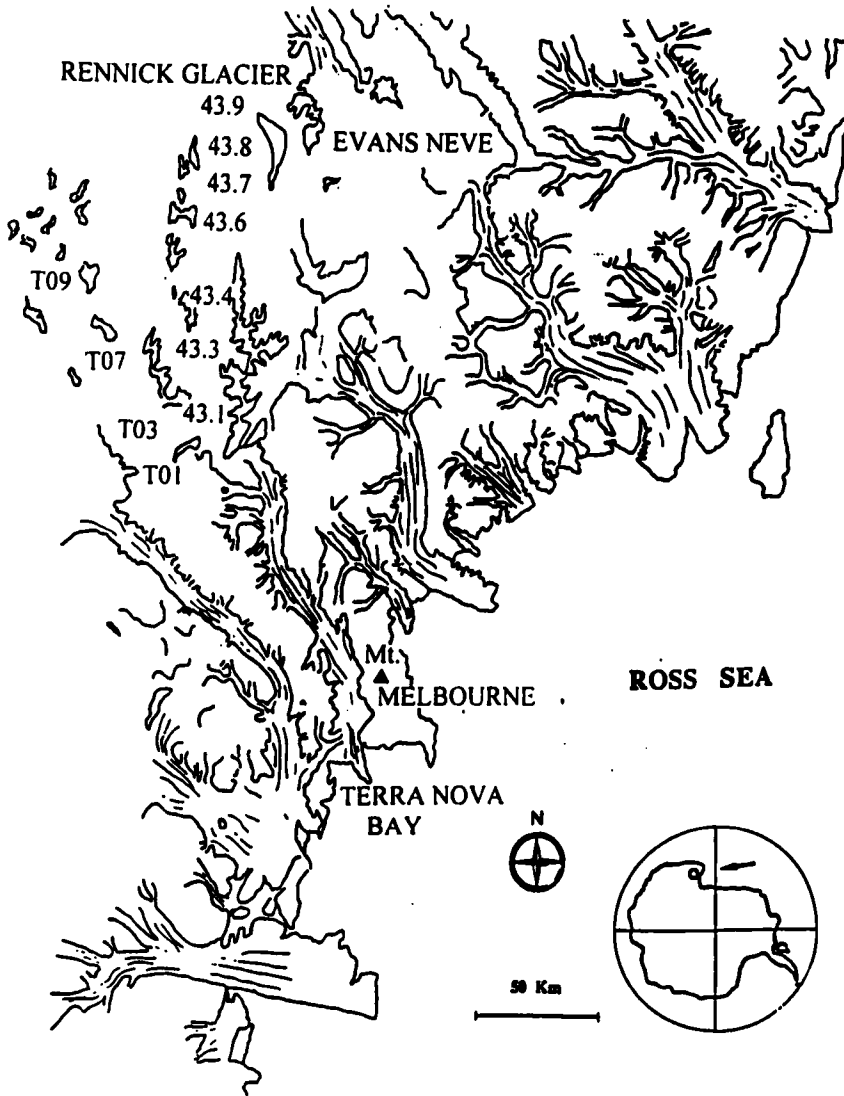


FIGURE 1 Snow sampling points of the 1995/96, 1996/97 and 1998/99 Italian Antarctic expeditions

Anhydrous sodium sulphate was heated at 450°C for 12 hours and then kept at 120°C until use. All apparatus was cleaned before use by repeatedly washing with chromic and concentrated sulphuric acid mixture, purified water, acetone, methylene chloride and n-hexane.

TABLE I Sampling stations coordinates

Rennick Glacier (Expedition 1995/96)	Lat. S	Long E
T01	73° 45.128'	160° 15.222'
T03	73° 30.222'	160° 00.124'
T07	73° 00.056'	159° 30.032'
T09	72° 45.236'	159° 14.936'
Rennick Glacier (Expedition 1996/97)	Lat. S	Long E
SN-43.1	73° 19.51'	162° 29.54'
SN-43.3	73° 04.66'	162° 38.39'
SN-43.4	72° 55.89'	162° 38.61'
SN-43.6	72° 40.86'	162° 44.90'
SN-43.7	72° 33.47'	162° 46.63'
SN-43.8	72° 26.10'	162° 45.28'
SN-43.9	72° 19.49'	162° 26.26'
Mt. Melbourne (Expeditions 1996/97 and 1998/99)	Lat. S	Long E
SN-4A	74° 31.815'	164° 45.942'
SN-4B	74° 28.328'	164° 46.369'
SN-4C	74° 25.930'	164° 44.979'
SN-4D	74° 23.810'	164° 41.871'
SN-4DE	74° 22.260'	164° 40.390'
SN-4E	74° 21.219'	164° 41.000'

### Fluorescence spectra

The normalized fluorescence intensity  $I_n$  (defined as  $I_{\max}/I_{\text{Raman}} \times 100$ , in which  $I_{\max}$  is the maximum intensity approximately at  $440 \pm 20$  nm,  $I_{\text{Raman}}$  is the Raman scattering peak intensity) of the surfactant fluorescent organic matter with marine humic character, was measured with apparatus and techniques described elsewhere<sup>[10]</sup>.

### Sodium ion analysis

The sodium ion concentrations in Antarctic snow were determined by Ion Chromatography using a Dionex 4500i ion chromatograph with conductivity detector (CDM-2) and eluent degas module (EDM-2). A Dionex CS10 column

(eluent = 1.0 ml/min of 20 mM HCl + 0.5 mM diaminopropionic acid) followed by a CMMS-2 micromembrane suppressor was used for cation separation<sup>[11]</sup>. Chromatographic data acquisition and elaboration were performed by a Dionex AI-450 integration software.

### **Analysis of organic compounds**

Only the internal part of each sample, which did not come in contact with the walls of the containers was analyzed to avoid contamination. The samples were melted at room temperature in a glass column (2 m length, 14 cm I.D.), kept under high purity grade nitrogen flow to avoid contamination of the sample from the laboratory atmosphere.

The extraction of the organic compounds from melted snow was carried out by a replicated extractant enrichment method, especially designed for Antarctic aqueous samples<sup>[12]</sup>. Fractionation of the organic extracts was performed as previously described<sup>[13]</sup> and the recovery of the entire analytical procedure was shown elsewhere<sup>[9]</sup>. The analyses were repeated five times for each sample.

### **Derivatization of aldehydes and alcohols**

The fraction containing aldehydes was derivatized by using O-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine hydrochloride (PFBHA) to obtain the corresponding oximes (PFBO)<sup>[14]</sup>; the alcohols were transformed into their trimethylsilyl derivatives<sup>[15]</sup>.

### **HRGC and GC-MS analysis**

GC and GC-MS analyses were performed on Varian 3400 (Palo Alto, U.S.A.) gas chromatographs, one equipped with a Finnigan ion trap detector and the other with FID. The injection was made by using a Septum Programmable Injector (SPI, Varian) according to the following temperature program: injection at 40°C then a rapid increase to 300°C. The column temperature program was: 40°C for 1 min., then linear increase to 300°C at 4°C/min., and finally isotherm at 300°C for 15 min. Supelco PTE-5 capillary columns (30m, 0.25mm ID, 0.25 µm thickness) were used; carrier gas: high purity grade helium. Electron impact mass spectra were obtained at 70 eV of ionization energy. All peaks were identified by using gas chromatographic Van den Dool and Kratz<sup>[16]</sup> indices with eight n-alkanes as standards (C<sub>8</sub>, C<sub>12</sub>, C<sub>16</sub>, C<sub>20</sub>, C<sub>24</sub>, C<sub>28</sub>, C<sub>32</sub>, C<sub>34</sub>) and a reference

calibration table. Mass spectra were compared with those reported in the N.B.S. library and in a second library made in our laboratory on ITD.

The quantities of organic compounds were determined by comparing their peak areas with the nearest n-alkane peaks as standards.

### **Blanks and detection limits**

Precautions were taken to avoid contamination in the laboratory.

Blanks were performed on highly purified water (40 liters) inserted in two stainless steel reservoirs in Antarctica, frozen at  $-30^{\circ}\text{C}$  and carried to our laboratory together with snow samples. As shown in a previous paper<sup>[9]</sup> blank concentration of organic compounds were  $0.9 \pm 0.2$  ng/l for phthalates, 0.7–0.9 ng/l for alkylbenzenes and 0.7 – 1.9 ng/l for aldehydes and n-alkanes.

Detection limits of 2 ng/l for n-alkanes, aldehydes and alcohols and 1 ng/l for alkylbenzenes and phthalates were reported in the tables in order to account for their blank concentrations.

## **RESULTS AND DISCUSSION**

### **Composition of “fresh” snow collected near Terra Nova Bay (Mt. Melbourne)**

Apparently, this is one of the first study on “fresh” snow at Terra Nova Bay. This new approach was presented in order to evaluate possible differences in the chemical composition between “fresh” and surface snow and to evidence the marine contribution to the transport of selected organic compounds found in the snow.

Table II reports the concentrations (ng/l) of a large number of organic compounds, extractable with n-hexane, measured in the samples taken on Mt. Melbourne, just after a snow-fall, during the 1996/97 and 1998/99 Italian Antarctic expeditions. The snow was sampled along a transect at increasing altitudes, from 360 up to 2670 meters (a.s.l.).

The results show substantially the same chemical composition found in surface snow, sea-water and pack-ice taken during previous campaigns<sup>[13,17,18]</sup>. In fact, little differences observed for n-alkanes and phthalates are not significant.

TABLE II Organic compounds in "fresh" snow samples taken near the coast on Mt. Melbourne (concentration ng/l)

Sample label Height above sea level	Expedition 1996/97					Expedition 1998/99				
	SN-4A (360 m)	SN-4B (710 m)	SN-4C (1188 m)	SN-4D (1490 m)	SN-4DE (2280 m)	SN-4E (2670 m)	SN-4A (360 m)	SN-4C (1188 m)	SN-4DE (280 m)	
<b>n-Alkanes</b>										
n-C8	bdl	2 <sup>a</sup>	3 ± 1	bdl	2 <sup>a</sup>	bdl	4 ± 1	6 ± 1	6 ± 1	
n-C10	10 ± 2	8 ± 2	5 ± 1	6 ± 1	3 ± 1	8 ± 2	3 ± 1	bdl	14 ± 3	
n-C12	3 ± 1	5 ± 1	19 ± 4	2 <sup>a</sup>	3 ± 1	3 ± 1	9 ± 2	23 ± 5	10 ± 2	
n-C13	2 <sup>a</sup>	bdl	bdl	bdl	2 <sup>a</sup>	bdl	bdl	bdl	bdl	
n-C14	6 ± 1	3 ± 1	3 ± 1	2 <sup>a</sup>	2 <sup>a</sup>	5 ± 1	2 <sup>a</sup>	2 <sup>a</sup>	2 <sup>a</sup>	
n-C15	5 ± 1	2 <sup>a</sup>	3 ± 1	3 ± 1	3 ± 1	4 ± 1	2 <sup>a</sup>	2 <sup>a</sup>	6 ± 1	
n-C16	24 ± 5	31 ± 6	15 ± 3	21 ± 4	10 ± 2	7 ± 1	13 ± 3	18 ± 4	31 ± 6	
n-C17	7 ± 1	3 ± 1	2 <sup>a</sup>	3 ± 1	3 ± 1	4 ± 1	8 ± 2	2 <sup>a</sup>	9 ± 2	
n-C18	4 ± 1	4 ± 1	3 ± 1	3 ± 1	2 <sup>a</sup>	3 ± 1	9 ± 2	5 ± 1	10 ± 2	
n-C19	2 <sup>a</sup>	3 ± 1	3 ± 1	3 ± 1	3 ± 1	3 ± 1	9 ± 2	4 ± 1	8 ± 2	
n-C20	6 ± 1	3 ± 1	3 ± 1	3 ± 1	3 ± 1	3 ± 1	3 ± 1	6 ± 1	7 ± 1	
n-C21	3 ± 1	2 <sup>a</sup>	3 ± 1	2 <sup>a</sup>	2 <sup>a</sup>	3 ± 1	12 ± 2	5 ± 1	5 ± 1	
n-C22	6 ± 1	3 ± 1	7 ± 1	4 ± 1	5 ± 1	3 ± 1	31 ± 6	3 ± 1	4 ± 1	
n-C23	3 ± 1	4 ± 1	3 ± 1	2 <sup>a</sup>	3 ± 1	3 ± 1	19 ± 4	24 ± 5	4 ± 1	
n-C24	26 ± 3	35 ± 4	29 ± 3	12 ± 1	8 ± 1	8 ± 1	42 ± 4	45 ± 5	10 ± 1	



Sample label Height above sea level	Expedition 1998/99						Expedition 1998/99					
	SN-4A (360 m)	SN-4B (710 m)	SN-4C (1188 m)	SN-4D (1490 m)	SN-4DE (2280 m)	SN-4E (2670 m)	SN-4A (360 m)	SN-4C (1188 m)	SN-4A (360 m)	SN-4E (2670 m)	SN-4DE (280 m)	SN-4DE (280 m)
n-C25	7 ± 1	6 ± 1	3 ± 1	3 ± 1	3 ± 1	3 ± 1	21 ± 2	34 ± 3	3 ± 1	3 ± 1	5 ± 1	5 ± 1
n-C26	12 ± 1	8 ± 1	5 ± 1	3 ± 1	4 ± 1	2 <sup>a</sup>	34 ± 3	136 ± 14	2 <sup>a</sup>	2 <sup>a</sup>	7 ± 1	7 ± 1
n-C27	10 ± 1	8 ± 1	6 ± 1	3 ± 1	3 ± 1	2 <sup>a</sup>	32 ± 3	126 ± 13	2 <sup>a</sup>	2 <sup>a</sup>	6 ± 1	6 ± 1
n-C28	18 ± 2	12 ± 1	11 ± 1	7 ± 1	6 ± 1	8 ± 1	88 ± 9	147 ± 15	8 ± 1	8 ± 1	15 ± 2	15 ± 2
n-C29	10 ± 2	10 ± 2	9 ± 2	4 ± 1	3 ± 1	2 <sup>a</sup>	24 ± 5	136 ± 27	2 <sup>a</sup>	2 <sup>a</sup>	5 ± 1	5 ± 1
n-C30	12 ± 2	9 ± 2	8 ± 2	4 ± 1	5 ± 1	2 <sup>a</sup>	17 ± 3	135 ± 27	2 <sup>a</sup>	2 <sup>a</sup>	6 ± 1	6 ± 1
n-C31	9 ± 2	10 ± 2	10 ± 2	4 ± 1	3 ± 1	2 <sup>a</sup>	14 ± 3	108 ± 22	2 <sup>a</sup>	2 <sup>a</sup>	7 ± 1	7 ± 1
n-C32	10 ± 2	12 ± 2	17 ± 3	7 ± 1	4 ± 1	2 <sup>a</sup>	12 ± 2	98 ± 20	2 <sup>a</sup>	2 <sup>a</sup>	15 ± 3	15 ± 3
Total n-alkanes ( <sup>b</sup> )	191	176	168	93	75	68	404	1001	68	68	190	190
Odd/even (n-C15 + n-C32)	0.46	0.38	0.41	0.36	0.53	0.63	0.56	0.74	0.63	0.52	0.52	0.52
Squalene	53 ± 11	14 ± 3	11 ± 2	16 ± 3	9 ± 2	2 <sup>a</sup>	187 ± 37	340 ± 68	2 <sup>a</sup>	2 <sup>a</sup>	74 ± 15	74 ± 15
Total aldehydes (C9 – C11)	61	35	49	32	27	23	56	81	23	23	97	97
Total alcohols (C10 – C16)	16	11	9	8	8	8	31	26	8	8	19	19
Total alkylbenzenes (C2 – C4)	225	220	211	191	171	167	413	525	167	167	555	555
Total phthalates	171	128	110	88	56	40	412	288	40	40	329	329

a. detection limit; bdl = below detection limit

b. detection limit values are not included in the sum

Particular care is given to the odd/even ratio for n-alkanes. It was much less than 1 for the range n-C<sub>15</sub> ÷ n-C<sub>32</sub> and this value is indicative of their biogenic origin<sup>[19]</sup>. Moreover, in all samples n-alkanes have a distribution pattern strongly dominated by C<sub>16</sub>, C<sub>24</sub> and C<sub>28</sub>, in agreement with that obtained from previously collected snow<sup>[9]</sup>. It's important to remark that this composition of n-alkanes is typical of marine environment at Terra Nova Bay and the discovery of this particular distribution in the snow confirms the biogenic origin of these compounds. The n-alkanes may be, therefore, used as "markers" of marine contribution to the chemical composition of snow.

The concentration values reported in Table II are of the same order of magnitude than those measured in surface snow<sup>[8,9]</sup>. However, the comparison of the samples collected during the 1996/97 expedition with those of the 1998/99 expedition, shows some differences. The concentration of organic compounds in the 1996/97 samples decreases as altitude increases and their content is lower with respect to the latter samples. It should be noted that this trend was not evidenced during previous expeditions; it appears, therefore, casual and could be explained by the variation of climatic conditions, by the more or less presence of marine components and by wind direction. A similar variability was also noted by other authors for the concentrations of anionic and cationic inorganic compounds<sup>[20]</sup>.

TABLE III Mean percentage of organic compound classes found in snow samples collected on Mt. Melbourne and Rennick Glacier

<i>Organic compounds</i>	<i>Mt. Melbourne</i>		<i>Rennick Glacier</i>	
	<i>surface snow</i>	<i>fresh snow</i>	<i>surface snow</i>	<i>fresh snow</i>
n-Alkanes	41	30	30	16
Other aliphatics	30	22	23	27
Aldehydes and alcohols	5	6	11	7
Alkylbenzenes	13	26	19	41
Phthalates	11	16	17	9

On the basis of these results, it appears interesting to compare the mean percentages of the classes of organic compounds relative to surface snow collected on Mt. Melbourne through several years with those of "fresh" snow. Table III shows such values for surface snow (1990/91 and 1993/94 expeditions) and "fresh" snow (1996/97 and 1998/99 expeditions), respectively. In the class indicated as "other aliphatics", branched and cyclic alkanes and squalene were enclosed. The percentage of alkylbenzenes increases going from surface snow (13%) to "fresh" snow (26%). This behaviour can be explained considering that

alkylbenzenes are involved in post-depositional processes, such as loss of more volatile compounds<sup>[21]</sup>.

### **Origin of organic compounds found in “fresh” snow (Mt. Melbourne)**

Organic compounds present in snow samples collected on Mt. Melbourne may derive from various sources (marine aerosol, terrestrial material and so on). The presence of biogenic compounds, such as aldehydes, squalene and n-alkanes with the prevalence of C<sub>16</sub>, C<sub>24</sub>, C<sub>28</sub> indicates that marine matrices make up a large part of “fresh” snow composition. The transfer of these compounds from aqueous environment to the atmosphere and, successively, to snow precipitations could be explained considering their possible association with marine aerosol or their direct transport in gaseous form. The latter mechanism involves compounds both transferred in the gas-phase owing to their high volatility and/or stripped by air bubbles during marine aerosol formation. These compounds distribute quite homogeneously in Antarctic atmosphere, independently of altitude and distance from the coast. For example the concentration of gaseous alkylbenzenes is comparable in all the snow samples taken at different altitudes on Mt. Melbourne. However a large number of compounds found in snow samples are exclusively associated with liquid aerosol, as previously shown from laboratory experiments<sup>[22]</sup>. In particular, n-alkanes with carbon atom number equal to or more than 16 and phthalates are completely transferred from salt solutions to air through aerosol formation, even at usual laboratory temperatures (20°C). In Antarctic climatic conditions, where temperatures lower than 0°C can be observed even in the summer period, the number of organic compounds associated with marine aerosol is probably higher than that above indicated. Such hypothesis has been confirmed by the experiments of Ciccioli *et al.*<sup>[5]</sup> on aerosol samples collected at Terra Nova Bay. An evidence of marine aerosol contribution to the snow composition is the high level of NaCl found in all the examined samples. However, the concentration of n-alkanes and phthalates in the snow is different from that measured in sea-water<sup>[18]</sup> and it depends on distance from the coast and altitude above sea level (see Table II). These results can be explained considering the different composition of marine aerosol<sup>[5]</sup> with respect to sea-water and its variability depending on the distance from the coast.

For a better understanding of this phenomenon, it's necessary to calculate the ratios between the concentration of n-alkanes and phthalates in snow and sea-water samples with respect to the concentration of sodium ion in the same matrices.

More exactly, we define the enrichment ratio (Er) of compound X using the expression:

$$E_{\text{Na}^+}(X) = \frac{([X]/[\text{Na}^+])_{\text{snow}}}{([X]/[\text{Na}^+])_{\text{seawater}}}$$

Since sodium ion is not enriched during the aerosolization process, its concentration was taken as a quantitative index of marine aerosol content in the snow. The enrichment ratios for n-alkanes (C<sub>14</sub>-C<sub>32</sub>) and phthalates were obtained using their mean concentrations. The ratios between the concentration of n-alkanes and phthalates in sea-water and that of sodium ion are  $1.225 \times 10^{-8}$  and  $4.396 \times 10^{-8}$  respectively<sup>[9]</sup>.

Table IV shows the values calculated for "fresh" snow collected during the campaign 1998/99 because sodium ion concentrations are not available for the samples collected during the 1996/97 expedition.

TABLE IV Enrichment ratios with respect to Na<sup>+</sup> concentration for n-alkanes and phthalates in "fresh" snow (Mt. Melbourne, expedition 1998/99)

Sample label	Height above sea level	SN-4A (360 m)	SN-4C (1188 m)	SN-4DE (2670 m)
[Na <sup>+</sup> ]	(μg/l) <sup>a</sup>	5226	1571	186
n-Alkanes		6367	75343	84611
Phthalates		1793	4170	40236

a. sodium concentration in "fresh" snow samples.

We can appreciate that an hyperbolic like function, which reminds the trend expected by spray drop adsorption model (SDAM)<sup>[23]</sup>, fits well the data for phthalates. Taking into account that the increases of the surface/volume ratio as a function of the diminution of the sphere radius is described by a hyperbolic trend, the present model predicts that in a similar way the concentration of surface material, adsorbed on the drop surface after its formation, increases with respect to that enclosed in the inner drop<sup>[24]</sup>. Therefore the surfactant concentration at the surface increases as the diameter of the drop decreases. The fine particles of marine aerosol, mainly constituted by surfactant material, reach even high altitude<sup>[25]</sup> and can be considered responsible for the enrichment of phthalates with increasing the altitude above sea-level.

In addition, the greater content of n-alkanes found in snow with respect to phthalates could be attributed to their higher percentage in sea-water and to their high hydrophobicity which favours their adsorption on the natural fluorescent surfactant matter, as shown by laboratory studies<sup>[22]</sup>. The fluorescence intensity measures (In), which can be considered as an index of the concentration of fulvic substances, are in agreement with the above suggested model. According to this model, it could be predicted an enrichment of surfactant matter in fine and hyper-

fine marine aerosol particles as shown by the In enrichment ratios ( $E_{In}$ ) in respect to sodium ion reported in Table V. The  $E_{In}$  was calculated using the procedure previously described:

$$E_{In} = \frac{(In/[Na^+])_{snow}}{(In/[Na^+])_{seawater}}$$

The presence of this material confirms 1) the marine aerosol contribution to the chemical composition of the snow, 2) the validity of SDAM on the basis of that the surfactant matter is concentrated in fine and hyperfine aerosol particles and 3) the enrichment of n-alkanes which don't show surface active properties but can interact with surfactants and follow the same fate.

TABLE V Normalized fluorescent intensity (In) and enrichment ratios of the fluorescent material ( $E_{In}$ ) with respect to  $Na^+$  concentration in "fresh" snow (Mt. Melbourne, expedition 1998/99)

<i>Sample label Height above sea level</i>	<i>SN-4A (360 m)</i>	<i>SN-4C (1188 m)</i>	<i>SN-4DE (2670 m)</i>
In	18.81	17.01	17.31
$E_{In}$	1308	3934	33833

### Composition of surface snow and "fresh" snow collected in the inland zones of Antarctica

In order to verify the marine contribution to the transport of organic compounds from the coast towards the inner zones of Antarctica, snow samples collected on Rennick Glacier during several Italian expeditions were studied.

Surface snow was taken during the 1995/96 expedition at different altitudes, from 2210 and 1860 meters (a.s.l.) (sampling points T01-T09 in Figure 1) and the concentrations of biogenic and anthropogenic organic compounds are shown in Table VI.

No difference was observed between the chemical composition of Mt. Melbourne and Rennick Glacier samples as regards the compounds extractable with n-hexane.

Typical trends were not observed for the concentrations of organic compounds with increasing the distance from the coast and altitude. However, it should be noted that sampling points lie in a transept which doesn't follow the same development direction of the glacier; in addition, it's not exactly known if these samples are referred to a single event or to several snowfalls occurred in different periods. More interestingly, the "markers"  $C_{16}$ ,  $C_{24}$  and  $C_{28}$  were the most abundant compounds among n-alkanes and the odd/even carbon number ratio was much lower than one, pointing out a biogenic origin of such chemicals. The data shown in Table VI evidence a significant marine contribution to the chemical composition of snow collected far away from the sea.

TABLE VI Organic compounds in surface snow samples taken on Rennick Glacier, expedition 1995/96 (concentration ng/l)

<i>Sample label</i>	<i>T01</i>	<i>T03</i>	<i>T07</i>	<i>T09</i>
<i>Height above sea level</i>	<i>(1860 m)</i>	<i>(2010 m)</i>	<i>(2260 m)</i>	<i>(2250 m)</i>
<i>Distance from the coast</i>	<i>(130 Km)</i>	<i>(150 Km)</i>	<i>(190 Km)</i>	<i>(240 Km)</i>
Total n-alkanes (C12 – C32)	118	130	136	128
Odd/even (n-C15 + n-C32)	0.44	0.58	0.56	0.51
Squalene	52 ± 10	8 ± 2	22 ± 4	38 ± 8
Total aldehydes (C9 – C11)	26	27	36	33
Total alcohols (C10 – C16)	10	29	27	6
Total alkylbenzenes (C2 – C4)	70	63	95	108
Total phthalates	76	112	37	69

The same compounds identified in surface snow are also present in “fresh” snow (see Table VII) collected during the successive expedition on Rennick Glacier as far as 270 Km from the coast (see points 43.1 – 43.9, Figure 1). In the latter case, sampling was effected as soon as possible after a large snowfall. Data concerning shape, size and structure of snow crystals confirmed that it was not effected by post-depositional events<sup>[26]</sup>. The composition of n-alkanes is the same already found in all the coastal and inland samples examined up to day, where it was noted the predominance of markers C<sub>16</sub>, C<sub>24</sub> and C<sub>28</sub> and an odd/even ratio much lower than one. These results demonstrate the marine origin of the compounds identified in “fresh” snow samples collected as far as 270 km from the coast, even if several compounds are present at blank concentrations in the SN-43.8 and SN-43.9 samples. For this reason the concentration of total n-alkanes does not include the values of such compounds and the odd/even ratios have not been reported for the latter two samples.

These data show that the concentration of most organic compounds decreases as the distance from the coast increases and altitude decreases. This trend is similar to that observed for sodium ion, which represent the marine aerosol quantity in the snow (see Table VII). A quite difference behaviour is observed for alkylbenzenes whose concentration is high and substantially the same in all samples. The maximum concentration of organic compounds was found in the snow taken at 2210 meters a.s.l., in agreement with the results obtained by Udisti et al.<sup>[20]</sup> for inorganic compounds. This behaviour can be explained taking into account the contribution of wet air masses coming from the sea which could ascend the Campbell Glacier and meet the cold and dry air masses of the plateau at the maximum altitude, giving rise to a snowfall enriched in marine organic compounds. Beyond such altitude, snow resulted poorer and poorer in compounds associated with marine aerosol.

TABLE VII Concentration of sodium ion ( $\mu\text{g/l}$ ) and organic compounds (ng/l) in "fresh" snow taken on Rennick Glacier, expedition 1996/97\*

	SN 43.1 (2210 m) (150 Km)	SN 43.3 (1990 m) (170 Km)	SN 43.4 (1890 m) (190 Km)	SN 43.6 (1710 m) (2200 Km)	SN 43.7 (1600 m) (2400 Km)	SN 438 (1490 m) (260 Km)	SN 43.9 (1350 m) (270 Km)
[Na <sup>+</sup> ] ( $\mu\text{g/l}$ )	6580	1363	498	611	260	35	26
n-Alkanes							
n-C8	bdl	2 <sup>a</sup>	bdl	bdl	2 <sup>a</sup>	bdl	2 <sup>a</sup>
n-C10	3 $\pm$ 1	2 <sup>a</sup>	3 $\pm$ 1	2 <sup>a</sup>	4 $\pm$ 1	3 $\pm$ 1	3 $\pm$ 1
n-C12	bdl	2 <sup>a</sup>	2 <sup>a</sup>	bdl	2 <sup>a</sup>	2 <sup>a</sup>	2 <sup>a</sup>
n-C13	bdl	bdl	3 $\pm$ 1	bdl	bdl	2 <sup>a</sup>	bdl
n-C14	3	3	3 $\pm$ 1	3 $\pm$ 1	3 $\pm$ 1	3 $\pm$ 1	2 <sup>a</sup>
n-C15	2 <sup>a</sup>	2 <sup>a</sup>	3 $\pm$ 1	3 $\pm$ 1	3 $\pm$ 1	2 <sup>a</sup>	3 $\pm$ 1
n-C16	14 $\pm$ 3	8 $\pm$ 2	10 $\pm$ 2	8 $\pm$ 2	11 $\pm$ 2	9 $\pm$ 2	7 $\pm$ 1
n-C17	2 <sup>a</sup>	2 <sup>a</sup>	2 <sup>a</sup>	3 $\pm$ 1	2 <sup>a</sup>	2 <sup>a</sup>	2 <sup>a</sup>
n-C18	3 $\pm$ 1	3 $\pm$ 1	3 $\pm$ 1	3 $\pm$ 1	2 <sup>a</sup>	2 <sup>a</sup>	3 $\pm$ 1
n-C19	2 <sup>a</sup>	2 <sup>a</sup>	2 <sup>a</sup>	3 $\pm$ 1	2 <sup>a</sup>	3 $\pm$ 1	2 <sup>a</sup>
n-C20	2 <sup>a</sup>	3 $\pm$ 1	3 $\pm$ 1	3 $\pm$ 1	2 <sup>a</sup>	2 <sup>a</sup>	3 $\pm$ 1
n-C21	2 <sup>a</sup>	3 $\pm$ 1	2 <sup>a</sup>	2 <sup>a</sup>	3 $\pm$ 1	2 <sup>a</sup>	2 <sup>a</sup>
n-C22	6 $\pm$ 1	3 $\pm$ 1	4 $\pm$ 1	3 $\pm$ 1	3 $\pm$ 1	3 $\pm$ 1	3 $\pm$ 1
n-C23	3 $\pm$ 1	2 <sup>a</sup>	3 $\pm$ 1	2 <sup>a</sup>	2 <sup>a</sup>	2 <sup>a</sup>	2 <sup>a</sup>
n-C24	8 $\pm$ 1	10 $\pm$ 1	6 $\pm$ 1	7 $\pm$ 1	6 $\pm$ 1	5 $\pm$ 1	6 $\pm$ 1

Sample label Height above sea level Distance from the sea	SN 43.1 (2210 m) (150 Km)	SN 43.3 (1990 m) (170 Km)	SN 43.4 (1890 m) (190 Km)	SN 43.6 (1710 m) (2200 Km)	SN 43.7 (1600 m) (2400 Km)	SN 438 (1490 m) (260 Km)	SN 43.9 (1350 m) (270 Km)
n-C25	4 ± 1	4 ± 1	4 ± 1	2 <sup>a</sup>	3 ± 1	2 <sup>a</sup>	2 <sup>a</sup>
n-C26	5 ± 1	6 ± 1	5 ± 1	3 ± 1	3 ± 1	3 ± 1	2 <sup>a</sup>
n-C27	5 ± 1	5 ± 1	5 ± 1	2 <sup>a</sup>	3 ± 1	3 ± 1	2 <sup>a</sup>
n-C28	12 ± 1	8 ± 1	8 ± 1	6 ± 1	7 ± 1	7 ± 1	5 ± 1
n-C29	6 ± 1	5 ± 1	4 ± 1	4 ± 1	3 ± 1	2 <sup>a</sup>	2 <sup>a</sup>
n-C30	7 ± 1	6 ± 1	5 ± 1	5 ± 1	3 ± 1	3 ± 1	2 <sup>a</sup>
n-C31	5 ± 1	4 ± 1	3 ± 1	4 ± 1	2 <sup>a</sup>	2 <sup>a</sup>	2 <sup>a</sup>
n-C32	7 ± 1	5 ± 1	3 ± 1	5 ± 1	3 ± 1	2 <sup>a</sup>	2 <sup>a</sup>
Total n-alkanes (a <sup>b</sup> )	91	76	78	63	58	42	33
Odd/even (n-C15 + n-C32)	0.52	0.65	0.60	0.63	0.64	--	--
Squalene	8 ± 2	2 <sup>a</sup>	4 ± 1	7 ± 1	2 <sup>a</sup>	3 ± 1	5 ± 1
Total aldehydes (C9 - C11)	34	23	26	19	17	14	12
Total alcohols (C10 - C16)	13	11	11	8	8	8	5
Total alky/benzenes (C2 - C4)	185	177	162	158	169	156	148
Total phthalates	58	50	42	37	32	18	14

\* detection limit values are not included in the sum

a. detection limit; bdl = below detection limit



By comparing the mean percentages of organic compounds identified in "fresh" and surface snow collected above Rennick Glacier, some differences can be pointed out. As observed for Mt. Melbourne samples, the most important difference concerns alkylbenzenes (see Table III), which were present at much higher percentages in fresh snow (41%) than in surface snow (19%).

The data of Table III show that alkylbenzenes are more abundant than alkanes and phthalates in "fresh" snow taken from Rennick Glacier with respect to Mt. Melbourne samples. This behaviour can be due to the greater volatility of alkylbenzenes, which are present in the gas phase, with respect to n-alkanes and phthalates.

In order to explain the transport mechanism of the latter compounds associated to marine aerosol, their Er in respect to sodium ion concentration were calculated. Er values increase with increasing the distance from the coast, with the only exception of SN-43.6 sample, and the Er sequence (n-alkanes » phthalates) is quite similar to the one found for "fresh" snow taken from Mt. Melbourne. The behaviour of n-alkanes can be due to their strong affinity for the natural fluorescent surfactant matter (fulvic acids) which is abundant in fine and hyperfine aerosol particles<sup>[27]</sup>. In fact, studies effected on snow samples taken from Evans Nevè (altitude 2400 m, distance from Terra Nova Bay about 200 Km), near to Rennick Glacier (see Figure 1), evidenced that fulvic acid concentrations are comparable to those found in the snow collected at high altitudes on Mt. Melbourne<sup>[28]</sup>.

The results obtained for "fresh" snow confirm the usefulness of these samples to evaluate the real composition of Antarctic atmosphere and the important role both of gaseous marine components, such as alkylbenzenes, and of fine and hyperfine marine aerosol particles which can be transported to long distances from the coast and widely contribute to the composition of non volatile compounds in the snow.

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