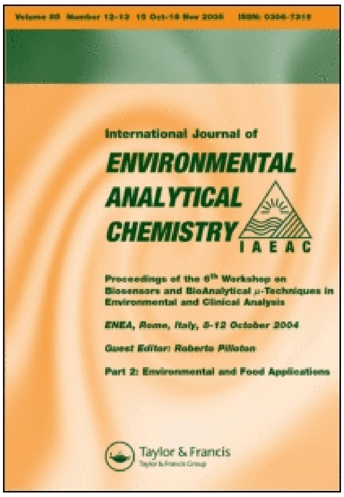

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Pier G. Desideri[a]; Luciano Lepri[a]; Roberto Udisti[a]; Leonardo Checchini[a]; Massimo Del Bubba[a]; Renato Cini[b]; Angela M. Stortini[b]
[a] Department of Public Health, Epidemiology and Environmental Analytical Chemistry. University of Florence, Florence, Italy [b] Department of Organic Chemistry, Laboratory of Technical Physical Chemistry, University of Florence, Florence, Italy

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ANALYSIS OF ORGANIC COMPOUNDS IN ANTARCTIC SNOW AND THEIR ORIGIN

PIER G. DESIDERI[a]*, LUCIANO LEPRI[a], ROBERTO UDISTI[a],
LEONARDO CHECCHINI[a], MASSIMO DEL BUBBA[a], RENATO CINI[b] and
ANGELA M. STORTINI[b]

[a]*Department of Public Health, Epidemiology and Environmental Analytical Chemistry. University of Florence, Via G. Capponi 9, 50121 Florence, Italy and* [b]*Department of Organic Chemistry, Laboratory of Technical Physical Chemistry, University of Florence, Via G.Capponi 9, 50121 Florence, Italy*

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Organic compounds extractable with n-hexane were identified and quantitatively determined in pack, surface and deep snow samples taken at different depths and collected at several altitudes above sea level from Antarctica during the 1993/94 Italian expedition. The comparison between the composition of organic compounds in snow and the ones in pack and sea-water samples pointed out that the three matrices substantially contain the same biogenic and anthropogenic organic compounds. The contribution of marine aerosol to organic content in the snow is confirmed by the enrichment ratios calculated for the more representative classes of identified compounds (n-alkanes, phthalates and low molecular weight alkylbenzenes). The changes in the composition of organic compounds in snow as the altitude increases seem to depend on the dimensional spectrum of the aerosol. Thus, smallest particles, richest in surfactant material, reach the highest altitudes.

Keywords: Antarctica; snow; pack; chromatographic analysis; marine aerosol

INTRODUCTION

The transport of organic compounds from temperate zones to the polar regions is an interesting subject as can be seen from the papers published in the last 15 years [1–7]. The two principal theories are: 1) the direct transport of organic substances through the atmosphere at high altitude; 2) the indirect transport by means of sea-water/air exchange. Further knowledge of the transport mechanism of organic compounds in Antarctica can be obtained from analysis of snow

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* Corresponding author. Fax: +39–55–2476972. E-mail: pgdesideri@cesit1.unifi.it.

which is the only possible wet deposition of organic substances present in the Antarctic atmosphere. In addition, because of its particular orographic conformation, snow samples can be collected both at various distances from the sea and at different altitudes. For these reasons, during the 1993/94 Antarctic expedition, several surface snow samples were collected from stations at sea-level and at increasing altitudes up to 2960 m. Samples were taken at two stations in depths of one, two and three meters, representing the snowfall over a period of 8 – 10 years. The composition of organic compounds in snow was compared to pack samples collected in the same period and to sea-water composition analyzed in previous years.

EXPERIMENTAL

Sampling sites

The sampling stations for surface snow at different altitudes were the following (see Figure 1) :

SN-6	Sea-level	Wood Bay;	Lat. 74° 30′S;	Long. 165° 10′ E
SN-10	220 m	Vegetation Island;	Lat. 74° 47′ S;	Long. 163° 38′ E.
SN-4	200 m	Mount Melbourne;	Lat. 74° 32′ S;	Long. 164° 46′ E
SN-4	600 m	Mount Melbourne;	Lat. 74° 28′ S;	Long. 164° 47′ E
SN-27	790 m	Mc Carty Ridge;	Lat. 74° 36′ S;	Long. 163° 03′ E
SN-4	1130 m	Mount Melbourne;	Lat. 74° 26′ S;	Long. 164° 45′ E
SN-36	2960 m	Hercules Nevè;	Lat. 73° 06′ S;	Long. 165° 28′E.

SN-27 and SN-36 stations were also used for deep snow samples.

The surface snow samples were collected after eliminating the top layer (about 5 cm) to avoid contamination of the sample. A scoop was used to collect a layer of snow approximately 5 cm thick. A total volume of about 40 liters was received. For the –1 m, –2 m and –3 m samples, a horizontal layer about 10 cm thick was collected. The samples were immediately frozen and kept at –30°C until analysis.

The sampling stations of pack-ice were the following (Figure 1) :

Station B	Gerlache Inlet (Terra Nova Bay)	Lat. 74° 58′ S;	Long. 164° 10′ E
Station E	Wood Bay	Lat. 74° 22′ S;	Long. 165° 24′ E

The following pack samples were collected: B-1 (depth 1 m), B-2 (depth 2 m), B-3 (depth 3 m), E-1(depth 1 m), E-2 (depth 2 m).

The pack samples were taken by a manually operated steel corer, after eliminating the top layer of snow. The cores (100 × 10 cm) were immediately placed in steel containers, frozen and kept at –30°C until analysis.

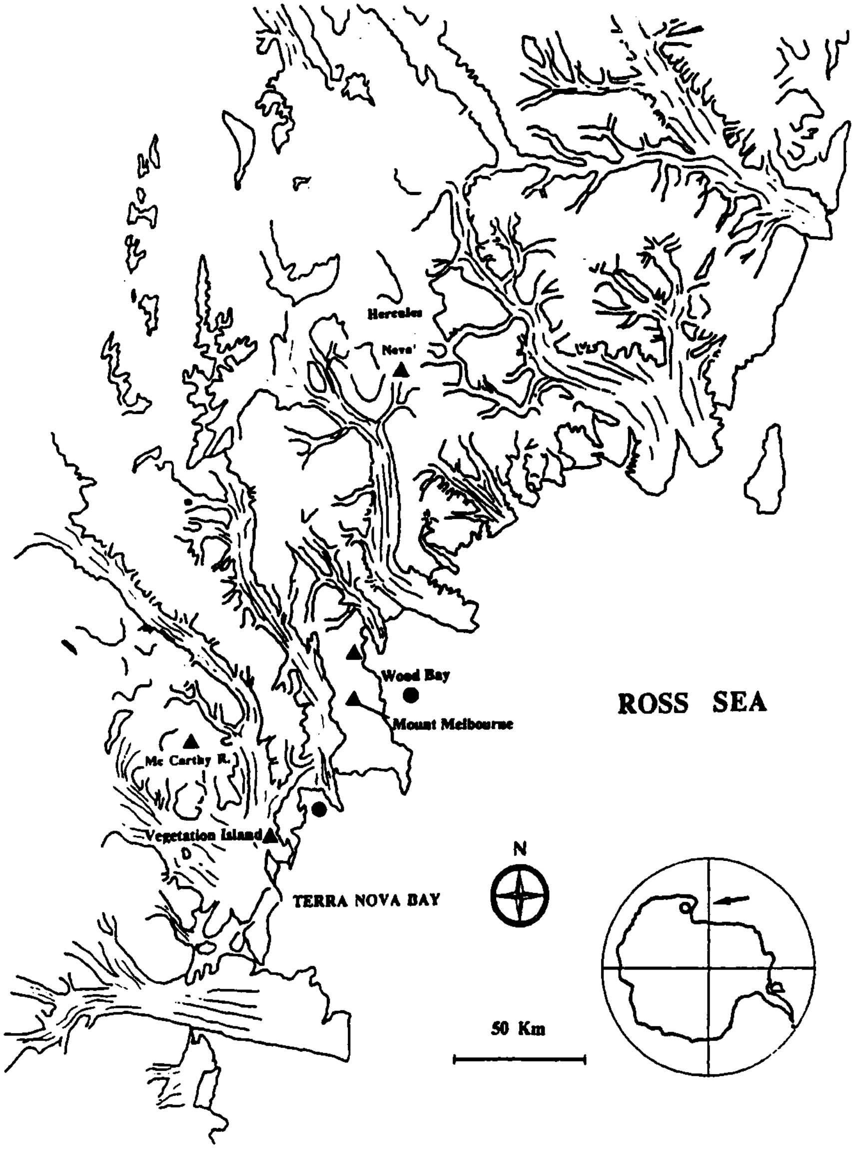

FIGURE 1 Snow (▲) and pack (•) sampling points of the Italian Antarctic Expedition 1993/94

Reagents and materials

20 Liter stainless steel reservoirs (Inox Sabat, Bologna, Italy) were used for storage of snow samples. Howhever, it should be pointed out that the samples were divided in two separate reservoirs and analysed as one sample in the laboratory afterwards. Stainless steel cylinders (1.20 × 0.15 m) were used to store the pack-ice cores.

Solvents (n-hexane, toluene, ethyl acetate, acetone, methylene chloride) were all pesticide grade purchased from Merck (Darmstadt, Germany) and bidistilled before use. Standard organic compounds are commercially available from Supelco (Bellefonte, U.S.A.) and Alltech (Deerfield, U.S.A.). 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.

Fluorescence spectra

The normalized fluorescence intensity In (defined as $I_{max}/ I_{Raman} \times 100$, in which I_{max} is the maximum intensity approximately at 440 ± 20 nm., I_{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 [8].

Sodium ion analysis

The sodium ion concentrations in the Antarctic snow and pack 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[9].

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 column walls were washed with 20 ml acetone after the melted snow or pack was taken out of column, and the resulting water/acetone mixture was extracted with 3 ml of n-hexane.

The extraction of the organic compounds from melted snow and pack was carried out by a replicated enrichment method, especially designed for Antarctic aqueous samples [10,11].

The fractionation of the organic extracts was performed as described previously [12]. The analyses were repeated five times for each sample. The extraction efficiency for the different classes was calculated by using a standard mixture containing aliphatic and aromatic hydrocarbons and phthalates at concentration levels of 10 ng/l.

In contrast to the pack, surface and deep snow does not require a preliminary fractionation of the organic compounds in homogeneous classes for their identification and quantitative determination. Therefore, Table I shows the recovery percentages of the examined organic compounds both after n-hexane extraction (A%) and subsequent fractionation on silica microcolumn (B%).

TABLE I Recovery efficiencies for standard organic compounds from purified water after extraction with n-hexane (A) and fractionation on silica column (B)

Standard	*A (%)*	*B (%)*
n-ALKANES		
nC-14	86 ± 4[a]	79 ± 7
nC-16	87 ± 5	80 ± 8
nC-18	89 ± 4	82 ± 7
nC-20	90 ± 4	82 ± 8
nC-22	90 ± 5	83 ± 6
nC-24	91 ± 6	84 ± 8
nC-26	91 ± 5	84 ± 7
nC-28	92 ± 5	85 ± 8
nC-30	93 ± 5	85 ± 8
ALKYL BENZENES		
Ethylbenzene	75 ± 4	63 ± 7
Propylbenzene	78 ± 5	65 ± 8
Butylbenzene	80 ± 6	70 ± 8
Hexylbenzene	82 ± 5	74 ± 9
PHTHALATES		
Di-iso-butylphthalate	62 ± 5	58 ± 7
Di-n-butylphthalate	64 ± 6	60 ± 7
Bis(2-ethylhexyl)phthalate	86 ± 6	80 ± 9

[a] Standard deviations calculated from five runs.

On the whole the total recovery is high for most of the compounds and increases with increasing the carbon atom number of n-alkanes and alkylbenzenes. Di-n-butylphthalate and di-isobutylphthalate, which have less hydrophobic characteristics, were recovered at lowest percentages.

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)[13]; the alcohols were transformed into their trimethylsilyl derivatives [14].

HRGC and GC-MS analysis

For the identification and quantitative determination of organic compounds, a HRGC-5160 Mega Series (Carlo Erba, Milan, Italy) gas-chromatograph equipped with a FID detector (300°C) was used. The injection was made by using a cold split-splitless liquid injector (Carlo Erba) according to Grob and Grob technique[15]. Injector temperature program: 40°C, then rapid increase in temperature to 300°C and splitting of the solvent after 30 sec. Column temperature program: 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 (1 atm.) The chromatographic peaks were analyzed with a Mega-2 computer system (Carlo Erba) with Spectra Physics software. GC-MS analyses were performed on a Varian 3400 (Palo Alto, U.S.A.) gas chromatograph coupled with a Finnigan ion trap detector; carrier gas: high purity grade helium. 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 identical to that described above. 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[16] indices with eight n-alkanes as standards (C-8, C-12, C-16, C-20, C-24, C-28, C-32, C-34) and a reference calibration table. Mass spectra with those reported in the N.B.S. library and in a second library made in our laboratory on ITD were compared. The exact name is reported in the tables only for those compounds positively identified with the above methods, while only the class is given for the others.

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 Antarctide, frozen at –30°C and carried to the our laboratory together with the snow and pack samples. The results are reported in Table II. Using the analytical conditions described previously, we were able to achieve a detection limit of 0.7 ng/l for all the compounds.

TABLE II Organic compounds (ng/l) in blanks. Medium values of five determinations with standard deviation

n-ALKANES		*BENZENES*	
nC-10	0.7*	Ethylbenzene	0.7*
nC-11	0.7*	m/p-Xylene	0.9±0.2
nC-12	0.7*	o-Xylene	0.7*
nC-14	1.1 ± 0.2	Mesytilene	0.7*
nC-15	1.4 ± 0.3	1,2,4-Trimethylbenzene	0.9 ± 0.2
nC-16	1.7 ± 0,4		
nC-17	1.9 ± 0,5	*PHTHALATES*	
nC-18	1.6 ± 0.4		
nC-19	0.9 ± 0.2	Di-iso-butylphthalate	0.9 ± 0.2
nC-20	0.7*	Di-n-butylphthalate	0.9 ± 0.2
nC-22	0.7*		
ALDEHYDES		*PAH*	
Nonanal	1.5 ± 0.4	Naphthalene	0.7*

* detection limit.

RESULTS AND DISCUSSION

Surface snow composition

Tables III and IV report the concentrations (ng/l) of the n-alkanes, aldehydes, alcohols, alkylbenzenes and phthalates found in the seven surface snow samples listed according to the altitude above sea level. These compounds represent almost all the organic substance classes extractable with n-hexane.

TABLE III Biogenic organic compounds in surface snow (ng/l); medium values of five determinations with standard deviation. Antarctic expedition 1993/94

Sample label above Sea level	*SN-6 (s.l.)*	*SN-4 (200 m)*	*SN-10 (220 m)*	*SN-4 (600 m)*	*SN-27 (790 m)*	*SN-4 (1130 m)*	*SN-36 (2960 m)*
n-Alkanes							
nC-14	10 ± 1	6 ± 1	39 ± 3	104 ± 7	29 ± 2	89 ± 6	9 ± 1
nC-15	23 ± 2	5 ± 1	53 ± 4	9 ± 1	5 ± 1	6 ± 1	5 ± 1
nC-16	100 ± 7	78 ± 5	251 ± 18	277 ± 19	51 ± 4	256 ± 18	218 ± 15
nC-17	6 ± 1	5 ± 1	65 ± 5	8 ± 1	5 ± 1	7 ± 1	16 ± 2
nC-18	5 ± 1	8 ± 1	6 ± 1	5 ± 1	7 ± 1	8 ± 1	5 ± 1
nC-19	7 ± 1	6 ± 1	9 ± 1	5 ± 1	6 ± 1	9 ± 2	5 ± 1
nC-20	5 ± 1	26 ± 2	122 ± 6	98 ± 5	5 ± 1	7 ± 1	6 ± 1
nC-21	5 ± 1	5 ± 1	25 ± 2	6 ± 1	5 ± 1	6 ± 1	7 ± 1
nC-22	18 ± 2	5 ± 1	38 ± 3	14 ± 1	8 ± 2	12 ± 2	23 ± 2
nC-23	14 ± 1	5 ± 1	32 ± 2	19 ± 1	12 ± 1	13 ± 1	31 ± 2
nC-24	109 ± 5	127 ± 6	224 ± 11	540 ± 27	197 ± 10	326 ± 16	88 ± 7
nC-25	51 ± 3	7 ± 1	39 ± 3	39 ± 2	36 ± 2	25 ± 2	66 ± 3
nC-26	24 ± 2	10 ± 2	43 ± 2	52 ± 3	54 ± 3	30 ± 2	118 ± 11
nC-27	19 ± 2	9 ± 2	52 ± 3	51 ± 3	60 ± 3	31 ± 2	100 ± 10
nC-28	192 ± 10	76 ± 4	50 ± 3	305 ± 15	162 ± 8	217 ± 11	128 ± 11
nC-29	24 ± 2	19 ± 2	48 ± 2	51 ± 3	86 ± 4	43 ± 2	109 ± 10
nC-30	14 ± 2	6 ± 1	51 ± 5	47 ± 5	91 ± 9	33 ± 3	183 ± 16
nC-31	17 ± 2	8 ± 2	22 ± 2	41 ± 4	78 ± 8	23 ± 2	95 ± 10
nC-32	5 ± 1	5 ± 1	6 ± 1	66 ± 7	76 ± 8	23 ± 2	95 ± 10
nC-33	6 ± 1	2*	9 ± 2	66 ± 7	76 ± 7	75 ± 7	97 ± 9
Total n-alkanes	654	418	1184	1803	1049	1239	1404
Odd/even (C15-C32)	0.35	0.20	0.44	0.16	0.45	0.18	0.50
Squalene	898 ± 73	17 ± 3	149 ± 13	93 ± 8	13 ± 2	16 ± 2	179 ± 15
Aldehydes							
Nonanal	102 ± 20	16 ± 3	212 ± 42	62 ± 12	68 ± 14	71 ± 14	227 ± 45
Decanal	41 ± 8	4 ± 1	63 ± 13	26 ± 5	17 ± 3	65 ± 13	96 ± 19
Undecanal	12 ± 2	2*	13 ± 3	4 ± 1	2*	7 ± 1	10 ± 2
Dodecanal	7 ± 1	2*	6 ± 1	4 ± 1	2*	9 ± 2	8 ± 2
Tetradecanal	bdl	bdl	9 ± 2	bdl	bdl	bdl	6 ± 1
Total Aldehydes	162	23	326	96	88	150	347
ALCOHOLS							
1-Octanol	bdl	bdl	2*	bdl	bdl	bdl	2*
1-Decanol	5 ± 1	bdl	10 ± 2	bdl	bdl	4 ± 1	7 ± 1
1-Dodecanol	8 ± 2	bdl	28 ± 6	4 ± 1	7 ± 1	8 ± 2	18 ± 4
1-Tetradecanol	15 ± 3	2*	25 ± 5	4 ± 1	3 ± 1	5 ± 1	23 ± 5
1-Hexadecanol	16 ± 3	3 ± 1	26 ± 5	3 ± 1	4 ± 1	7 ± 1	25 ± 5
1-Octadecanol	10 ± 2	2*	27 ± 5	3 ± 1	4 ± 1	4 ± 1	24 ± 5
Total alcohols	54	7	118	14	18	28	99

* = detection limit; bdl = below detection limit.

TABLE IV Alkylbenzenes and phthalates in surface snow (ng/l); medium values of five determinations with standard deviation. Antarctic expedition 1993/94

Sample label above Sea level	*SN-6 (s.l.)*	*SN-4 (200 m)*	*SN-10 (220 m)*	*SN-4 (600 m)*	*SN-27 (790 m)*	*SN-4 (1130 m)*	*SN-36 (2960m)*
BENZENES							
Ethylbenzene	28 ± 4	3 ± 1	39 ± 6	10 ± 2	9 ± 2	11 ± 2	23 ± 3
m/p-Xylene	44 ± 7	2 ± 1	87 ± 13	16 ± 2	18 ± 3	8 ± 2	48 ± 7
o-Xylene	23 ± 3	1^*	50 ± 8	6 ± 1	9 ± 2	4 ± 1	22 ± 3
Propylbenzene	14 ± 2	2 ± 1	22 ± 3	10 ± 2	21 ± 3	21 ± 3	28 ± 4
1-Methyl-3-ethylbenzene	50 ± 8	4 ± 1	63 ± 9	33 ± 5	63 ± 9	20 ± 3	100 ± 13
1-Methyl-4-ethylbenzene	15 ± 2	2 ± 1	22 ± 3	14 ± 2	26 ± 4	8 ± 2	42 ± 6
1-Methyl-2-ethylbenzene	6 ± 1	bdl	35 ± 5	2 ± 1	3 ± 1	bdl	8 ± 1
Mesytilene	28 ± 4	3 ± 1	47 ± 6	21 ± 3	42 ± 5	14 ± 2	67 ± 9
1,2,4-Trimethylbenzene	20 ± 3	4 ± 1	75 ± 10	16 ± 2	40 ± 5	9 ± 1	44 ± 6
1,2,3-Trimethylbenzene	70 ± 9	9 ± 2	119 ± 15	69 ± 9	127 ± 17	43 ± 6	210 ± 27
Ethyl-dimethylbenzene	8 ± 1	bdl	14 ± 2	6 ± 1	10 ± 2	4 ± 1	15 ± 2
2-Ethyl-1,4-dimethylbenzene	15 ± 2	2 ± 1	29 ± 4	13 ± 2	24 ± 3	9 ± 2	42 ± 5
2-Methyl-2-isopropylbenzene	9 ± 1	2 ± 1	16 ± 2	9 ± 2	13 ± 3	bdl	17 ± 3
1-Methyl-3-n-propylbenzene	5 ± 1	bdl	9 ± 1	bdl	8 ± 2	3 ± 1	12 ± 2
C4benzene	23 ± 3	3 ± 1	40 ± 4	5 ± 1	10 ± 1	5 ± 1	14 ± 2
C6benzene	21 ± 2	1^*	63 ± 7	6 ± 1	14 ± 2	4 ± 1	15 ± 2
Total benzenes	379	38	730	236	437	163	707
PHTHALATES							
Dimethylphthalate	24 ± 4	2 ± 1	15 ± 2	bdl	bdl	bdl	bdl
Diethylphthalate	5 ± 1	bdl	20 ± 3	8 ± 1	3 ± 1	3 ± 1	7 ± 1
Di-isobutylphthalate	210 ± 32	24 ± 4	532 ± 80	108 ± 16	66 ± 10	140 ± 21	112 ± 17
Di-n-butylphthalate	89 ± 13	2 ± 1	280 ± 42	112 ± 17	89 ± 13	84 ± 13	80 ± 12
Dihexylphthalate	4 ± 1	bdl	20 ± 3	11 ± 2	2 ± 1	bdl	bdl
Diheptylphthalate	6 ± 1	bdl	14 ± 2	10 ± 2	3 ± 1	5 ± 1	bdl
Bis(2-ethylhexyl)phthalate	252 ± 38	45 ± 7	380 ± 57	104 ± 16	61 ± 9	140 ± 21	346 ± 52
Total phthalates	590	73	1261	353	224	372	545

* = detection limit; bdl = delow detection limit.

Detection limits of 2 ng/l (n-alkanes, aldehydes and alcohols) and 1 ng/l (alkylbenzenes and phthalates) were reported in Tables III and IV in order to account for the blank concentrations of these organic compounds.

The alkylbenzenes and phthalates are surely anthropogenic while n-alkanes, which have odd/even ratios much lower than 1, are probably biogenic [12]. Aldehydes and alcohols are biogenic as well [17]. Substantially the same compounds were found in all samples even if some are present in a few samples only at detection levels. The most abundant n-alkanes are C-16, C-24 and C-28 while di-n-butyl-, di-isobutyl- and di-(2-ethylhexyl)phthalate represent almost all the phthalates (92–97%). The compounds with three carbon atoms in the substituent groups (C3) make up most of the alkylbenzenes (52–72%) while the C4 account for 14–17%; the greatest range is shown by C2 (11–28%).

The percentages of the more prevalent classes of organic compounds are shown in Figure 2.

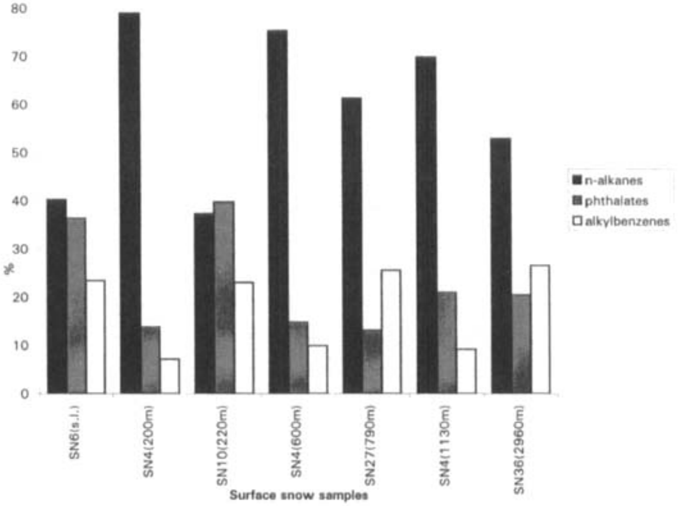

FIGURE 2 Percentages of n-alkanes, alylbenzenes and phthalates in the surface samples collected at different altitudes during the Antartic expedition 1993/94

Samples SN-6 (s.l.) and SN-10 (220 m) contain the three classes in different percentages with respect to the other samples since the phthalates/n-alkanes ratio is very close to 1. This may be due to the fact that SN-10, even if collected at 220 m and, therefore, at an altitude very similar to that of SN-4 (200 m), is closer to the coast as the sample SN-6. It should be noted that the surface snow collected during the Antarctic expeditions 1987/88, 1988/89 and 1990/91 contain the same compounds reported in Tables III and IV. The mean concentration (ng/l) of n-alkanes, alkylbenzenes and phthalates in these samples is 642 (range 369–1231), 341 (range 115–867) and 363 (range 117–539), respectively. Such values agree with those calculated from Tables III and IV and the same sequence was also observed for the percentages of these classes of compounds: n-alkanes > phthalates > alkylbenzenes [12].

Deep snow composition

Tables V and VI show the organic compounds and their concentrations found in snow taken at stations SN-27 and SN-36 at different depths. With few exceptions, the compounds are the same as those identified in the surface snow at all sampling stations. Here the n-alkanes, followed by alkylbenzenes and phthalates, are also the dominating classes of compounds.

Figure 3 shows the percentages of these classes in the snow samples collected at station SN-27 from the surface and at depths of 1, 2 and 3 meters.

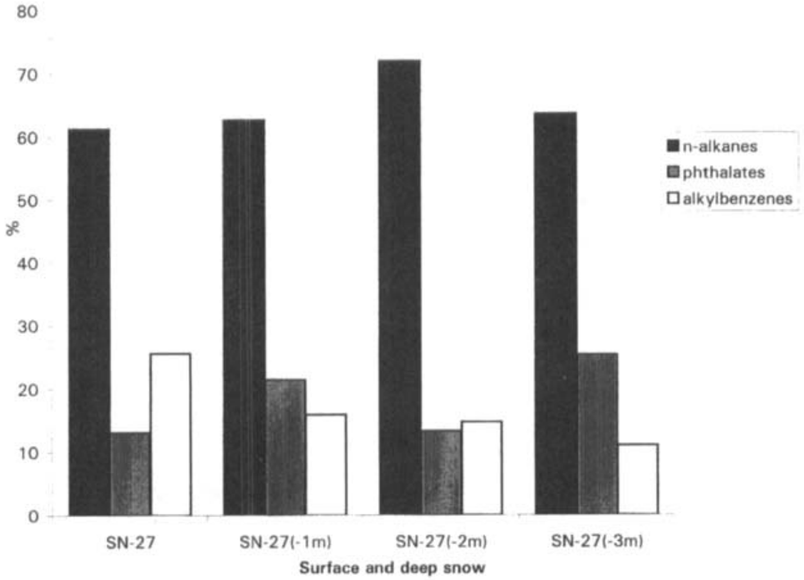

FIGURE 3 Percentages of n-alkanes, alkylbenzenes and phthalates in samples of surface (SN-27) and deep snow (-1m, –2m, –3m) collected during the Antartic expedition 1993/94

The composition of the snow samples taken at SN-36 station is similar to the one reported above with the exception of sample taken at 1 m where phthalates prevail. SN-27 samples, however, contain benzylbutylphthalate which is not present in SN-36 samples.

TABLE V Biogenic organic compounds in snow at different depths (ng/l); medium values of five determinations with standard deviation. Antarctic expedition 1993/94

Sample label *Snow depth (meters)*	*SN-27* *(-1 m)*	*SN-27* *(-2 m)*	*SN-27* *(-3 m)*	*SN-36* *(-1 m)*	*SN-36* *(-2 m)*	*SN-36* *(-3m)*
n-ALKANES						
nC-14	128 ± 12	121 ± 11	bdl	29 ± 3	15 ± 1	186 ± 17
nC-15	6 ± 1	12 ± 1	7 ± 1	5 ± 1	7 ± 1	21 ± 2
nC-16	370 ± 33	480 ± 43	396 ± 36	43 ± 4	598 ± 54	582 ± 52
nC-17	17 ± 1	9 ± 1	86 ± 8	5 ± 1	28 ± 2	38 ± 3
nC-18	5 ± 1	7 ± 1	11 ± 1	6 ± 1	5 ± 1	13 ± 1
nC-19	8 ± 1	9 ± 1	7 ± 1	5 ± 1	7 ± 1	9 ± 1
nC-20	104 ± 7	94 ± 7	21 ± 1	6 ± 1	5 ± 1	7 ± 1
nC-21	5 ± 1	6 ± 1	21 ± 1	23 ± 2	28 ± 2	24 ± 2
nC-22	29 ± 2	29 ± 2	46 ± 3	63 ± 4	31 ± 2	27 ± 2
nC-23	15 ± 1	16 ± 1	80 ± 6	54 ± 4	37 ± 3	26 ± 2
nC-24	430 ± 22	468 ± 33	319 ± 22	45 ± 2	162 ± 8	525 ± 26
nC-25	34 ± 2	37 ± 2	131 ± 7	83 ± 4	86 ± 4	58 ± 3
nC-26	47 ± 2	42 ± 2	125 ± 6	72 ± 4	100 ± 5	86 ± 4
nC-27	51 ± 3	38 ± 2	138 ± 7	91 ± 5	92 ± 5	76 ± 4
nC-28	369 ± 18	338 ± 17	194 ± 10	41 ± 2	447 ± 22	370 ± 19
nC-29	51 ± 2	35 ± 2	82 ± 4	74 ± 4	91 ± 5	90 ± 5
nC-30	37 ± 2	17 ± 2	57 ± 6	71 ± 7	74 ± 7	83 ± 8
nC-31	36 ± 4	10 ± 1	66 ± 7	60 ± 6	25 ± 3	74 ± 7
nC-32	23 ± 2	7 ± 1	8 ± 1	50 ± 5	127 ± 13	181 ± 18
nC-33	8 ± 1	6 ± 1	93 ± 9	63 ± 6	36 ± 4	17 ± 2
Total n-alkanes	1773	1772	1888	889	2001	2493
Odd/even(C15-C32)	0.16	0.12	0.60	1.17	0.28	0.23
Squalene	41	295	86	196	215	102
ALDEHYDES						
Nonanal	205 ± 41	131 ± 26	109 ± 22	484 ± 97	89 ± 18	238 ± 48
Decanal	50 ± 10	41 ± 8	bdl	198 ± 40	43 ± 9	97 ± 19
Undecanal	11 ± 2	7 ± 1	bdl	39 ± 8	5 ± 1	14 ± 3
Dodecanal	5 ± 1	3 ± 1	bdl	25 ± 5	bdl	7 ± 1
Tetradecanal	4 ± 1	3 ± 1	bdl	12 ± 2	bdl	4 ± 1
Total aldehydes	275	185	109	758	137	360
ALCOHOLS						
1-Octanol	35 ± 7	9 ± 2	4 ± 1	5 ± 1	4 ± 1	23 ± 5
1-Decanol	11 ± 2	10 ± 2	2^*	2^*	bdl	9 ± 2
1-Dodecanol	8 ± 2	12 ± 2	2^*	4 ± 1	bdl	bdl
1-Tetradecanol	5 ± 1	7 ± 1	9 ± 2	2^*	6 ± 1	5 ± 1
1-Hexadecanol	14 ± 3	17 ± 3	bdl	7 ± 1	9 ± 2	3 ± 1
1-Octadecanol	17 ± 3	25 ± 5	bdl	6 ± 1	bdl	4 ± 1
Total alcohols	90	80	17	26	19	44

* = detection limit; bdl = below detection limit

TABLE VI Organic compounds in snow at different depths (ng/l); medium values of five determinations with standard deviation. Antarctic expedition 1993/94

Sample label	*SN-27*	*SN-27*	*SN-27*	*SN-36*	*SN-36*	*SN-36*
Snow depth (meters)	*(-1 m)*	*(-2 m)*	*(-3 m)*	*(-1 m)*	*(-2 m)*	*(-3m)*
BENZENES						
Ethylbenzene	15 ± 2	14 ± 2	11 ± 2	44 ± 7	11 ± 2	63 ± 9
m/p-Xylene	26 ± 4	23 ± 3	19 ± 3	77 ± 12	26 ± 4	61 ± 9
o-Xylene	11 ± 2	12 ± 2	9 ± 1	39 ± 6	13 ± 2	24 ± 4
Propylbenzene	17 ± 3	15 ± 2	16 ± 2	29 ± 4	bdl	94 ± 14
1-Methyl-3-Ethylbenzene	91 ± 14	50 ± 8	55 ± 8	79 ± 12	76 ± 11	147 ± 22
1-Methyl-4-Ethylbenzene	20 ± 3	21 ± 3	24 ± 4	31 ± 5	32 ± 5	61 ± 9
1-Methyl-2-Ethylbenzene	1*	2 ± 1	bdl	4 ± 1	bdl	27 ± 4
Mesytilene	43 ± 6	35 ± 5	33 ± 4	64 ± 8	49 ± 6	112 ± 15
1,2,4-Trimethylbenzene	2 ± 1	3 ± 1	4 ± 1	42 ± 5	2 ± 1	58 ± 8
1,2,3-Trimethylbenzene	138 ± 18	104 ± 14	112 ± 15	161 ± 21	158 ± 21	290 ± 38
Ethyl-Dimethylbenzene	13 ± 1	9 ± 1	10 ± 1	18 ± 2	12 ± 1	21 ± 2
2-Ethyl-1,4-Dimethylbenzene	28 ± 3	29 ± 3	22 ± 2	51 ± 6	30 ± 3	63 ± 7
1-Methyl-2-isopropylbenzene	13 ± 2	12 ± 2	4 ± 1	26 ± 3	15 ± 2	27 ± 4
1-Methyl-3-n-propylbenzene	bdl	bdl	bdl	bdl	9 ± 1	16 ± 2
C4benzene	11 ± 1	12 ± 1	3 ± 1	47 ± 5	9 ± 1	21 ± 2
C6benzene	22 ± 2	22 ± 2	5 ± 1	10 ± 1	6 ± 1	26 ± 3
Total benzenes	451	363	327	722	448	1111
PHTHALATES						
Dimethylphthalate	bdl	bdl	bdl	95 ± 14	bdl	15 ± 2
Diethylphthalate	15 ± 2	6 ± 1	bdl	47 ± 7	30 ± 5	7 ± 1
Di-isobutylphthalate	180 ± 27	66 ± 10	125 ± 19	245 ± 37	89 ± 13	135 ± 20
Di-n-butylphthalate	127 ± 19	58 ± 9	90 ± 14	189 ± 28	126 ± 19	100 ± 15
Dihexylphthalate	29 ± 4	bdl	bdl	67 ± 10	32 ± 5	5 ± 1
Benzylbutylphthalate	23 ± 3	15 ± 2	52 ± 8	bdl	bdl	bdl
Diheptylphthalate	23 ± 3	6 ± 1	17 ± 3	57 ± 9	28 ± 4	7 ± 1
Bis(2-ethylhexyl)phthalate	209 ± 31	176 ± 26	468 ± 70	560 ± 84	404 ± 61	312 ± 47
Total phthalates	606	327	752	1260	709	581

* = detection limit; bdl = below detection limit.

Pack composition

The comparison between the composition of snow and marine matrices (pack and sea-water) is useful for a better understanding of the origin of the substances found in the snow.

Pack has the same composition as sea-water even though it is slightly richer in organic compounds since it probably includes the surface marine microlayer[18].

Such a microlayer has more organic content than the underlying water and it is never collected with the surface sea-water, normally taken at 0.5 m depth.

Tables VII and VIII show the classes of organic compounds found in the pack samples at depths of 1, 2 and 3 meters. The composition of the five samples is very similar and the individual compounds are mainly the same as found in the snow. It should be noted that the pack composition is different from most of the snow samples since there are more phthalates than n-alkanes and alkylbenzenes (see Figure 4).

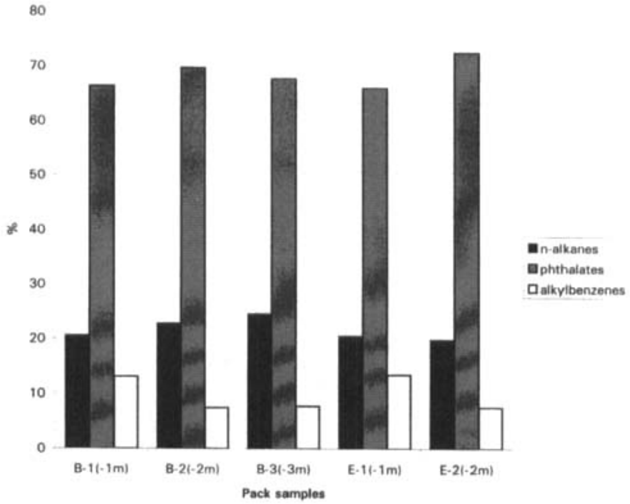

FIGURE 4 Percentages of n-alkanes, phthalates and alkylbenzenes in pack samples collected during the Antartic expedition 1993/94

Sea-water composition

Previous papers [12,19,20] described the sea-water composition under the pack and in the open sea samples collected in Terra Nova Bay and Ross Sea (Antarctic expeditions 1987/88, 1988/89, 1990/91). The water under the pack is always less concentrated in organic compounds than the pack above it and the sea-water taken from the open sea. The data indicate that the composition of sea-water in Antarctica whether near or far from the coast is very similar and no substantial changes have been observed during our research period.

The mean concentrations (μg/l) of the three prevalent classes of compounds in sea-water are: n-alkanes 136±15, phthalates 488±170 and alkylbenzenes 118±13.

TABLE VII Biogenic organic compounds in pack-ice (ng/l); medium values of five determinations with standard deviation. Antarctic expedition 1993/94

Sample label *Pack depth*	*B-1* *(-1 m)*	*B-2* *(-2 m)*	*B-3* *(-3 m)*	*E-1* *(-1 m)*	*E-2* *(-2 m)*
n-ALKANES					
nC-14	6 ± 1	13 ± 2	11 ± 2	7 ± 1	7 ± 1
nC-15	30 ± 2	5 ± 1	4 ± 1	13 ± 2	7 ± 1
nC-16	72 ± 5	8 ± 2	33 ± 2	46 ± 3	29 ± 2
nC-17	9 ± 2	4 ± 1	7 ± 2	5 ± 1	4 ± 1
nC-18	6 ± 1	7 ± 1	6 ± 1	4 ± 1	5 ± 1
nC-19	4 ± 1	6 ± 1	4 ± 1	5 ± 1	3 ± 1
nC-20	8 ± 2	5 ± 1	23 ± 2	33 ± 2	56 ± 3
nC-21	4 ± 1	5 ± 1	3 ± 1	6 ± 1	4 ± 1
nC-22	7 ± 2	6 ± 1	5 ± 1	4 ± 1	5 ± 1
nC-23	19 ± 2	13 ± 2	6 ± 1	17 ± 2	8 ± 1
nC-24	38 ± 2	14 ± 2	32 ± 2	31 ± 2	10 ± 1
nC-25	50 ± 3	45 ± 3	18 ± 2	34 ± 2	32 ± 2
nC-26	18 ± 2	25 ± 2	19 ± 2	13 ± 2	15 ± 2
nC-27	24 ± 2	22 ± 2	18 ± 2	17 ± 2	19 ± 2
nC-28	43 ± 2	44 ± 3	47 ± 3	42 ± 2	59 ± 3
nC-29	31 ± 2	22 ± 2	20 ± 2	9 ± 1	11 ± 1
nC-30	5 ± 1	6 ± 1	4 ± 1	3 ± 1	6 ± 1
nC-31	3 ± 1	4 ± 1	5 ± 1	4 ± 1	5 ± 1
nC-32	15 ± 2	37 ± 4	38 ± 4	14 ± 2	47 ± 5
nC-33	7 ± 1	10 ± 1	13 ± 2	8 ± 1	15 ± 2
Total n-alkanes	399	301	316	315	347
Odd/even (C15-C32)	0.82	0.83	0.41	0.58	0.40
Squalene	999 ± 87	1035 ± 93	808 ± 75	847 ± 82	777 ± 80
ALDEHYDES					
Nonanal	14 ± 3	4 ± 1	6 ± 1	7 ± 1	6 ± 1
Decanal	4 ± 1	8 ± 2	6 ± 1	9 ± 2	13 ± 3
Undecanal	2*	4 ± 1	4 ± 1	5 ± 1	2*
Total aldehydes	20	16	16	21	21
ALCOHOLS					
1-Dodecanol	9 ± 2	18 ± 4	7 ± 1	4 ± 1	5 ± 1
1-Tetradecanol	7 ± 1	18 ± 4	4 ± 1	6 ± 1	3 ± 1
1-Hexadecanol	11 ± 2	5 ± 1	5 ± 1	8 ± 2	6 ± 1
1-Octadecanol	13 ± 3	11 ± 2	9 ± 2	24 ± 5	21 ± 4
Total alcohols	40	52	25	42	35

* = detection limit; bdl = below detection limit.

TABLE VIII Alkylbenzenes and phthalates in pack-ice (ng/l); medium values of five determinations with standard deviation. Antarctic expedition 1993/94

Sample label *Pack depth*	*B-1* *(-1 m)*	*B-2* *(-2 m)*	*B-3* *(-3 m)*	*E-1* *(-1 m)*	*E-2* *(-2 m)*
BENZENES					
Ethylbenzene	25 ± 4	15 ± 2	4 ± 1	22 ± 3	28 ± 4
m/p-Xylene	53 ± 8	34 ± 5	29 ± 4	54 ± 8	37 ± 6
o-Xylene	17 ± 3	10 ± 2	11 ± 2	20 ± 3	12 ± 2
Propylbenzene	6 ± 1	8 ± 1	3 ± 1	7 ± 1	3 ± 1
1-Methyl-3-ethylbenzene	25 ± 3	7 ± 1	7 ± 1	22 ± 3	18 ± 2
1-Methyl-4-ethylbenzene	15 ± 2	3 ± 1	3 ± 1	3 ± 1	4 ± 1
Mesytilene	14 ± 2	3 ± 1	9 ± 2	18 ± 2	3 ± 1
1,2,4-Trimethylbenzene	9 ± 1	2^*	6 ± 1	13 ± 2	10 ± 2
1,2,3-Trimethylbenzene	42 ± 5	3 ± 1	4 ± 1	5 ± 1	9 ± 1
Ethyl-dimethylbenzene	10 ± 1	2^*	4 ± 1	7 ± 1	bdl
2-Ethyl-1,4-dimethylbenzene	12 ± 2	3 ± 1	7 ± 1	13 ± 1	2^*
2-Methyl-2-isopropylbenzene	6 ± 1	4 ± 1	3 ± 1	8 ± 1	3
1-Methyl-3-n-propylbenzene	8 ± 1	3 ± 1	4 ± 1	10 ± 1	2^*
C4benzene	7 ± 1	2^*	5 ± 1	3 ± 1	2^*
C6benzene	5 ± 1	bdl	2^*	3 ± 1	bdl
Total benzenes	254	99	101	208	133
PHTHALATES					
Dimethylphthalate	12 ± 2	bdl	8 ± 1	bdl	bdl
Diethylphthalate	16 ± 2	13 ± 2	bdl	15 ± 2	bdl
Di-isobutylphthalate	440 ± 66	420 ± 63	261 ± 39	349 ± 52	409 ± 61
Di-n-butylphthalate	501 ± 75	228 ± 34	304 ± 46	450 ± 68	576 ± 86
Diheptylphthalate	13 ± 2	bdl	bdl	21 ± 3	25 ± 4
Bis(2-ethylhexyl)phthalate	306 ± 46	257 ± 39	300 ± 45	178 ± 27	257 ± 39
Total phthalates	1288	918	873	1013	1267

* = detection limit; bdl = below detection limit.

Origin of the organic compounds in the snow

Recently, Shaw [21] evidenced the presence of marine aerosol as the principal micro component carrier in Antarctic snow, especially during salt storms.

The fact that the same compounds are present in snow, pack and sea-water underlines the influence of the marine matrices on the snow composition. The presence of biogenic marine compounds such as aldehydes, n-alkanes, squalene and fluorescent humic material [22] in the snow strongly supports this hypothesis.

However, the composition of pack and sea-water is very different from snow where n-alkanes are the predominant substances in most of the samples. In addition, the two samples nearest to the coast (SN-6 and SN-10) and, therefore, more directly exposed to the marine aerosol, have a composition which is midway between those of sea-water and pack and the composition of the other snow samples. These data agree with the hypothesis that the composition of marine aerosol is different from that of sea-water and changes with the distance from the coast.

For a better understanding of the marine contribution to the organic content of snow, the ratios between the concentrations of organic compounds in snow and in sea-water samples with respect to the concentrations of sodium ion in the same matrices were calculated.

The enrichment of compound x is shown in the following expression:

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

where $([X)/(Na^+])_{snow}$ is the ratio between the concentration of compound X and that of sodium ion in the snow while $([X)/(Na^+])_{seawater}$ is the same ratio in sea-water. $[Na^+]$ was taken as an index of the marine aerosol trapped in our snow samples.

Table IX shows the enrichment of the three classes of organic compounds in surface snow calculated by using their mean concentrations and that of the sodium ion in snow at different altitudes and in sea-water. The ratios between the concentration of n-alkanes, phthalates and alkylbenzenes in sea-water and that of the sodium ion are 1.225×10^{-8}, 4.396×10^{-8} and 1.063×10^{-8}, respectively.

TABLE IX Enrichment ratios for selected organic compounds between surface snow and sea-water

Sample label above Sea level	*SN-4 (200 m)*	*SN-4 (600 m)*	*SN-27 (790 m)*	*SN-4 (1130 m)*	*SN-36 (2960 m)*
$[Na^+]$(μg/l)*	2288	1998	556	1029	44
n-Alkanes	14700	73500	154000	98000	2600000
Alkylbenzenes	1880	11300	74300	15100	1510000
Phthalates	680	4100	9100	8200	282000

* sodium concentration in the surface snow samples.

The data in Table IX show high enrichments for all the substances even though they vary from class to class and, in particular, the n-alkanes have the highest value. Chiavarini et al. [23,24] found in aerosol samples, collected from November 1994 to January 1995 near the Italian Base at Terra Nova Bay, a ratio of 2.83×10^{-3} between the average phthalate concentration and sodium ion. From the above mentioned data, the enrichment of phthalates in the aerosol with respect to sea-water is about 60000 and demonstrates the strong enrichment of organic substances with respect to sodium ion passing from sea-water to the aerosol.

The differences between the enrichments observed for the three classes of compounds can be seen as differences in a) volatility, b) surface activity, c) interaction with particles and distribution according to the size of particles, d) scavenging by the snow of the compounds in the gas or particulate phases.

Aerosol studies performed in our laboratory [25] on these compounds pointed out that, considering the extremely low temperatures in Antarctica, the n-alkanes and phthalates identified are all in the particulate phase. On the other hand, the alkylbenzenes which at 20°C in the laboratory were completely transported from the solution to the air in the gaseous phase, may be present, even partially, in the same phase in the Antarctic atmosphere.

The greater enrichment of n-alkanes with respect to phthalates observed in snow seems to depend on the more defined affinity of the hydrocarbons to the particulate matter of the aerosol owing to their higher hydrophobicity. This behaviour was demonstrated in laboratory studies mentioned above [25].

With increasing altitude, an enrichment increase is observed for all the classes of compounds with the exception of samples SN-4 (1130 m). Such a phenomenon can depend on the affinity of these compounds for the organic biogenic fraction of the marine aerosol (humic material, fatty acid esters etc.) which is found prevalently in the fine particles (diameter less than 1 μm) of the same aerosol[26]. In order to know which class of compounds has the greatest enrichment as the altitude increases, the ratios between the enrichment values at 1130 m (SN-4) and 2960 m (SN-36) and those at 200 m (SN-4) were calculated. These values are 6.7 at 1130 m and 177 at 2960 m for the n-alkanes and 12 and 414 for the phthalates in the same samples. Since the surface tension of phthalates is much higher than that of n-alkanes, it is important to remember that the surfactant material, adsorbed on the drop surface immediately after its formation, increases with respect to that enclosed in the inner drop section with the same function which describes the increase of the surface/volume ratio of a sphere versus the diminution of the sphere diameter [27].

Therefore, as the diameter of drops decreases, the quantity of surfactant increases considerably and a selective enrichment for the various substances with respect to the size of particles, according to their structural characteristics, can occur if no loss of surfactant due to its physical properties is expected.

The smallest particles of the marine aerosol, enriched in organic surfactant material, reach and stay longer in the high atmosphere [28] and are responsible for the greater enrichment noted for the phthalates with respect to the hydrocarbons as the altitude above sea level increases.

An increase in the enrichment for the alkylbenzenes is also observed at higher altitudes with respect to n-alkanes (see values at 2960 m compared to 200 m). This behaviour can be due to the higher volatility of alkylbenzenes which can be found in the Antarctic atmosphere even in the gas phase.

The reversal of the enrichment values for the stations at 790 m and 1130 m can be attributed to local meteorological factors which cause the fast rising of air masses containing bigger sized marine aerosol particles.

It should be pointed out that the three SN-4 samples at 200, 600 and 1130 m show an homogeneous trend for all the classes of compounds and this is of considerable interest since these snow samples were collected at similar distances from the coast along the slopes of Mount Melbourne. In these stations, the maximum fluorescence intensity of the soluble fraction of the humic component was also measured and the corresponding enrichment values were calculated using the procedure previously described [8].

In fact the value

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

gives an estimate of the enrichment of fluorescent material in the snow with respect to sea-water.

Table X shows the normalized fluorescence intensity and the enrichment in the snow with respect to the same component in sea water. The data demonstrate increased enrichment values as the altitude increases. Since the humic component calculated here (essentially fulvic acids) is directly correlated to the presence of marine aerosol [29], the enrichment of fluorescent material with respect to the altitude can be another confirmation of the transport of the above described compounds through marine aerosol.

TABLE X Enrichment of the fluorescent material (Eln) in the marine aerosol trapped in the snow samples

Sample label above Sea level	*SN-4 (200 m)*	*SN-4 (600 m)*	*SN-4 (1130 m)*
In	22.18	19.69	23.33
Eln	3512	3571	8214

Table XI gives the enrichments for n-alkanes, phthalates and alkylbenzenes in six snow samples taken at depth of 1, 2 and 3 m. The entire thickness of the snow cores corresponds to a time period of approximately ten years [30] and since the enrichment values do not vary much with the depth, this is in agreement with the theory that these compounds are transported by marine aerosol from the Ross Sea.

TABLE XI Enrichment ratios for selected organic compounds between deep snow and sea-water

Sample label *Snow depth*	*SN-27* *(-1 m)*	*SN-27* *(-2 m)*	*SN-27* *(-3 m)*	*SN-36* *(-1 m)*	*SN-36* *(-2 m)*	*SN-36* *(-3 m)*
$[Na^+]$(μg/l)*	1126	1131	842	23	47	26
n-Alkanes	128000	128000	183000	3100000	3435000	7537000
Alkylbenzenes	37600	30100	36700	295300	897000	387100
Phthalates	12300	66000	20200	1246000	343000	490000

* sodium concentration in the surface snow samples.

Another confirmation is the minimum percentage variation of these classes of compounds with the depth which is correlated to the transport, at the same altitude, of marine aerosol particles within a narrow size range.

The comparison of the lower altitude (790 m) data with the higher one (2960 m) also confirms the above mentioned facts. For the latter station, in fact, the enrichment of the compounds is substantially higher in agreement with the deposition of the smallest particles and richest in organic material at higher levels.

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