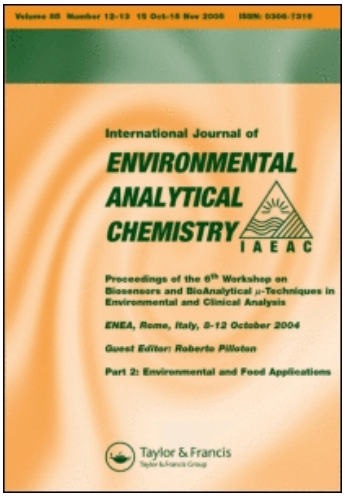


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# Horizontal and vertical distributions of Biogenic and Anthropogenic Organic compounds in the Ross Sea (Antarctica)

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# HORIZONTAL AND VERTICAL DISTRIBUTIONS OF BIOGENIC AND ANTHROPOGENIC ORGANIC COMPOUNDS IN THE ROSS SEA (ANTARCTICA)

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Horizontal and vertical distributions of organic compounds extractable with *n*-hexane were investigated at five sampling stations (Ross Sea) during the Italian Antarctic Expedition 1997/98. Samples were collected from seven depths under pack ice and from two or three depths at the other stations located at different distances from the coast. The lowest concentrations of biogenic and anthropogenic compounds were found at station Y3, the furthest from the coast, while the highest concentrations were observed under pack ice (B2-2 station) or in the Polynya zone (Y1 station). The levels of organic compounds in the particulate phase were higher than those in the dissolved phase for all the investigated samples. Concentrations of biogenic organic compounds (long-chain aldehydes and alcohols, fatty acid esters and *n*-alkanes) were well related to fluorescence intensity, which is usually reported as a biological activity index. The odd-to-even carbon-number ratio for *n*-alkanes was lower than 1 at stations B2-2, Y1, Y5 and Y6 (located less than 150 km far from the coast) with the predominance of *n*-C16, *n*-C24 and *n*-C28, indicative of autochthonous pelagic species. An odd-to-even ratio higher than unity and a different *n*-alkane profile were observed at station Y3 (about 300 km from the Ross Ice Shelf and 600 km from Terra Nova Bay). Low levels of pollutants (i.e. phthalates) were found, mainly in the particulate phase up to a depth of 50 m, confirming a local source of the phthalates found at significant concentrations during previous expeditions.

*Keywords:* Antarctica; Sea water; Chromatographic analysis; Organic compounds

## INTRODUCTION

The determination of organic compounds in aqueous matrices of Antarctica as tracers for biogenic and anthropogenic sources is of paramount importance to foresee their origin and the composition of marine aerosol, which is involved in the transport of biogenic and anthropogenic compounds from the marine environment to the coastal and inner zones of the continent [1,2].

The analyses of sea water, sediment and pack ice samples, collected in Terra Nova Bay (Ross Sea) during previous Antarctic expeditions [3–7], evidenced a large

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number of biogenic organic compounds and some classes of contaminants such as phthalates and alkylbenzenes. High concentrations of phthalates were found in pack ice collected during the 1990/1991 Italian Antarctic Expedition, and their origin was related to local pollution sources [8].

Among biogenic compounds, particular care was given to the class of aliphatic hydrocarbons which show an odd-to-even carbon-number ratio much lower than 1 and a distribution pattern dominated by C16, C24 and C28 *n*-alkanes in snow, sea water and pack ice samples collected in Terra Nova Bay and snow samples taken from an inner zone of the continent [1,2,8].

To obtain a representative picture of horizontal and vertical distributions of biogenic and anthropogenic organic compounds in a larger zone such as the Ross Sea area, several samples were collected during the Italian Antarctic Expedition 1997/1998 at five stations located at different distances from the coast (up to 300 km far from the Ross Ice Shelf ).

A further aim of this article was to highlight the concentration and/or composition variations of the investigated organic compounds, comparing the present results with those obtained during previous expeditions [3,8], taking into account that all samples were collected in the same season, close to the ice-melting period.



## EXPERIMENTAL

### Sampling Sites

During the XIII Italian Antarctic Expedition (1997/1998), sea-water samples were collected in November 1997 at different depths at B2-2 station (under pack ice), located in the Gerlache Inlet (Terra Nova Bay), and at the stations Y1, Y3, Y5 and Y6, located in Ross Sea at different distances from the coast (see Fig. 1). The geographical coordinates and maximum depth of the sampling stations are reported in Table I.

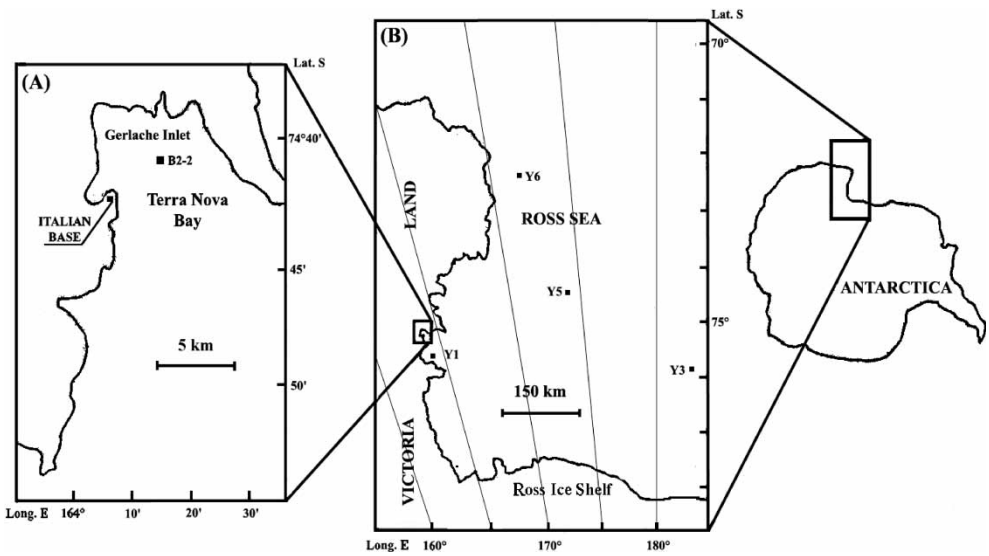


FIGURE 1 Italian Antarctic Expedition 1997/1998: sampling stations.

TABLE I Italian Antarctic Expedition 1997/1998: sampling stations

| *Sampling station* | *Latitude* | *Longitude* | *Maximum depth* (m) |
|---|---|---|---|
| B2-2 Gerlache Inlet (Terra Nova Bay) | 74°41.632′S | 164°11.178′E | 430 |
| Y1 Ross Sea (Polynya) | 75°04′S | 164°13′E | 950 |
| Y3 Ross Sea (Challenger Basin) | 75°54.20′S | 177°34.44′W | 628 |
| Y5 Ross Sea (Joides Basin) | 74°00.45′S | 174°48.72′E | 582 |
| Y6 Ross Sea (Joides Basin) | 72°02′S | 172°15′E | 415 |

The following samples were collected: B2-2: depth, 2 m (concerning the water layers directly below the pack ice), 10 m, 25 m, 50 m, 100 m, 200 m and 380 m; Y1: depth, 25 m, 80 m and 250 m; Y3: depth, 25 m, 140 m and 250 m; Y5: depth, 25 m and 90 m; Y6: depth, 25 m, 70 m and 200 m.

At the main station B2-2, which was also used as the sampling site in previous expeditions [3,8], the largest number of samples and the maximum depth were investigated. Sampling stations in Ross Sea were studied for the first time, and the number of collected samples was lower than at B2-2 site because of time constraints during the oceanographic cruise.



## Sampling

Sea water was sampled using 25-L stainless steel Go-Flo type bottles (Idromar, Genoa, Italy) fixed on a Kevlar wire. After the collection, the samples were immediately transferred into 25-L stainless steel reservoirs (Inox Sabat, Bologna, Italy), frozen and stored at −30°C until the analysis. Sea-water samples from Gerlache Inlet were taken under the pack, making a hole (diameter: 1 m) in the ice. The offshore samplings were performed by an oceanographic ship with a starting depth of 25 m so as to avoid any pollution from the boat.

## Reagents and Materials

Solvents used for extraction and fractionation processes were of 'organic residue analysis' grade and purchased from Baker (Holland), and distilled three times before use.

Anhydrous sodium sulphate (Merck, Germany) was heated for 24 h at 450°C to remove any organic matter and kept at 120°C until use. The same procedure was adopted for the purification of glass-fiber filters (GF/F Whatman, UK).

All glassware and steel apparatus were cleaned before use by repeatedly washing with hot chromic and concentrated sulphuric acid mixture, purified water (Steroglass, Perugia, Italy) and acetone, methylene chloride and *n*-hexane.

Standard organic compounds were commercially available from Supelco (Bellefonte, USA) and Alltech (Deerfield, USA).

## Filtration

After defrosting, samples were filtered through glass-fiber filters (previously purified as above described) and weighted. Filtration was carried out by using a stainless steel apparatus (Sartorius, Florence, Italy) under pressure of nitrogen. Filters were then washed with ultrapure water to remove sea salt, partially dried under a gentle nitrogen

flow and finally maintained in a dryer. Filters were weighed repeatedly until the masses were within 5% of each other, and the suspended material was determined by difference.

### Extraction and Fractionation of Organic Compounds

Before extraction, filters were spiked with a standard mixture containing tetradecene (400 ng) and di-heptylphthalate (200 ng) for recovery determination. After adding purified water (3 mL) and methanol (1 mL), filters were broken up using an ultrasonic probe for 15 min, and the particulate matter was extracted under magnetic stirring with 3 mL of a *n*-hexane/methylene chloride mixture 1/1 v/v. After centrifugation (3500 rpm, 5 min), the hydrophobic phase was recovered, and the extraction procedure was repeated two more times. The three organic solutions were combined, dried over anhydrous sodium sulphate and cold-evaporated to 100 µL under a gentle nitrogen flow in standardized conditions.

The extraction of organic compounds from filtered sea water was performed with *n*-hexane by the replicated extractant enrichment method, especially designed for Antarctic aqueous samples [9], enabling 18 L of water to be extracted with 6 mL of solvent.

Fractionation of organic compounds was performed as described elsewhere [10] using a silica gel 60 HR (Merck) column (0.6 × 10 cm), previously activated at 150°C for 3 h. The organic extract (100 µl) was applied at the top of the column, and the compounds were fractionated using the following eluents:

1. 4 mL of *n*-hexane: *n*-alkanes.
2. 7.5 mL of *n*-hexane/toluene 5.6/9.4 v/v: alkylbenzenes.
3. 7 mL of *n*-hexane/ethyl acetate 9/1 v/v: aldehydes, ketones, phthalates, fatty acid esters.
4. 8 mL of *n*-hexane/ethyl acetate 6/4 v/v: alcohols and sterols.

The quantitative determination of the analytes was repeated five times on each fraction or organic extract (when fractionation was unnecessary). The extraction efficiency for the different classes of compounds was calculated using a standard mixture containing aliphatic and aromatic hydrocarbons and phthalates at concentration levels of 10 ng/L [8].

### Derivatization of Aldehydes and Alcohols

The fraction containing aldehydes was derived by using *O*-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine hydrochloride (PFBHA) to yield the corresponding oximes (PFBO) [11]; the alcohols were transformed into their trimethylsilyl derivatives [12].

### HRGC and GC-MS Analysis

GC and GC-MS analyses were performed on two Varian 3400 (Palo Alto, CA, USA) gas chromatographs, equipped with a Finnigan ion trap and a FID detector, respectively. The injection was made 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 a linear increase

to 300°C at 4°C/min, and finally an isotherm at 300°C for 15 min. Supelco PTE-5 capillary columns (30 m, 0.25 mm ID, 0.25 μm thickness) were used; carrier gas: high-purity-grade helium. Electron impact mass spectra were obtained at an ionization energy of 70 eV.

All peaks were identified using gas-chromatographic Van den Dool and Kratz [13] indices with eight *n*-alkanes as standards (C8, C12, C16, C20, C24, C28, C32, C34) and a reference calibration table. Mass spectra were compared with those reported in the NBS library and in a second library made in our laboratory on ITD.

The amounts 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 L) inserted in two stainless steel reservoirs in Antarctica, frozen at −30°C and carried to our laboratory together with sea-water samples. Analysis of the highly purified water revealed a negligible concentration of organic compounds, when compared with the blanks. As shown in a previous paper [1], the blank concentrations of organic compounds were $0.9 \pm 0.2$ ng/L for di-iso- and di-*n*-butylphthalate, 0.7–0.9 ng/L for ethylbenzene, *o*-xylene and mesytilene, $0.9 \pm 0.2$ ng/L for *m*/*p*-xylene and 1,2,4-trimethylbenzene, and 0.7–1.9 ng/L for nonanal, dodecanol and C14–C22 *n*-alkanes.

The concentration levels reported in Tables II–V were obtained by subtracting the blanks (2 ng/L for *n*-alkanes, aldehydes and alcohols, and 1 ng/L for alkylbenzenes and phthalates) from the values obtained by the gas chromatograms.

Detection limits were calculated by doubling blank concentrations, and, consequently, 2 ng/L for *n*-alkanes, aldehydes and alcohols and 1 ng/L for alkylbenzenes and phthalates were considered. For instance, the detection limit of 2 ng/L for *n*-alkanes corresponds to 4 ng/L values obtained by the gas-chromatographic analysis.



## RESULTS AND DISCUSSION

### Horizontal Distribution of Organic Compounds in the Sub-surface Water

In order to study the horizontal distribution of organic compounds in the investigated area, the samples collected at −25 m were compared, since this depth was the only one common for all the sampling sites. In particular, Table II shows the detailed composition of the sample collected under pack ice, at the main station B2-2.

The major part of organic compounds found in this sample was probably biogenic. In this regard, one should note the presence of sterols, fatty acid esters, *n*-alkanes, branched and monounsaturated hydrocarbons and squalene, which are well-known phytoplankton and zooplankton-derived compounds [14–17]. The presence of aldehydes and ketones may be the result of the photolysis of dissolved organic material (DOM) [18] usually present in Antarctic sea water [19]. Such compounds were the same as those found in sea-water samples collected under pack ice in Terra Nova Bay during a previous expedition [8] and are present in all the examined stations.

TABLE II Mean concentration (ng/L) and standard deviation ($n = 5$) of organic compounds identified in a sea-water sample from the B2-2 station at a depth of 25 m

| *Compounds* | *B2-2* | |
|---|---|---|
| | *Solution* | *Particulate phase* |
| *n*C-14 | 2[a] | 5 ± 1 |
| *n*C-15 | 2[a] | 11 ± 3 |
| *n*C-16 | 19 ± 3 | 39 ± 6 |
| *n*C-17 | 5 ± 2 | 22 ± 4 |
| *n*C-18 | 4 ± 1 | 15 ± 2 |
| *n*C-19 | 4 ± 1 | 28 ± 6 |
| *n*C-20 | 3 ± 1 | 21 ± 2 |
| *n*C-21 | 2[a] | 22 ± 3 |
| *n*C-22 | 8 ± 2 | 10 ± 1 |
| *n*C-23 | 2[a] | 11 ± 2 |
| *n*C-24 | 10 ± 3 | 28 ± 5 |
| *n*C-25 | 3 ± 1 | 9 ± 1 |
| *n*C-26 | 3 ± 1 | 16 ± 3 |
| *n*C-27 | 3 ± 1 | 14 ± 3 |
| *n*C-28 | 10 ± 2 | 22 ± 4 |
| *n*C-29 | 3 ± 1 | 14 ± 2 |
| *n*C-30 | 3 ± 1 | 15 ± 2 |
| *n*C-31 | 4 ± 1 | 5 ± 2 |
| *n*C-32 | 5 ± 1 | 21 ± 5 |
| *n*C-33 | bdl | 5 ± 1 |
| *n*C-34 | bdl | 9 ± 2 |
| Odd/even (C15–C32) | 0.4 | 0.7 |
| Branched alkanes and alkenes[b] | 49 | 318 |
| Squalene | 59 ± 7 | 164 ± 16 |
| Nonanal | 4 ± 1 | 2[a] |
| Decanal | 2[a] | bdl |
| Undecanal | 5 ± 1 | 2[a] |
| Dodecanal | 5 ± 1 | 6 ± 1 |
| Tetradecanal | 3 ± 1 | 29 ± 4 |
| Aliphatic ketones[b] | 5 | 22 |
| Aliphatic alcohols[b] | 20 | 42 |
| Alkyl-cyclohexanol[b] | 6 ± 2 | 6 ± 1 |
| Hexadecanol | 3 ± 1 | 27 ± 3 |
| Docosanol | 3 ± 1 | 14 ± 2 |
| Sterols[b] | 7 | 89 |
| Alkyl phenols[b] | 8 | 67 |
| Octanoic acid methyl ester | 5 ± 1 | 2[a] |
| Tetradecanoic acid methyl ester | 25 ± 4 | 11 ± 2 |
| Pentadecanoic acid methyl ester | 10 ± 2 | 11 ± 3 |
| Hexadecanoic acid methyl ester | 50 ± 9 | 137 ± 19 |
| Octadecanoic acid methyl ester | 7 ± 1 | 24 ± 6 |
| Di-isobutylphthalate | 2 ± 1 | 5 ± 1 |
| Di-*n*-butylphthalate | 2 ± 1 | 6 ± 1 |
| Bis-(2-ethylhexyl)phthalate | 4 ± 1 | 9 ± 2 |

[a]Detection limit. [b]Compounds for which only the class was identified. bdl: below detection limit.



### *Aliphatic Hydrocarbons*

The horizontal profile of *n*-alkanes determined at Ross Sea stations, at 25 m depth, is shown in Fig. 2. As previously observed at the main station B2-2, straight-chain compounds such as C16 and, to a minor extent, C24, C28 and C32 *n*-alkanes were generally present at higher concentrations with respect to the other components. However, in the particulate matter of sample Y1, high levels of C19, C20 and C21 *n*-alkanes were also observed.

TABLE III Mean concentrations of the organic compound classes (ng/L) in sea-water samples collected at 25 m depth

| | *Stations* | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | *B2-2* | | *Y1* | | *Y6* | | *Y5* | | *Y3* | |
| | *S* | *P* (0.94 mg/L) | *S* | *P* (0.40 mg/L) | *S* | *P* (0.40 mg/L) | *S* | *P* (0.17 mg/L) | *S* | *P* (0.25 mg/L) |
| Total *n*-alkanes | 95 | 342 | 99 | 253 | 82 | 257 | 76 | 347 | 79 | 201 |
| Odd-to-even ratio (C15–C32) | 0.4 | 0.7 | 0.6 | 0.8 | 0.6 | 0.8 | 0.5 | 0.7 | 1.2 | 1.4 |
| Total aliphatic hydrocarbons | 203 | 824 | 145 | 612 | 137 | 334 | 105 | 424 | 106 | 275 |
| Total oxygenated compounds | 168 | 491 | 68 | 266 | 55 | 172 | 46 | 159 | 18 | 85 |
| Total alkylbenzenes | 3 | 8 | 9 | 13 | 5 | 10 | 3 | 6 | bdl | bdl |
| Total phthalates | 8 | 20 | 18 | 21 | 6 | 14 | 5 | 13 | 3 | 7 |

bdl: below detection limit; S: solution; P: particulate matter.



The odd-to-even carbon number ratio for *n*-alkanes in the range C15–C32 was less than 1 for the samples B2-2, Y1, Y6 and Y5 and greater than unity for the offshore sample Y3, the farthest from the coast. This ratio can provide useful information about the origin of *n*-alkanes. Values of about 1 suggest contamination by petroleum hydrocarbons, while an odd- or even-carbon predominance was attributed to terrestrial plants (or marine algae) [20,21] and to Antarctic pelagic species [22], respectively. In particular, several authors found that even-chain compounds dominated the hydrocarbons of marine organisms in Ross Sea [23] and in Antarctic Peninsula [24]. Therefore, *n*-alkanes of samples B2-2, Y1, Y6 and Y5 were probably biogenic.

Sample Y3, collected about 300 km from the Ross Ice Shelf and 600 km from Terra Nova Bay, showed a different distribution of *n*-alkanes, with odd-carbon predominance in the C23–C31 range. The odd-to-even carbon number ratios were 1.2 and 1.4 for dissolved and particulate hydrocarbons, respectively. The presence of such hydrocarbons could be due to the long-range transport of terrestrially (high plants) influenced aerosol and/or to autochthonous marine organisms containing hydrocarbons dominated by odd-chain compounds. It should be underlined that odd-to-even ratios ranging from 0.7 to 1.4 were found for pelagic species in Bransfield Strait (between Weddel and Bellingshausen Sea) [25].

The marked even-carbon dominance in a wide zone of Ross Sea agrees with the results obtained for samples of sea water, pack ice and snow collected in the area of Terra Nova Bay during previous expeditions [1,2,8]. The prevalence of C16, C24 and C28 *n*-alkanes in this area can affect the composition of aliphatic hydrocarbons in marine aerosol and, consequently, in coastal snow, where such hydrocarbons were found at higher concentrations with respect to the others.

Concentrations of *n*-alkanes were included between 76 and 104 ng/L (mean $89 \pm 13$ ng/L) and between 201–365 ng/L (mean $284 \pm 81$ ng/L) for dissolved and particulate phase, respectively. Similar levels of *n*-alkanes (36–260 ng/L) were found in the same area [8] during a previous expedition and in sea-water samples taken at the Davis Station (Eastern Antarctica), as reported by Green *et al.* [26] (70–170 ng/L). However, lower (4.1–10.5 ng/L) and higher (1.1–21.8 μg/L) levels were obtained by Sanchez-Pardo *et al.* [27] and Cripps [28], respectively, for the Bransfield strait area.

TABLE IV Mean concentrations of the organic compound classes (ng/L) in the water column at B2-2 sampling station

| | *Depth* | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 2 m | | 10 m | | 25 m | | 50 m | | 100 m | | 200 m | | 380 m | |
| | *S* | *P* (0.32 mg/L) | *S* | *P* (0.38 mg/L) | *S* | *P* (0.94 mg/L) | *S* | *P* (1.43 mg/L) | *S* | *P* (0.76 mg/L) | *S* | *P* (0.37 mg/L) | *S* | *P* (0.27 mg/L) |
| Total *n*-alkanes | 55 | 129 | 104 | 173 | 95 | 342 | 94 | 432 | 34 | 66 | 32 | 97 | 32 | 92 |
| Odd-to-even ratio (C15–C32) | 0.7 | 0.7 | 0.4 | 0.6 | 0.4 | 0.7 | 0.6 | 0.8 | – | 0.7 | – | 0.7 | – | 0.6 |
| Total aliphatic hydrocarbons | 110 | 422 | 173 | 461 | 203 | 824 | 147 | 646 | 108 | 170 | 93 | 179 | 62 | 204 |
| Total oxygenated compounds | 40 | 86 | 76 | 312 | 167 | 489 | 62 | 667 | 54 | 113 | 33 | 48 | 32 | 43 |
| Total alkylbenzenes | 20 | 19 | 6 | 10 | 3 | 9 | bdl | bdl | bdl | bdl | bdl | bdl | bdl | bdl |
| Total phthalates | 18 | 32 | 10 | 15 | 8 | 20 | 5 | 24 | bdl | 10 | bdl | 7 | bdl | 3 |

S: solution; P: particulate matter; bdl: below detection limit; nc: not calculated.

TABLE V Mean concentrations of the organic compound classes (ng/L) in the water column at Y1, Y3, Y5 and Y6 stations (Ross Sea)

| *Y1* | | | | | | *Y3* | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| (−25 m) | | (−80 m) | | (−250 m) | | (−25 m) | | (−70 m) | | (−200 m) | |
| *S* | *P* (0.40 mg/L) | *S* | *P* (0.44 mg/L) | *S* | *P* (0.70 mg/L) | *S* | *P* (0.04 mg/L) | *S* | *P* (0.20 mg/L) | *S* | *P* (0.11 mg/L) |
| 99 | 253 | 77 | 194 | 44 | 85 | 82 | 257 | 64 | 175 | 32 | 80 |
| 0.6 | 0.8 | 0.7 | 0.7 | nc | 0.7 | 0.6 | 0.8 | 0.6 | 0.7 | 0.5 | 0.7 |
| 145 | 612 | 100 | 316 | 52 | 102 | 137 | 334 | 93 | 250 | 45 | 96 |
| 68 | 266 | 40 | 144 | 10 | 82 | 55 | 172 | 20 | 53 | 13 | 30 |
| 9 | 13 | bdl | 3 | bdl | bdl | 5 | 10 | bdl | 2 | bdl | bdl |
| 18 | 21 | bdl | 9 | bdl | bdl | 6 | 14 | bdl | 8 | bdl | bdl |

| *Y5* | | | | | | *Y6* | | | |
|---|---|---|---|---|---|---|---|---|---|
| (−25 m) | | (−90 m) | | (−25 m) | | (−140 m) | | (−250 m) | |
| *S* | *P* (0.17 mg/L) | *S* | *P* (0.15 mg/L) | *S* | *P* (0.25 mg/L) | *S* | *P* (0.44 mg/L) | *S* | *P* (0.02 mg/L) |
| 76 | 347 | 55 | 135 | 79 | 201 | 55 | 131 | 25 | 62 |
| 0.5 | 0.7 | 0.5 | 0.7 | 1.2 | 1.4 | 1.3 | 1.3 | nc | 1.2 |
| 105 | 424 | 74 | 182 | 106 | 275 | 64 | 168 | 32 | 77 |
| 46 | 159 | 13 | 32 | 18 | 85 | 13 | 32 | 9 | 25 |
| 3 | 6 | bdl | bdl | bdl | bdl | bdl | bdl | bdl | bdl |

S: solution; P: particulate matter; bdl: below detection limit; nc: not calculated.

This variability is probably related to the seasonal change in phytoplankton production.

Samples collected in stations B2-2- and Y1 were slightly richer in aliphatic hydrocarbons and oxygenated compounds than the other samples. This occurrence might be due to the release, at the beginning of the ice-melting period, of organic matter entrapped in the pack ice during its formation process. In fact, sample Y1 was collected in a zone of drifting pack ice (Polynya zone).

### *Anthropogenic Compounds*

As regards anthropogenic compounds, phthalates and low-molecular-weight alkylbenzenes were determined, albeit only at trace levels. The phthalates were the result of a worldwide dissemination of di-*n*-butylphthalate, di-isobutylphthalate and bis-(2-ethylhexyl)-phthalate [29,30]. Importantly, the same organic compounds were identified in each sample, even if some were present only at detection levels. Therefore, the average concentrations of the most prevalent classes of compounds are shown in Table III.



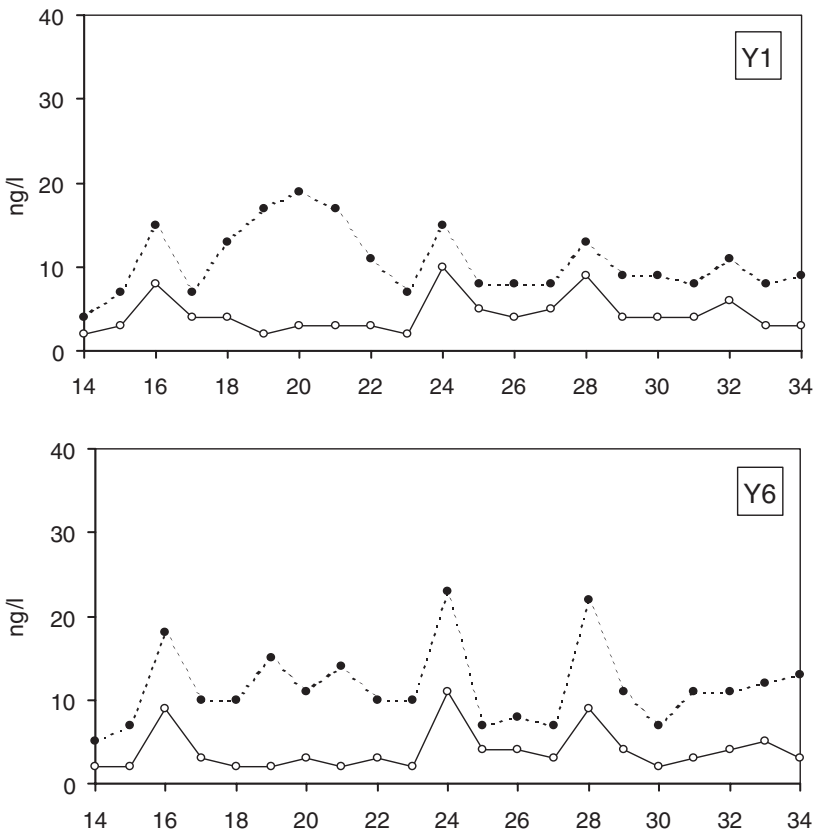


FIGURE 2 Horizontal profile of *n*-alkanes for the sea-water samples collected at Y1, Y6, Y5 and Y3 stations, at a depth of 25 m. Continuous line and white symbols: dissolved phase. Dashed line and black symbols: particulate phase.

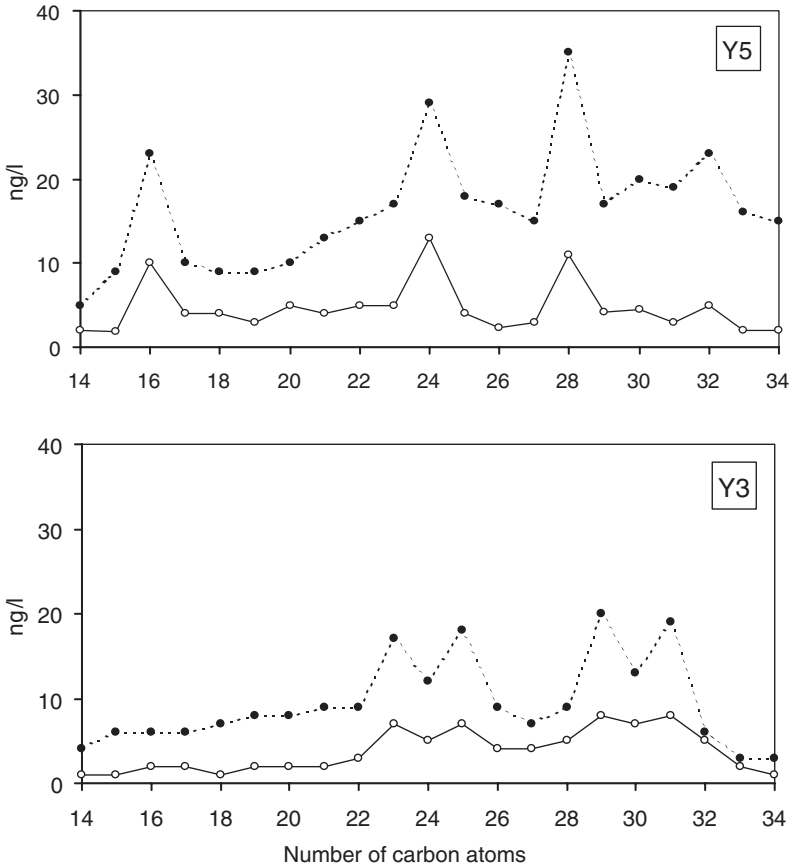


FIGURE 2 Continued.



Phthalates were found at very low levels at stations Y5 and Y6, and were practically absent at the Y3 site. These data confirm that the high concentrations of phthalates, found in pack ice and/or in sea-water samples, collected near the coast (not far from the Italian Base) during the previous expeditions [3,4], were due to local anthropogenic sources, rather than to the long-range transport.

The concentration levels of contaminants determined in the present paper were in agreement with what would be expected for an unpolluted area, indicating that a natural remediation occurred during the time that elapsed between the two expeditions (7 years).

## Vertical Distribution of Organic Compounds at the Five Stations

### *B2-2 Station (Gerlache Inlet, Terra Nova Bay)*

Samples were collected from seven depths at this station, and these were used to study the vertical profiles of the particulate matter and of dissolved and particulate organic compounds. Concentrations of particulate matter were in the range 0.27–1.43 mg/L, and such values were consistent with those found by others at the same stations [31,32] or at different sampling sites [33]. Such a material, probably derived from

sea-ice algae, plays an important role in sediment formation [34], as confirmed by data obtained during previous expeditions in the same area, where the same compounds were found in the sediments [7].

The chemical composition of the samples was identical for all the sub-surface water layers. The most prevalent classes of organic compounds found in the water column at the B2-2 sampling site (under pack ice) are listed in Table IV.

As regards biogenic compounds, their concentrations in dissolved and particulate phases were found to be at a maximum at depths between 25 and 50 m, where the highest concentrations of suspended matter were also observed. In contrast, the concentrations of anthropogenic compounds were found to be at a maximum at a depth of 2 m.

A general enrichment in the particulate phase was evident for all the classes of compounds identified.

Odd-to-even ratios for dissolved *n*-alkanes ranged from 0.4 to 0.8, indicating that distributions were characterized by a predominance of even carbon number in the C15–C32 range. It should be noted that similar odd-to-even ratios were found for sea-ice algae, which usually develop in the core section of pack at the sea-water interface [26].

Further information can be obtained by expressing the vertical profiles of the different classes of organic compounds as milligrams per gram of particulate matter (see Fig. 3A). The concentration of *n*-alkanes was found to be at a maximum (0.455 mg/g) at a depth of 10 m and at a minimum (0.087 mg/g) at 100 m. Fatty acids esters behaved similarly, showing low and rather homogeneous values (0.029–0.060 mg/g) at the different depths with a maximum (0.309 mg/g) at 50 m. These profiles were different from the vertical distribution of suspended material (see Fig. 3B) indicating that the chemical composition of particulate matter was modified through the water column.



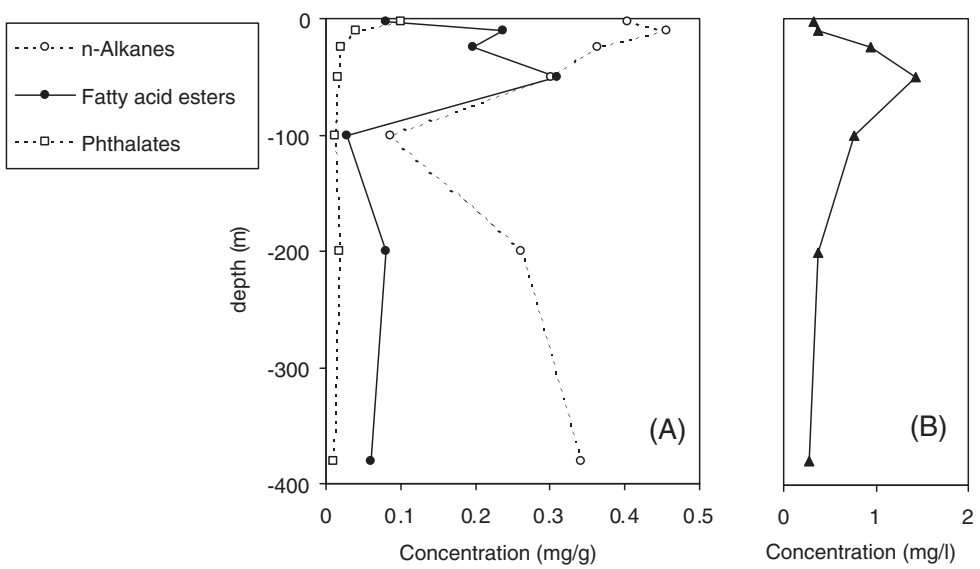


FIGURE 3 Vertical profiles of (A) *n*-alkanes, fatty acid esters and phthalates in the particulate phase and (B) particulate matter at the B2-2 station.

Such behaviour is in agreement with the different depth profiles of large and small particles observed in other oceanic regions, together with the qualitative and quantitative compositional differences of these particles [35].

The concentration of phthalates adsorbed on the particulate matter decreased rapidly with depth, aside from the concentration of the same material, suggesting that such compounds are not primary constituents of particulate matter.

### *Compositional Differences of n-alkanes through the Water Column at B2-2 Station*

Useful information can be obtained from the detailed vertical profiles of *n*-alkanes in the C14–C34 range (see Fig. 4). Different trends were observed for dissolved and

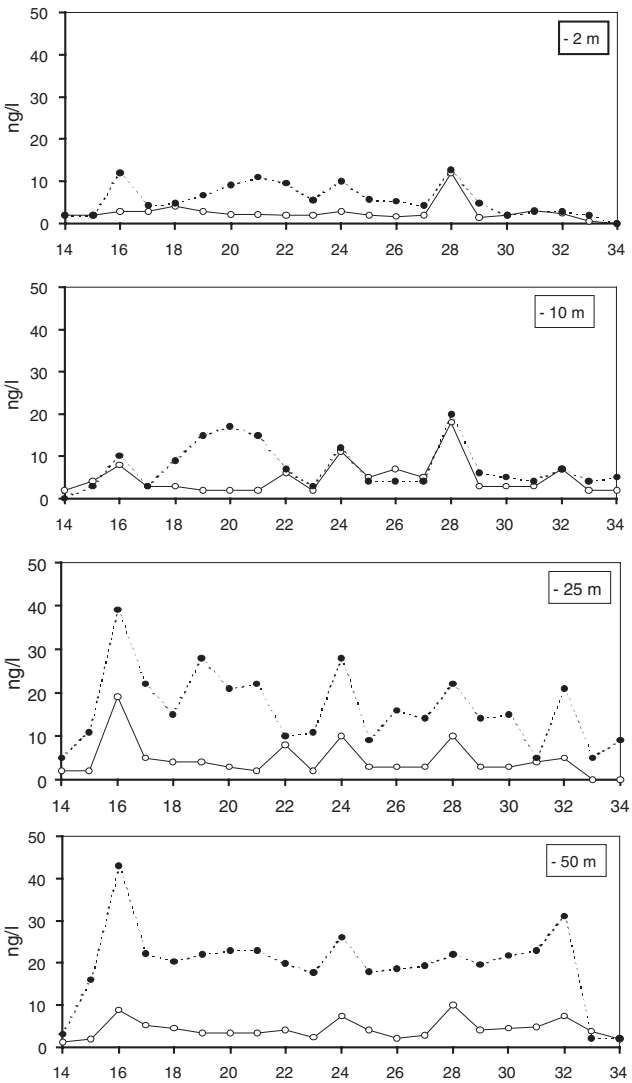


FIGURE 4 Vertical profile of *n*-alkanes in sea-water samples collected at different depths (B2-2 station). Continuous line and white symbol: dissolved phase. Dashed line and black symbol: particulate phase.

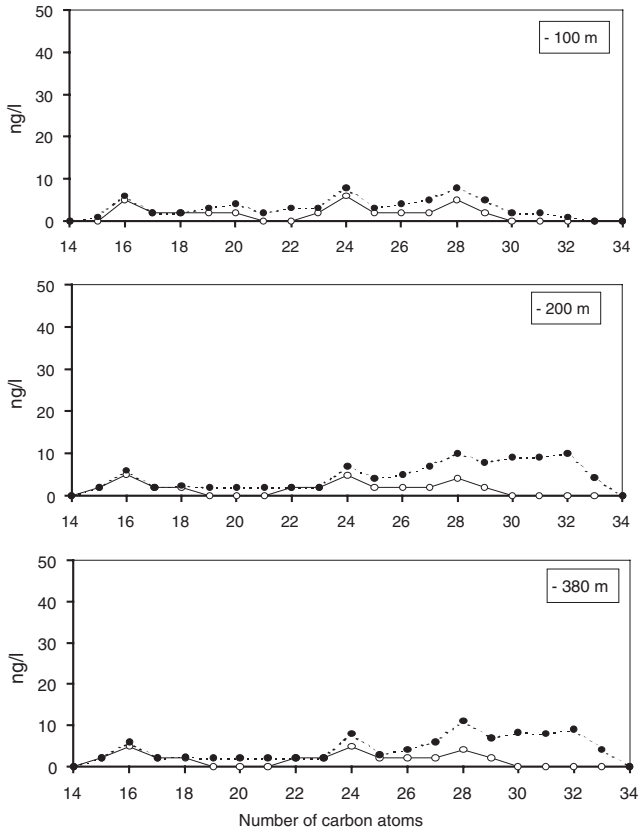


FIGURE 4 Continued.



particulate hydrocarbons through the water column; in addition, their composition tended to vary with depth. A common finding was the high concentration of C16, C24 and C28 *n*-alkanes in all the samples and their predominance in the dissolved phase indicating a contribution of autochthonous pelagic species. Particulate matter contained significant concentrations of C19–C22 *n*-alkanes at low depths (2 and 10 m) and of C29–C32 *n*-alkanes in deep-water layers (200 and 380 m). No enrichment in odd-carbon-numbered C29–C32 components was observed, which seems to exclude any contribution from terrestrial sources. It should be noted that the samples collected at a depth of 200 m and above all of 380 m are very close to the maximum depth of the sampling station (430 m), and therefore, the sediments may have some influence on the *n*-alkane composition of the above-mentioned samples.

### *Y1, Y3, Y5 and Y6 Stations (Ross Sea)*

The vertical distributions of the most prevalent classes of organic compounds determined at the sampling stations Y1, Y6, Y5 and Y3 are listed in Table V.

Samples were collected from only two (Y5) or three (Y1, Y6 and Y3) depths and therefore can only give partial information on the distribution of the analysed compounds at the different depths. In spite of these limitations, it can be seen that

the concentrations of biogenic compounds were always at a maximum at a depth of 25 m, as found in B2-2 station. These findings were in agreement with the data from fluorescence intensity, which can be considered as a measure of the algal productivity. In fact, fluorescence intensity was found to be at a maximum near a depth of 25 m for all the Ross Sea stations [36], apart from the profiles of aliphatic hydrocarbons and the distance from the coast.

The odd-to-even ratio for *n*-alkanes was less than 1 for sites Y1, Y5 and Y6, was higher than unity for the Y3 station and did not vary with depth. As regards dissolved *n*-alkanes, the odd-to-even ratio was not calculated for samples collected at stations Y1 and Y3 in the deepest water layers (250 m), since their hydrocarbon concentration was very low, and several of these were below the detection limit.

Contaminants were present at very low levels at a depth of 25 m and decreased with depth and/or distance from the coast.



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