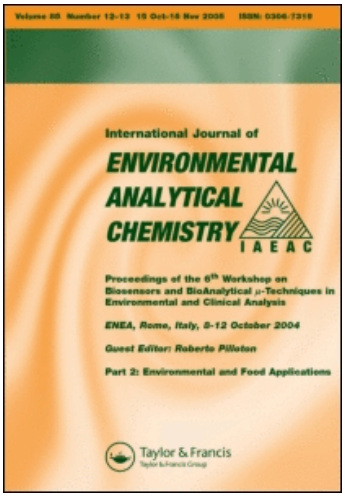

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ORGANIC COMPOUNDS IN ANTARCTIC SEA-WATER AND PACK-ICE

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Pack-ice and sea-water samples collected at different depths from Terra Nova Bay and Ross Sea, during 1990/1991 Italian Antarctic Expedition, were analyzed using HRGC and GC-MS. Several classes of biogenic and anthropogenic organic compounds were identified and measured in both matrices. The results showed the changes in the organic composition at varying depths of pack-ice and sea-water and the enrichment of organic compounds in the pack.

KEY WORDS: Antarctica, pack-ice, seawater, organic pollutants, chromatographic analysis.

INTRODUCTION

The analysis of samples of pack-ice and of the immediately underlying sea-water, taken from Terra Nova Bay during the 1988/1989 Italian Antarctic Expedition, revealed the presence of numerous organic compounds in both matrices[1]. Only the sea-water surface in direct contact with the pack-ice was taken and the pack samples were cored and stored without any sectioning.

The aim of this study was to identify and measure the organic compounds present in: 1) pack-ice samples collected from different areas (Terra Nova and Wood Bay), (Figure 1-B, D and E) and in cores of 1 m, taken at different depths down to 3 m and stored separately; 2) sea-water samples taken at different depths under the pack-ice in Terra Nova Bay; 3) sea-water samples from Ross Sea collected at considerable distance from the coast (Figure 1-A) at different depths (20, 500, 1500 meters).

The results may contribute to understand the behaviour of organic compounds in Antarctic waters and during the ice formation.

EXPERIMENTAL

Sampling

The sampling stations for pack-ice and sea-water were the following (Figure 1):

Station B: Lat. 74°40' S; Long 164°07' E.
Station D: Lat. 74°36' S; Long 164°35' E.

Station E: Lat. 74°21' S; Long 165°14' E.
Station A: Lat. 70°53' S; Long 177°21' E.

The following samples were collected: pack-ice, B-1 (depth 1 m), B-2 (depth 2 m), D-1 (depth 1 m), D-2 (depth 2 m), D-3 (depth 3 m), E-1 (depth 1 m), E-2 (depth 2 m); sea-water, SWA (depth 20 m, 500 m and 1500 m), SWB (depth 0.5 m, 25 m, 250 m), SWE (depth 0.5 m).

The pack-ice samples were collected by a manually operated steel corer, after eliminating the top layer of snow. The cores (100 × 10 cm) were immediately placed in steel containers. The sea-water samples were collected in 30 liter "go-flow" bottles made of PVC with a Teflon coating. Each sample was transferred into 25 liter steel reservoirs, frozen and kept at –30°C until the time of analysis.

Reagents and materials

25 Liter stainless steel reservoirs (Inox Sabat, Bologna, Italy) were used for storage of sea-water samples. Stainless steel cylinders (1.20 × 0.15 m) were used to store the pack-ice cores. Solvents (n-hexane, methylene chloride, chloroform, acetone) were all pesticide grade purchased from Merck (GFR). Standard organic compounds are commercially available from Supelco (USA) and Alltech (USA).

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

Extraction of organic compounds

The extraction of the organic compounds from the sea-water samples was performed by the replicated extractant enrichment method, which is very suitable for environmental

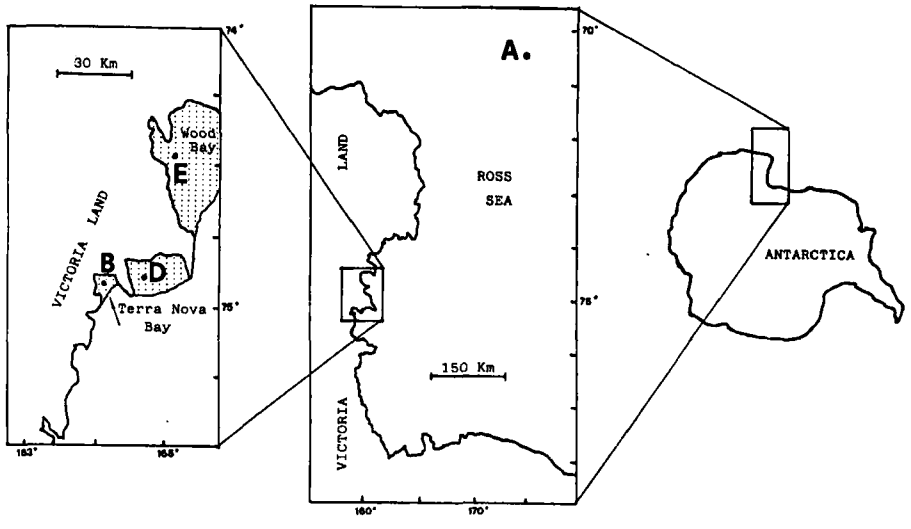

Figure 1 Sampling stations for offshore sea-water (Ross Sea, Antarctica) (A) and for pack-ice and sea-water under the pack (B, D and E).

matrices with low concentration of organic compounds, such as the Antarctic matrices. The extraction was performed by adding 3 ml of n-hexane to 3 liters of sea-water sample and then stirring the resulting mixture magnetically for 10 minutes in a special glass apparatus[2]. After leaving the mixture to stand for 5 min. the n-hexane phase was collected into a microburette (first extract). A second extraction of the same sample was performed with 1 ml of n-hexane and the resulting extract is added to the first. The enrichment of the extractant was achieved by using the n-hexane recovered from the above mentioned extraction of 3 liters of sea-water to treat equal portions of the same sea-water sample up to 9 liters[2]. This procedure was used on a total of eighteen liters of unfiltered sea-water divided in two fractions of nine liters each. Both extracts were combined, dried under sodium sulphate and cold evaporated to 100 µl under nitrogen flow in standardized conditions. The pack-ice cores, melted in a glass column at room temperature and under nitrogen flow, resulted in about 5 liters of solution. The liquid was extracted with 3 ml n-hexane following the above mentioned method and the extract was treated as above.

Fractionaction of the organic extracts

The fractionaction of the organic extracts of both matrices was performed on a silicagel 60 HR for TLC (Merck) column (0.6 × 10 cm) previously activated to 120°C for 12 hours. The n-hexane extract (100 µl) was deposited at the top of the column and the organic compounds were fractionated using the following eluents:

l) 5 ml of n-hexane:	n-alkanes
2) 5 ml of n-hexane/toluene 9.4/5.6 v/v:	polycyclic aromatic hydrocarbons
3) 5 ml of n-hexane/ethyl acetate 9/1 v/v:	aldehydes, ketones, phthalates, fatty acid esters
4) 5 ml of n-hexane/ethyl acetate 6/4 v/v:	alcohols, phthalates

The volume of each fraction was cold evaporated to 100 µl under nitrogen flow.

The entire analytical procedure was repeated five times for every sample.

The recoveries obtained for the different classes of compounds, calculated by using a standard mixture containing n-alkanes, polycyclic aromatic hydrocarbons, aliphatic aldehydes, ketones, alcohols, fatty acid esters and phthalates, at concentration levels of 10 ng/l, are indicated in Table 1.

Derivatization of aldehydes, ketones and alcohols

The fraction containing aldehydes and ketones was derivatized by using O-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine hydrochloride (PFBHA) to obtain the corresponding

Table 1 Recoveries of organic compounds from 9 liters of an aquaeous standard solution.

Organic compounds	*Recovery (%)*	*St. dev.*
n-Alkanes	85	5
PAHs	80	7
Aldehydes, ketones, alcohols	75	5
Phthalates	70	10

oximes (PFBO)[3]. The alcohols were transformed into their trimethylsilyl derivatives by treatment with N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA)[4].

HRGC and GC-MS analysis

For the determination of organic compounds, a HRGC-5160 Mega Series (Carlo Erba, Italy) gas chromatograph equipped with a FID detector was used. The injection was made by using a Cold-SSL injector (Carlo Erba) according to the following temperature program: injection at 40°C, then a rapid increase in temperature to 300°C and splitting 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.. Capillary columns Supelco PTE-5: (30 m, 0.25 mm i.d., 0.25 μm thickness). Carrier gas:helium. The chromatographic peaks were analyzed with a Mega-2 computer system (Carlo Erba) with Spectra Physics software. Confirmatory GC-MS analyses of aldehydes, ketones, alcohols and esters were performed on a Varian 3400 gas chromatograph coupled with a Finnigan ITD mass detector. Carrier gas:helium. An injector SPI (Varian) was used according to the following temperature program: injection at 40°C, then a rapid increase to 300°C. The column temperature program was the same as described above.

Identification of organic compounds

The identification and quantitative determination of organic compounds was realized using gas-chromatographic retention indices with 8 n-alkanes (C-8, C-12, C-16, C-20, C-24, C-28, C-32 and C-34) as standards and a reference calibration table and/or comparing their mass spectra with those reported in the N.B.S. library and a second library made in our laboratory on ITD.

The exact name is reported in the Tables only for those compounds positively identified with the above methods, while only the belonging class is given for the others.

RESULTS AND DISCUSSION

Pack-ice

Tables 2 and 3 show the organic compounds identified in the three pack-ice samples (B, D, E) with their concentrations. From samples B and E only two cores corresponding to depths of one (B-1, E-1) and two meters (B-2, E-2) were obtained while three cores of one meter each were taken in the same place for sample D. The results reveal that this Antarctic matrix is quite rich in both biogenic and anthropogenic organic compounds as was found in pack-ice samples taken from Terra Nova Bay during the Italian Antarctic Expediction 1988/89[1].

The distribution of biogenic compounds, such as aldehydes, ketones, alcohols and squalene is rather homogeneous in the three samples and indicates the validity of the obtained results. The alcohols exhibited the higher concentrations among the different classes of organic compounds. In a number of pack-ice cores squalene dominated the aliphatic hydrocarbon fraction, i.e. 62%–78% of the aliphatic fraction in D-2 and E-2 cores (Table 2).

Table 2 Aliphatic hydrocarbons in Antarctic pack-ice (ng/l); medium values of five determinations with standard deviation.

Compounds	*B-1* *1 m*	*B-2* *2 m*	*D-1* *1 m*	*D-2* *2 m*	*D-3* *3 m*	*E-1* *1 m*	*E-2* *2 m*
n-ALKANES							
n-C 14	bdl	2 *	6 ± 2	2 *	4 ± 1	2 *	2 *
n-C 15	bdl	bdl	5 ± 1	bdl	8 ± 2	3 ± 1	7 ± 2
n-C 16	2 *	8 ± 2	6 ± 2	9 ± 2	15 ± 4	26 ± 7	6 ± 2
n-C 17	2 *	3 ± 1	3 ± 1	8 ± 2	16 ± 4	5 ± 2	6 ± 2
n-C 18	2 *	2 *	3 ± 1	bdl	15 ± 4	6 ± 2	8 ± 2
n-C 19	2 *	bdl	2 *	bdl	12 ± 3	2 *	10 ± 3
n-C 20	bdl	5 ± 2	2 *	2 *	16 ± 4	5 ± 1	9 ± 2
n-C 21	5 ± 1	4 ± 1	7 ± 2	2 *	26 ± 6	10 ± 3	11 ± 2
n-C 22	3 ± 1	4 ± 1	4 ± 1	2 *	32 ± 6	11 ± 3	10 ± 2
n-C 23	4 ± 1	6 ± 2	5 ± 2	2 *	29 ± 5	7 ± 2	6 ± 1
n-C 24	4 ± 1	4 ± 1	21 ± 4	4 ± 1	42 ± 6	11 ± 2	10 ± 2
n-C 25	7 ± 2	10 ± 3	7 ± 2	2 *	30 ± 4	12 ± 3	6 ± 1
n-C 26	8 ± 2	3 ± 1	9 ± 3	2 *	27 ± 4	13 ± 3	6 ± 1
n-C 27	8 ± 2	2 *	7 ± 2	2 *	22 ± 4	10 ± 4	6 ± 1
n-C 28	10 ± 3	3 ± 1	8 ± 3	2 *	27 ± 5	9 ± 3	8 ± 2
n-C 29	9 ± 3	bdl	6 ± 2	2 *	33 ± 7	8 ± 3	5 ± 1
n-C 30	5 ± 2	bdl	4 ± 1	bdl	13 ± 3	5 ± 2	2 *
n-C 31	3 ± 1	bdl	2 *	bdl	18 ± 4	5 ± 1	4 ± 1
n-C 32	bdl	bdl	2 *	bdl	11 ± 3	2 *	2 *
Total n-alkanes	74	56	109	41	396	152	124
Odd/even predominance	1.17	0.86	0.75	0.86	0.98	0.70	1.00
Squalane	bdl	bdl	bdl	bdl	8 ± 1	bdl	bdl
Squalene	61 ± 13	41 ± 11	68 ± 18	67 ± 17	540 ± 135	39 ± 9	431 ± 86

* = detection limit; bdl = below detection limit.

The n-alkanes were quantified over the range C-14 to C-32 in accordance with Cripps[5] (C-15 to C-30) and Green *et al.*[6] (C-15 to C-33); the concentration range was between 41–396 ng/l (Table 2) and agrees with the data reported in previous studies[1,7]. Similar levels of n-alkanes (70–170 ng/l) were found by Green *et al.*[6] in sea-water samples taken at the Davis Station (Eastern Antarctica) but lower (4.1–10.4 ng/l) and higher (1.1–21.8 μg/l) levels were reported by Sanchez-Pardo *et al.*[8] and Cripps[9] respectively for the same area of Antarctica (Bransfield Strait). This variation in the concentration is probably related to complex combination of biological properties of the Southern Ocean.

The odd to even carbon number ratio for n-alkanes gave doubtful informations on their origin[10]. This ratio, evaluated in the range nC-15 to nC-32, was greater than unity for core B-1, near to unity for cores D-3 and E-2 and less than one for the others (B-2, E-1, D-1, D-2) (Table 2). In addition, the values for the cores B-2 and D-2 were not very significant since the concentrations of most alkanes are equal to or less than the detection limit.

Odd to even ratio with values in the range 0.7–1.4 were found on a number of pelagic species from the Bransfield Strait[10] but several authors[11,12] reported that even numbered n-alkanes predominated in Antarctic marine organism from Ross Sea and, therefore the n-alkanes in cores B-2, E-1, D-1 and D-2 are probably biogenic.

Table 3 Organic etherocompounds in Antarctic pack-ice (ng/l); medium values of five determinations with standard deviation.

Compounds	*B-1 1 m*	*B-2 2 m*	*D-1 1 m*	*D-2 2 m*	*D-3 3 m*	*E-1 1 m*	*E-2 2 m*
ALDEHYDES							
Nonanal	36 ± 9	69 ± 17	72 ± 22	49 ± 12	47 ± 15	27 ± 8	46 ± 14
Aliphatic aldehyde	3 ± 1	10 ± 3	30 ± 8	bdl	17 ± 5	23 ± 6	18 ± 5
Decanal	14 ± 4	23 ± 7	17 ± 4	19 ± 4	18 ± 4	12 ± 3	20 ± 5
Decenal	12 ± 3	12 ± 3	49 ± 10	22 ± 7	20 ± 5	11 ± 2	11 ± 3
Undecanal	7 ± 2	10 ± 2	8 ± 2	5 ± 1	11 ± 2	bdl	11 ± 2
Dodecanal	bdl	6 ± 1	3 ± 1	3 ± 1	3 ± 1	5 ± 2	6 ± 2
Tridecanal	7 ± 2	4 ± 1	2 *	3 ± 1	bdl	bdl	bdl
Tetradecanal	bdl	bdl	bdl	bdl	3 ± 1	2 *	3 ± 1
Total aliphatic aldehydes	79	134	181	101	119	80	115
KETONES							
2-Nonanone	2 *	9 ± 3	3 ± 1	4 ± 1	bdl	2 *	4 ± 1
Aliphatic ketone	2 *	5 ± 2	5 ± 1	38 ± 11	2 *	2 *	5 ± 2
Aliphatic ketone	bdl	5 ± 2	7 ± 2	3 ± 1	3 ± 1	bdl	4 ± 1
2-Decanone	6 ± 2	11 ± 3	15 ± 4	6 ± 2	bdl	3 ± 1	bdl
Aliphatic ketone	8 ± 2	42 ± 10	20 ± 5	59 ± 18	35 ± 10	22 ± 6	4 ± 1
2-Undecanone	5 ± 2	10 ± 2	4 ± 1	5 ± 2	3 ± 1	2 *	2 *
Aliphatic ketone	9 ± 3	5 ± 1	6 ± 2	3 ± 1	3 ± 1	10 ± 3	6 ± 1
2-Dodecanone	12 ± 3	21 ± 6	14 ± 4	7 ± 2	3 ± 1	13 ± 3	12 ± 3
2-Tridecanone	6 ± 2	4 ± 1	3 ± 1	3 ± 1	bdl	bdl	bdl
2-Tetradecanone	6 ± 2	2 *	12 ± 4	4 ± 1	2 *	11 ± 3	3 ± 1
Aliphatic ketone	3 ± 1	3 ± 1	bdl	8 ± 3	bdl	bdl	bdl
Total aliphatic ketones	56	114	89	132	51	65	40
ALCOHOLS							
1-Docosanol	49 ± 12	89 + 20	61 ± 14	92 ± 19	132 ± 37	66 ± 14	113 ± 23
1-Tetradecanol	29 ± 6	44 ± 9	25 ± 6	17 ± 4	15 ± 5	45 ± 10	16 ± 4
1-Hexadecanol	27 ± 7	32 ± 9	14 ± 4	42 ± 11	16 ± 5	25 ± 6	30 ± 8
1-Octadecanol	59 ± 18	24 ± 7	27 ± 8	57 ± 17	90 ± 24	41 ± 11	89 ± 22
1-Eicosanol	22 ± 7	13 ± 4	20 ± 6	12 ± 3	61 ± 17	51 ± 12	34 ± 11
Total aliphatic alcohols	186	202	147	220	314	228	282
PHTHALATES							
Di-iso-butylphthalate	248 ± 32	299 ± 36	495 ± 64	199 ± 22	361 ± 54	815 ± 98	283 ± 45
Di-n-butylphthalate	311 ± 56	123 ± 21	268 ± 46	142 ± 21	572 ± 63	351 ± 32	174 ± 21
Benzylbutylphthalate	1056 ± 84	3134 ± 345	236 ± 17	113 ± 11	152 ± 21	421 ± 21	107 ± 10
Bis(2-ethylhexyl)phthalate	54 ± 9	33 ± 3	196 ± 29	67 ± 6	231 ± 30	25 ± 3	60 ± 7
Total phthalates	1669	3589	1195	521	1316	1612	624

* = detection limit; bdl = below detection limit.

Further informations can be deduced from the n-alkane profiles for the more representative ice-cores. The hydrocarbon profile for core B-1 was dominated by nC23–nC30 alkanes and suggested an input from terrestrial vegetation in which odd carbon n-alkanes in the range nC25–nC33, derived from cuticular waxes of continental plants, are dominant[13]. Consequently, the continental contribution defines the n-alkane fingerprinting and the odd/even ratio in the core B-1. The n-alkane profiles of the other

cores, on the contrary, do not show any predominance of nC23–nC30 compounds. There is, however, evidence of specific species influencing the hydrocarbon composition (17% nC16 and 19% nC24 in cores E-1 and D-1 respectively). The dominance of one alkane in one seawater sample (14% nC17) and in some sediments (44% nC18) was already observed by Green *et al.*[6] and it is probably due to a particular algal or bacterial species[14] and, therefore, to biogenic local sources.

The trend of the concentration of biogenic compounds for the three samples as the depth changes is shown in Figure 2.

The alcohols have a uniform behaviour, since increase in all samples with depth. It is not possible to determine any specific trend for the two other classes of organic compounds. It is important to note that the content of the various classes generally corresponds to the one reported for the same compounds in the Antarctic environmental matrices. In fact the concentration range is between 78–181 ng/l for aldehydes, 40–132 ng/l for ketones, 147–314 ng/l for alcohols and agrees with the data reported in previous studies[1,7].

The range of phthalate concentrations was between 521–1669 ng/l with the exception of 3589 ng/l in core B-2 (Table 3). These values depend on the high levels of benzylbutylphthalate in all cores and, particularly, in core B-2 which is the nearest to the Italian Base. Consequently, the presence of benzylbutylphthalate, which was not found in previous pack-ice samples[1], is probably characteristic of a local anthropogenic origin. The other three phthalates (di-n-butyl-, di-iso-butyl-, di-2-ethylhexyl-), on the contrary, are ubiquitous environmental contaminants and are present in all Antarctic matrices examined up to now (seawater, pack-ice, snow, sediments). The concentration range is 408–1191 ng/l (Table 3), similar levels of these compounds were found in pack-ice (525–745 ng/l) and seawater (139–556 ng/l) samples taken during the Expedition 1988/89[1]. The range of the phthalate concentrations in the North Sea (Liverpool Bay) is 467–5840 ng/l near the Tees and Mersey estuaries[15]. These data demonstrate the pollution level of Terra Nova Bay. A source for phthalates is the long range atmospheric transport as shown by the high concentrations of these compounds in the snow[7] and in the particulate organic matter sampled at Terra Nova Bay Station[16]. This fact suggestes that areosol transport is the dominant mechanism for input of phthalates to Antarctic precipitation. Local human activity in Ross Sea and on land may even result in phthalates contamination of the marine environment.

Sea-water under the pack and offshore

Tables 4 and 5 show the concentrations of organic compounds found in four sea-water samples collected under the pack in two different areas, B and E. The latter area is the furthest from the Italian Base. The same Tables also report the organic substances identified in the offshore sea-water samples (area A) taken at depths of 20 m (SWA-20), 500 m (SWA-500) and 1500 m (SWA-1500).

In all the samples the following compounds were identified: n-alkanes, aldehydes, ketones and alcohols. High concentrations of phthalates were also found but such data have not been reported because the samples were contaminated by the "go-flow" bottles.

The range of the n-alkane concentrations is 36–260 ng/l (Table 4), and the hydrocarbon level is generally lower than the one found for the pack-ice cores. Almost all n-alkanes were quantified since their detection limit is lower in water (1 ng/l) than in pack-ice (2 ng/l) owing to the greater volumes of seawater samples.

The odd/even predominance for the n-alkanes is much lower than 1 in all samples indicating that their origin is biogenic. It should be noted that Green *et al.*[6] found

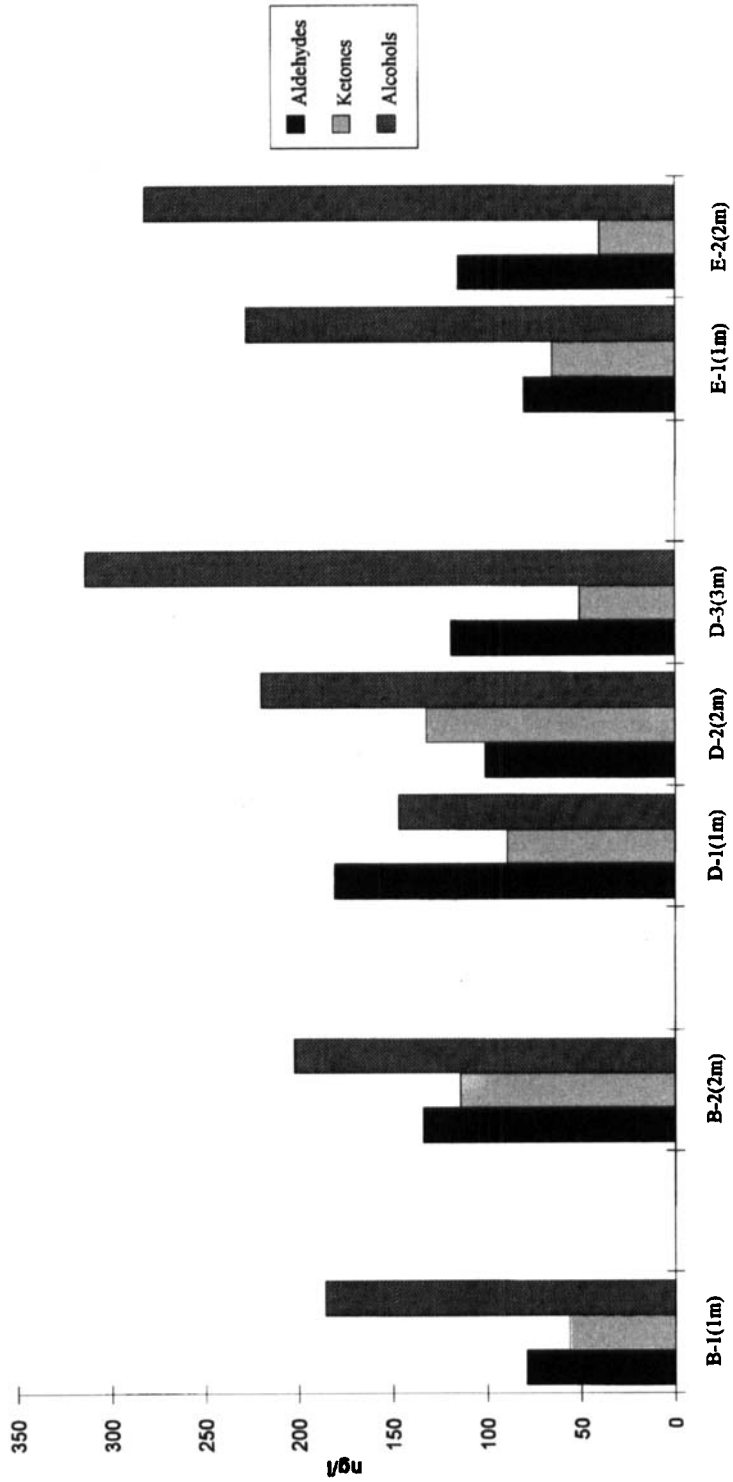

Figure 2 Concentrations (ng/l) of classes of biogenic organic compounds in pack-ice samples collected from different areas.

Table 4 Aliphatic hydrocarbons in offshore sea-water samples and in sea-water samples collected under pack-ice (ng/l); medium values of five determinations with standard deviation.

	SW samples collected under pack-ice				*Offshore SW samples*		
Compounds	*SWB 0.5 m*	*SWB 25 m*	*SWB 250 m*	*SWE 0.5 m*	*SWA 20 m*	*SWA 500 m*	*SWA 1500 m*
n-ALKANES							
n-C 14	1 *	1 *	1 *	1 *	5 ± 1.6	1 *	1 *
n-C 15	1 *	bdl	1 *	1 *	7 ± 1.9	2 ± 0.5	1 *
n-C 16	8 ± 1.8	6 ± 1.3	8 ± 1.9	7 ± 1.8	24 ± 7.0	14 ± 3.4	14 ± 3.6
n-C 17	3 ± 0.6	2 ± 0.4	2 ± 0.4	2 ± 0.5	12 ± 3.1	3 ± 0.7	bdl
n-C 18	2 ± 0.4	1 *	1 *	2 ± 0.5	10 ± 2.3	2 ± 0.4	1 *
n-C 19	2 ± 0.4	bdl	1 *	2 ± 0.4	10 ± 2.2	1 *	2 ± 0.4
n-C 20	1 *	1 *	1 *	1 *	13 ± 2.6	2 ± 0.4	2 ± 0.4
n-C 21	2 ± 0.3	1 *	2 ± 0.3	2 ± 0.4	13 ± 2.2	2 ± 0.4	2 ± 0.3
n-C 22	2 ± 0.2	1 *	1 *	2 ± 0.3	8 ± 1.4	1 *	2 ± 0.3
n-C 23	3 ± 0.2	1 *	1 *	3 ± 0.4	8 ± 1.2	1 *	3 ± 0.4
n-C 24	11 ± 1.3	8 ± 1.0	9 ± 1.3	7 ± 1.1	34 ± 4.4	10 ± 1.1	17 ± 2.2
n-C 25	4 ± 0.4	1 *	2 ± 0.3	4 ± 0.6	11 ± 1.2	2 ± 0.2	5 ± 0.5
n-C 26	4 ± 0.4	1 *	4 ± 0.4	3 ± 0.4	16 ± 2.4	2 ± 0.3	6 ± 0.8
n-C 27	3 ± 0.3	1 *	2 ± 0.2	3 ± 0.5	10 ± 1.4	2 ± 0.3	4 ± 0.6
n-C 28	8 ± 0.9	7 ± 1.0	8 ± 1.2	5 ± 0.8	22 ± 3.7	7 ± 1.1	13 ± 2.3
n-C 29	3 ± 0.4	1 *	2 ± 0.3	3 ± 0.6	10 ± 1.6	2 ± 0.4	3 ± 0.7
n-C 30	2 ± 0.4	bdl	1 *	1 *	13 ± 2.7	1 *	2 ± 0.5
n-C 31	2 ± 0.4	1 *	bdl	1 *	7 ± 1.7	1 *	1 *
n-C 32	7 ± 1.7	2 ± 0.4	5 ± 1.1	3 ± 0.8	27 ± 7.3	6 ± 1.5	7 ± 1.8
Total n-alkanes	69	36	52	53	260	62	86
Odd/even predominance	0.51	0.30	0.34	0.68	0.53	0.36	0.33

* = detection limit; bdl = below detection limit.

odd/even ratios between 0.4–0.8 for in Antarctic seawater particulate. The hydrocarbon profiles were similar and the alkanes nC16, nC24 and nC28 were dominant in all seawater samples. These data suggest a biogenic origin too.

Aliphatic aldehydes and ketones have a number of carbon atoms less than sixteen while the alcohols contain up to twenty (Table 5). The results indicate that there are no appreciable differences in the composition of organic compounds found in sea-water samples collected under the pack or offshore (Ross Sea). Figure 3 shows the trend of the concentration for the biogenic organic compounds at varying depths. The concentrations of the substances in the samples collected under the pack in two different areas (SWB and SWE) and at the same depth (0.5 m) are similar with the exception of the alcohols. The samples taken from area B at 0.5 m, 25 m and 250 m, contain the same quantities of biogenic compounds but different amounts of ketones.

Comparison of pack-ice and seawater

To obtain information about the possible enrichment of organic compounds in the pack, we compared the concentration range of each class of substances in the pack, in the seawater under the pack and in offshore seawater (see Figure 4). The results show that

Table 5 Organic etherocompounds in offshore sea-water samples and in sea-water samples collected under pack-ice (ng/l); medium values of five determinations with standard deviation.

	SW samples collected under pack-ice				*Offshore SW samples*		
Compounds	*SWB 0.5 m*	*SWB 25 m*	*SWB 250 m*	*SWE 0.5 m*	*SWA 20 m*	*SWA 500 m*	*SWA 1500 m*
ALDEHYDES							
Nonanal	2 ± 0.6	2 ± 0.7	4 ± 1.4	bdl	1 *	bdl	1 *
Aliphatic Aldehyde	bdl	bdl	2 ± 0.6	bdl	5 ± 1.7	2 ± 0.6	1 *
Decanal	5 ± 1.2	3 ± 0.8	2 ± 0.4	4 ± 1.0	9 ± 2.4	4 ± 1.2	5 ± 1.3
Decenal	2 ± 0.5	1 *	1 *	1 *	7 ± 2.1	1 *	1 ± 0.3
Undecanal	1 *	bdl	1 *	1 *	5 ± 1.3	2 ± 0.6	3 ± 1.0
Dodecanal	1 *	bdl	bdl	bdl	4 ± 0.9	1 *	1 *
Tridecanal	bdl	bdl	bdl	bdl	2 ± 0.4	2 ± 0.6	1 *
Tetradecanal	bdl	bdl	1 *	bdl	2 ± 0.5	1 *	1 *
Total aliphatic aldehydes	11	6	11	6	35	13	14
KETONES							
2-Nonanone	1 *	1 *	2 ± 0.6	1 *	14 ± 5.0	7 ± 2.4	4 ± 1.2
Aliphatic ketone	bdl	1 *	1 *	bdl	7 ± 2.0	2 ± 0.6	3 ± 1.0
Aliphatic ketone	2 ± 0.7	1 *	6 ± 1.7	1 *	17 ± 5.8	6 ± 2.2	5 ± 1.8
2-Decanone	1 *	2 ± 0.7	7 ± 2.0	bdl	24 ± 7.4	7 ± 2.0	12 ± 3.6
Aliphatic ketone	bdl	2 ± 0.7	3 ± 0.8	bdl	24 ± 9.1	12 ± 4.3	4 ± 1.4
2-Undecanone	8 ± 1.9	2 ± 0.6	3 ± 0.7	1 *	14 ± 3.8	3 ± 0.9	6 ± 1.6
Aliphatic ketone	bdl	2 ± 0.6	bdl	1 *	8 ± 2.5	2 ± 0.7	5 ± 1.7
2-Dodecanone	1 *	bdl	8 ± 1.6	bdl	6 ± 1.5	2 ± 0.6	1 *
2-Tridecanone	bdl	bdl	1 *	bdl	3 ± 0.8	2 ± 0.6	bdl
2-Tetradecanone	bdl	1 *	2 ± 0.4	bdl	3 ± 0.9	2 ± 0.7	bdl
Aliphatic ketone	2 ± 0.6	3 ± 0.8	2 ± 0.6	1 *	3 ± 1.0	4 ± 1.4	5 ± 1.7
Total aliphatic ketones	15	15	35	5	123	49	45
ALCOHOLS							
1-Docosanol	7 ± 2.0	4 ± 1.0	6 ± 1.6	41 ± 9.8	17 ± 4.9	36 ± 11.2	50 ± 15.5
1-Tetradecanol	11 ± 2.9	11 ± 2.9	10 ± 2.8	45 ± 9.9	35 ± 10.9	2 ± 0.6	6 ± 1.7
1-Hexadecanol	8 ± 2.2	9 ± 2.3	14 ± 4.1	10 ± 2.7	34 ± 9.2	5 ± 1.4	11 ± 3.1
1-Ottadecanol	19 ± 5.5	2 ± 0.5	18 ± 4.0	16 ± 4.5	43 ± 10.8	15 ± 3.9	10 ± 2.6
1-Eicosanol	14 ± 4.3	11 ± 2.9	7 ± 1.7	4 ± 1.2	39 ± 10.9	6 ± 1.9	3 ± 0.9
Total aliphatic alcohols	59	37	55	116	168	64	80

* = detection limit; bdl = below detection limit.

the concentration levels of each class of organic substances in the pack are consistently higher than those in seawater taken under the pack and in the offshore seawater. These data confirm previous results found for the same matrices[1] and the conclusion can be made that there is a real enrichment of organic compounds from seawater during the pack-ice formation. This agrees with the hypothesis that the pack forms from the surface down and incorporates all the organic compounds present at the marine surface microlayer which is, as known, more enriched in organic compounds than the underlying waters[17].

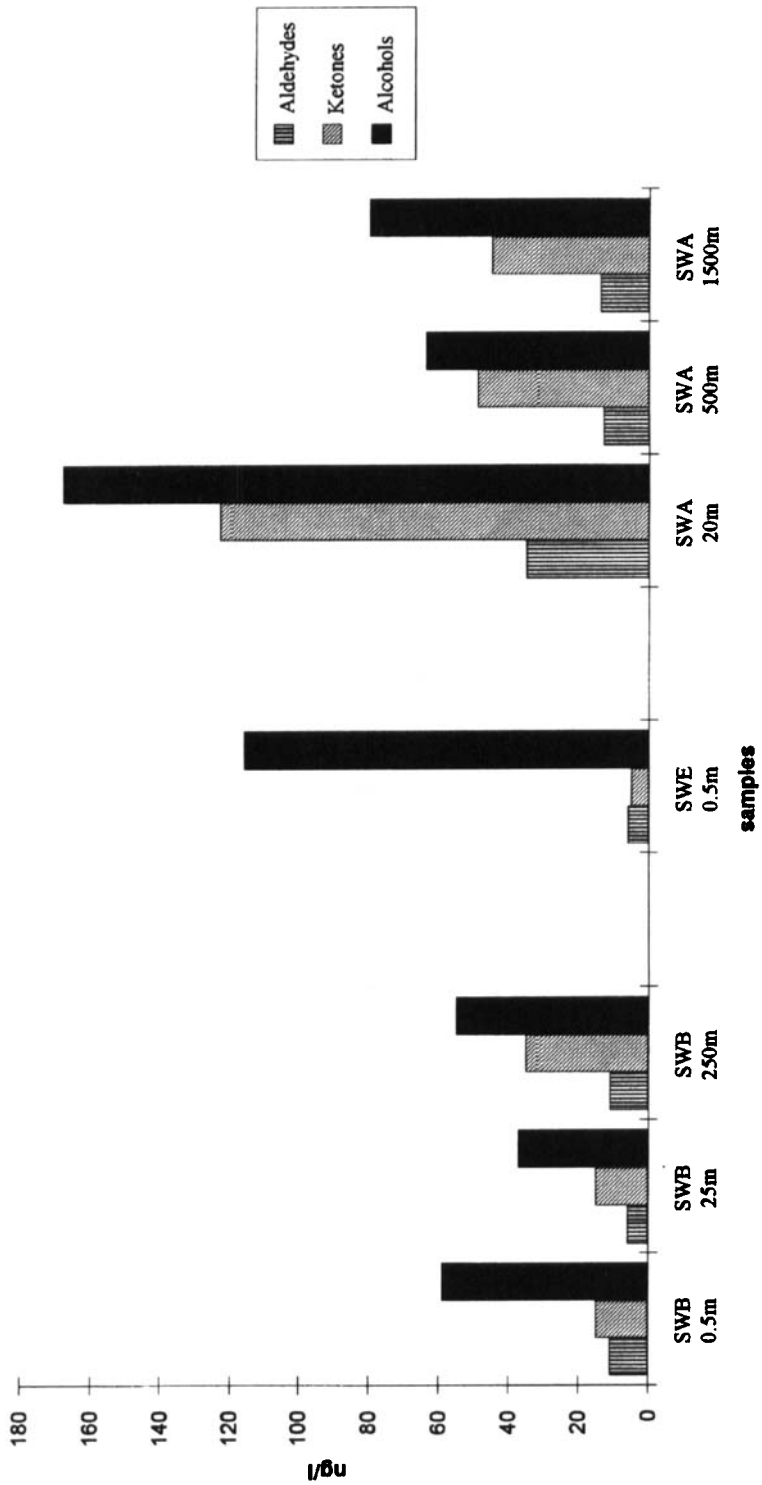

Figure 3 Concentrations (ng/l) of biogenic organic compounds in sea-water samples at different depths.

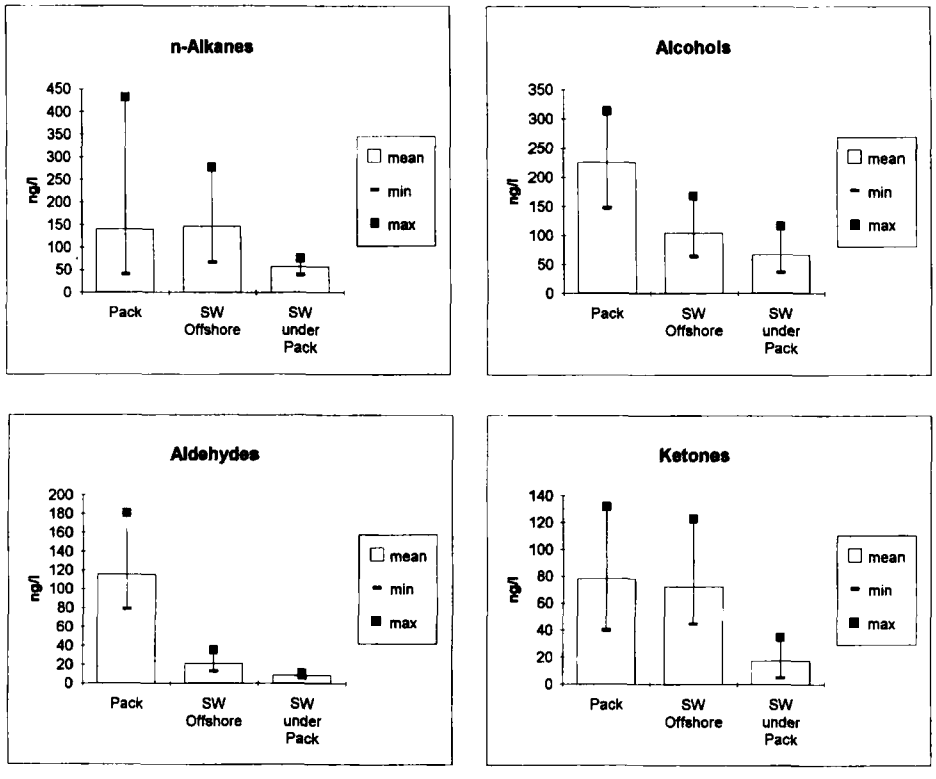

Figure 4 Comparison of concentration ranges of classes of organic compounds in pack-ice, offshore sea-water and sea-water collected under pack-ice.

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