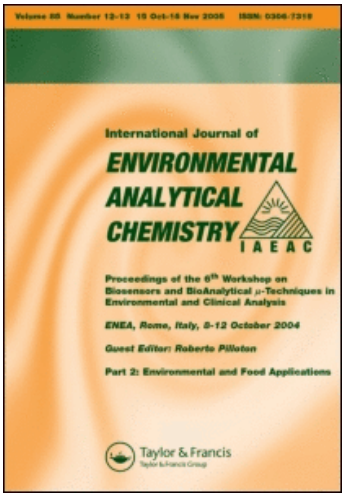

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Temporal evolution of DMS and DMSP in Antarctic Coastal Sea water

Andrea Gambaro[ab]; Ivo Moret[ab]; Rossano Piazza[a]; Carlo Andreoli[c]; Eleonora Da Rin[a]; Gabriele Capodaglio[ab]; Carlo Barbante[ab]; Paolo Cescon[ab]

[a] Dipartimento di Scienze Ambientali, Università Ca' Foscari, Dorsoduro 2137, I-30123 Venezia, Italy [b] C.N.R., Istituto per la Dinamica dei Processi Ambientali, Dorsoduro 2137, I-30123 Venezia, Italy [c] Dipartimento di Biologia, Università di Padova, Via Bassi 58/B, I-35121 Padova, Italy

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TEMPORAL EVOLUTION OF DMS AND DMSP IN ANTARCTIC COASTAL SEA WATER

ANDREA GAMBARO[a,b,*], IVO MORET[a,b], ROSSANO PIAZZA[a], CARLO ANDREOLI[c], ELEONORA DA RIN[a], GABRIELE CAPODAGLIO[a,b], CARLO BARBANTE[a,b] and PAOLO CESCON[a,b]

[a]*Dipartimento di Scienze Ambientali, Università Ca' Foscari, Dorsoduro 2137, I-30123 Venezia, Italy;* [b]*C.N.R., Istituto per la Dinamica dei Processi Ambientali, Dorsoduro 2137, I-30123 Venezia, Italy;* [c]*Dipartimento di Biologia, Università di Padova, Via Bassi 58/B, I-35121 Padova, Italy*

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The temporal evolution of concentrations of dimethylsulphide (DMS), its precursor dimethylsulphoniopropionate (DMSP) and chlorophyll *a* is surveyed weekly in the water column and in a landfast ice core at a coastal station of Gerlache Inlet (Terra Nova Bay, Antarctica) from 27 November 2000 to 14 February 2001. The DMS and DMSP profile concentrations in the water column are similar and show a clear temporal trend, with minimum values (< 0.7 nM) at all depths occurring on 27 November 2000 and maximum values (4.8×10^2 nM for DMS and 1.8×10^2 nM for DMSP) in surface water on 27 December 2000 for DMS and on 19 December 2000 for DMSP. When the sea-ice cover is present, the temporal evolution of DMSP closely follows that of chlorophyll *a* in the water column, supporting the idea that DMSP, and therefore DMS, has a phytoplanktonic origin. However, when the ice cover breaks up during the late austral summer, a second phytoplankton bloom occurs, while the DMSP concentration in the sea-water column remains very low. In the ice core, the results show higher concentrations of DMSP than those of the underlying sea water, highlighting the important role of sea ice in the sulphur cycle of the Antarctic ecosystem.

Keywords: Dimethylsulphide; Dimethylsulphoniopropionate; Chlorophyll *a*; Sea ice; Gerlache Inlet; Antarctica

INTRODUCTION

Dimethylsulphide (DMS) is considered the most important volatile organic sulphur compound, since it contributes about two-thirds of global natural sulphur emissions to the atmosphere [1] and thus has an important role in the global sulphur cycle and climate [2,3]. Over the past decade there have been many studies on the production and distribution of DMS in coastal, shelf and open ocean marine environments, and considerable efforts have been made to generate experimental data to construct

*Corresponding author. Fax: +39-041-2578549. E-mail: gambaro@unive.it

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global and regional inventories of DMS concentrations and ocean-to-atmosphere DMS fluxes [4]. A major limitation in estimating the global sea-to-air flux of DMS is the paucity of data for remote areas of the world's oceans. This is particularly true for the Southern Ocean, where the organic sulphur compounds in the Antarctic marine ecosystem have only recently been studied, principally in the open ocean. In particular, DiTullio and Smith [5] reported on the relationship between DMS and phytoplankton pigment concentrations in three transects sampled on the continental shelf of the Ross Sea, whereas Turner *et al.* [6] studied the distribution of DMS and dimethylsulphoniopropionate (DMSP) in sea water and sea ice on two cruises through the Drake Passage to the Bellingshausen Sea. The study of DiTullio and Smith [5] has shown that concentrations of DMS in the surface water of the Ross Sea can range over three orders of magnitude, from < 1 nM in the northern Ross Sea to 123 nM in the southern Ross Sea, showing a strong spatial gradient. However, other authors [6] reported a temporal gradient of DMS concentrations in Antarctic surface sea water.

It is increasingly recognized that DMS arises from a complex network of processes in sea water, the importance of which depends on the environment.

In sea water, DMS is believed to be produced mainly by marine phytoplankton through direct excretion, during viral or bacterial attack [7], or during grazing by zooplankton [8]. The most important process by which DMS is produced is enzymatic cleavage of DMSP [9]. The enzyme, DMSP-lyase, can be either bacterial or algal by origin. Although the role of DMSP within algal cells is not fully understood, it is thought to act as an osmolyte and as a cryoprotectant in many micro-algae, macroalgae and some salt-marsh grasses [10–13].

DMS is removed in the marine environment by photo-oxidation [14], by biological consumption [15], by sea–air exchange [16] and by adsorption onto sedimenting particles [17]. Several authors reported that no correlation was found between DMS concentration and other biological parameters such as chlorophyll *a*, phytoplankton cell number or nutrients [4]. This is because populations of phytoplankton are not homogeneous in the ocean and because different species of phytoplankton produce different amounts of DMSP [18] and chlorophyll.

The Ross Sea, a region of high seasonal production in the Southern Ocean, is characterized by blooms of the haptophyte *Phaeocystis antarctica* and of diatoms [19,20]. Smith and Dunbar [21] found that in the western Ross Sea, the phytoplankton community present in the surface water was dominated by pennate diatoms, in the south-central Ross Sea by *Phaeocystis antarctica*, and in the northern region by diatoms. Smith *et al.* [22], studying the seasonal cycle of phytoplankton biomass and primary productivity in the Ross Sea, found that phytoplankton biomass increased rapidly during the austral spring and that integrated chlorophyll reached a maximum during the summer (15 January) and decreased thereafter. Several authors reported that higher DMS and DMSP concentrations occurred at the same time as a bloom of *Phaeocystis* spp. [5,23]. In addition, sea ice offers a set of physico-chemical conditions for micro-organisms living in close association with it, either attached to ice crystals or suspended in the interstitial waters between ice crystals [24]. Horner [24] distinguished three main types of spatial distribution of microbial communities, each with specific algal assemblage: the *surface community*, which is dominated by several diatoms such as *Nitzchia*, *Navicula* and *Fragilariopsis* as well as colonies of *Phaeocystis* spp.; the *interior community*, which is coloured brown by the large amount of diatoms and dinoflagellates that it contains; and the *interstitial bottom*,

which accommodates pinnate and centric diatoms. The ice-covered regions can be divided into a zone of landfast ice in the shallow areas adjacent to the continent and the pack-ice, which extends into the deep-water regions. Although there is continuity between these two regions, the two kinds of ice differ in their physical and biological characteristics. Sea-ice habitats are (by convention) designated by their position within the sea ice and are generally categorized as surface, interior or bottom ice [25]. Andreoli *et al*. [26] found that the sea ice of Terra Nova Bay was colonized by microalgae. Diatoms were largely prevalent in the deepest layer, while archeomonads, Parmales and hypnozygotes of *Polarella glacialis* dominated in the middle and in uppermost layers. Because of the different microalgal composition between the deepest layer and overlying layers, and the constant presence of *Fragilariopsis cylindrus* in the middle and the uppermost layers, the sea ice of the Terra Nova Bay is more similar to landfast ice than to drifting pack ice. No DMS and DMSP studies have been carried out on the sea ice of the Terra Nova Bay. Trevena *et al*. [27] found high but spatially variable DMSPt (dissolved DMSP + particulate DMSP) concentrations in pack-ice cores from eastern Antarctica. They also found high correlations between DMSPt concentration, chlorophyll *a* and other photosynthetic marker pigments, which confirms that the high and variable DMSPt concentration found in sea ice could be mainly attributed to the high but patchy biomass distribution. The diatoms appear to be the principal producers of DMSP in the pack ice [27].

In this article, we report on a study of the temporal changes of DMS, DMSP and chlorophyll *a* concentrations along the water column and DMSP and chlorophyll *a* concentrations along the landfast sea-ice column in the coastal area of Terra Nova Bay (Gerlache Inlet), Antarctica. The aims of this work were to assess the seasonal trends of DMS and DMSP, and to understand the sources of volatile organic sulphur compounds in the coastal Antarctic marine ecosystem.

EXPERIMENTAL

Sampling

Seawater samples were collected weekly along the water column at a station in the Gerlache Inlet (74° 41′ 4.6″ S, 164° 10′ 10.1″ E) (Fig. 1) during the austral summer from 27 November 2000 to 14 February 2001. The station was covered by landfast sea ice (about 2.5 m) until about late January. The water depth at this site was about 300 m. The sea-water samples were collected with Teflon bottles, using a MERCOS Water Sampler system (IDROMAR, Genova, Italy) at 0.5, 7.5, 17.5, 27.5, 37.5, 47.5, 72.5, 97.5 m under the ice and at 3, 10, 20, 30, 40, 50, 75, 100 m when the sea was ice-free, later in the season (late January).

Seawater samples for DMS and DMSP determinations were stored at 4°C in 250-mL polyethylene fully filled containers until analysis (within 6 h) [28].

Five hundred millilitres of sea-water sample was fixed with concentrated Lugol's solution and stored in a dark glass bottles for phytoplankton determinations (composition and density) [29].

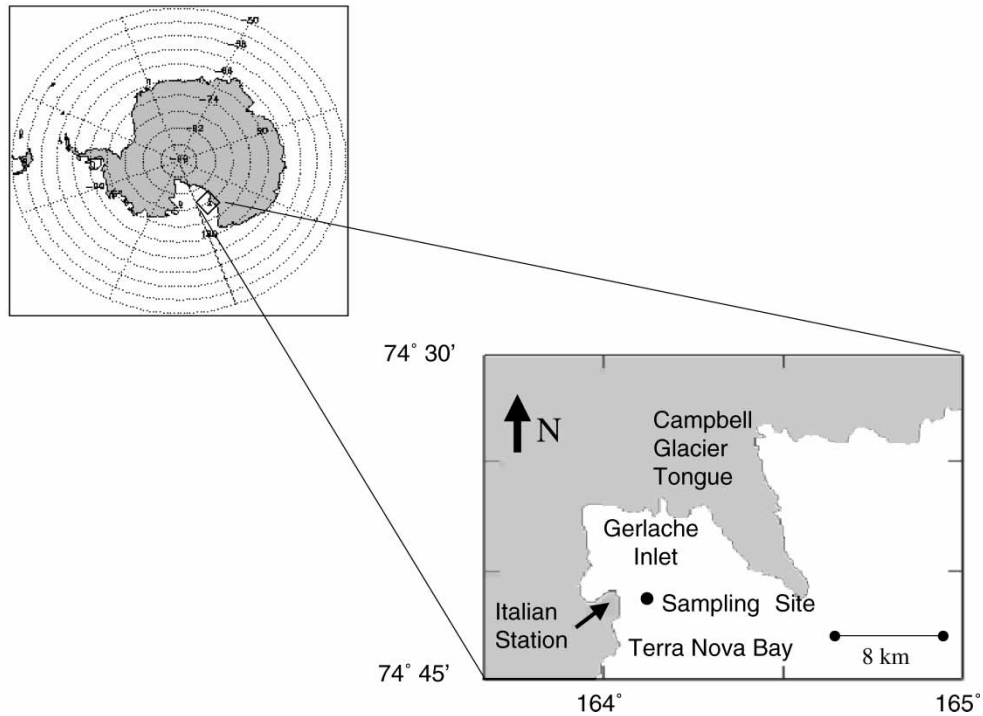

FIGURE 1 Sampling site in the Gerlache Inlet (Antarctica).

Two ice cores were sampled weekly at the above-mentioned station from 7 December 2000 to 11 January 2001 using an ice corer (Duncan, UK, Model BTC). Cores were wrapped in plastic bags and stored horizontally at −20°C until analysis.

Determination of DMS and DMSP

DMS in sea-water samples was determined using a purge-and-trap technique followed by gas-chromatographic quantification, using the procedures described in detail in Moret *et al.* [28,30].

Briefly, unfiltered sea-water samples (40–100 mL, depending on the DMS and DMSP concentrations) were stripped by nitrogen at 80°C in a Dynamic Thermal Stripper (Supelco, Bellafonte, CA). The volatile compounds were trapped at 85°C in a multibed adsorption tube containing graphitized carbon black (Carbopack B, Supelco Inc.) and a carbon molecular sieve (Carbosieve S-III, Supelco). The determination unit consisted of a Thermal Desorption Unit (Supelco) where DMS, previously trapped in the adsorption tube, was transferred to a 30-m megabore capillary column filled with a porous polymer (GS-Q, J&W Scientific, Folson, CA) mounted in a gas chromatograph (Carlo Erba, model 5160, Rodano, Italy) equipped with a flame-photometric detector.

The sample, having been stripped to remove DMS, was brought to pH 13 by 5 M NaOH to determine the total DMSP (dissolved plus particulate) according to the cold alkali treatment method proposed by Dacey and Blough [11].

The sea-ice cores (1.6 m) were cut to 16 aliquots of about 10 cm. The single aliquots were introduced into the Dynamic Thermal Stripper and, as reported above, analysed for DMSP concentration.

The repeatability of DMS and DMSP measurements, computed from three replicates of the same sea water and sea ice samples, was: 14% (as relative standard deviation, RSD) for DMS and DMSP in sea water and 17% (as RSD) for DMSP in sea ice.

Chlorophyll *a* and Phytoplankton Determination

A sea-water sample (1 L) and a portion of the sea-ice core (700–800 mL of thawed ice) were collected by vacuum filtration (< 0.5 atm.) onto glass-microfibre filters (GF/F Whatmann) and stored in the dark at $-20°C$. Chlorophyll *a*, in the presence of pheophytin *a*, was determined on the filter using the spectrophotometric method [31,32]. Quantitative analyses of all microalgae larger than 2 μm were carried out on settled samples using a Zeiss IM35 inverted microscope, as reported by Moro *et al*. [29].

RESULTS AND DISCUSSION

Chlorophyll *a* and DMSP in Sea Water

Figure 2 shows the chlorophyll *a* and DMSP concentrations in the samples collected along the water column between 27 November 2000 and 14 February 2001. It is important to note that the water was covered by land fast ice during the sampling from 27 November to 24 January, whereas from 31 January to 14 February, no sea ice was present.

The phytoplankton biomass was very low (chlorophyll *a* concentrations smaller than 0.01 μg/L) in all samples collected on 27 November. In the subsequent samplings, the phytoplankton biomass was observed to increase quickly at depths of 10–20 m, with chlorophyll *a* concentrations varying between 0.5 μg/L on 6 December and about 6.5 μg/L on 19 December, indicating the phytoplankton bloom. After the bloom, the chlorophyll *a* concentration gradually decreased in the first 40 m of the water column until 10 January when values < 1.5 μg/L were present. This is probably the senescence period for the previously developed phytoplankton species.

In the following weeks, the sea ice broke up in several parts, and the Gerlache Inlet was soon free of ice. From 24 January to 14 February, the chlorophyll *a* concentrations in the first 20 m rose again from about 2 μg/L to about 6 μg/L, showing the presence of a second bloom.

In the light of the temporal evolution of concentration profiles of chlorophyll *a*, it is interesting to observe the corresponding seasonal profiles of DMSP. DMSP concentrations, as for DMS and chlorophyll *a*, showed values (< 0.7 nmolS/L) below the detection limits of our methodology in all samples collected at different depths during the sampling of 27 November. The DMSP concentration along the water column then rose, especially in the first 50 m, reaching maximum values (about 150 nmolS/L, 10–30 m, 19 December) during the phytoplankton bloom. During this period, the DMSP was correlated with chlorophyll *a* concentration ($r^2 = 0.7$), showing that in the phytoplankton community, species containing DMSP were very abundant.

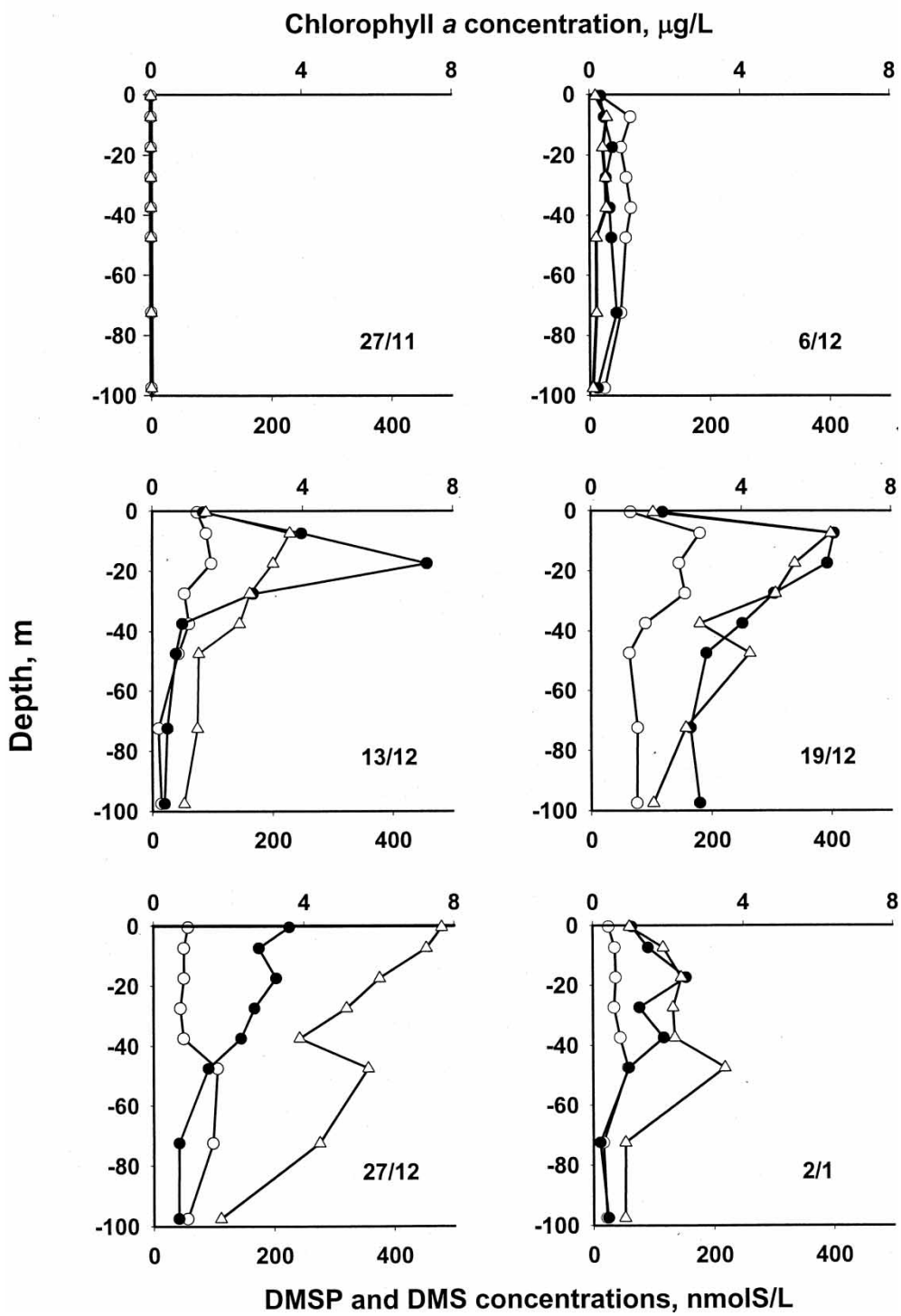

FIGURE 2 DMS (Δ), DMSP (○) and chlorophyll *a* (●) concentrations in the weekly collected samples along the water column in the Gerlache Inlet during the 2000–2001 Italian expedition.

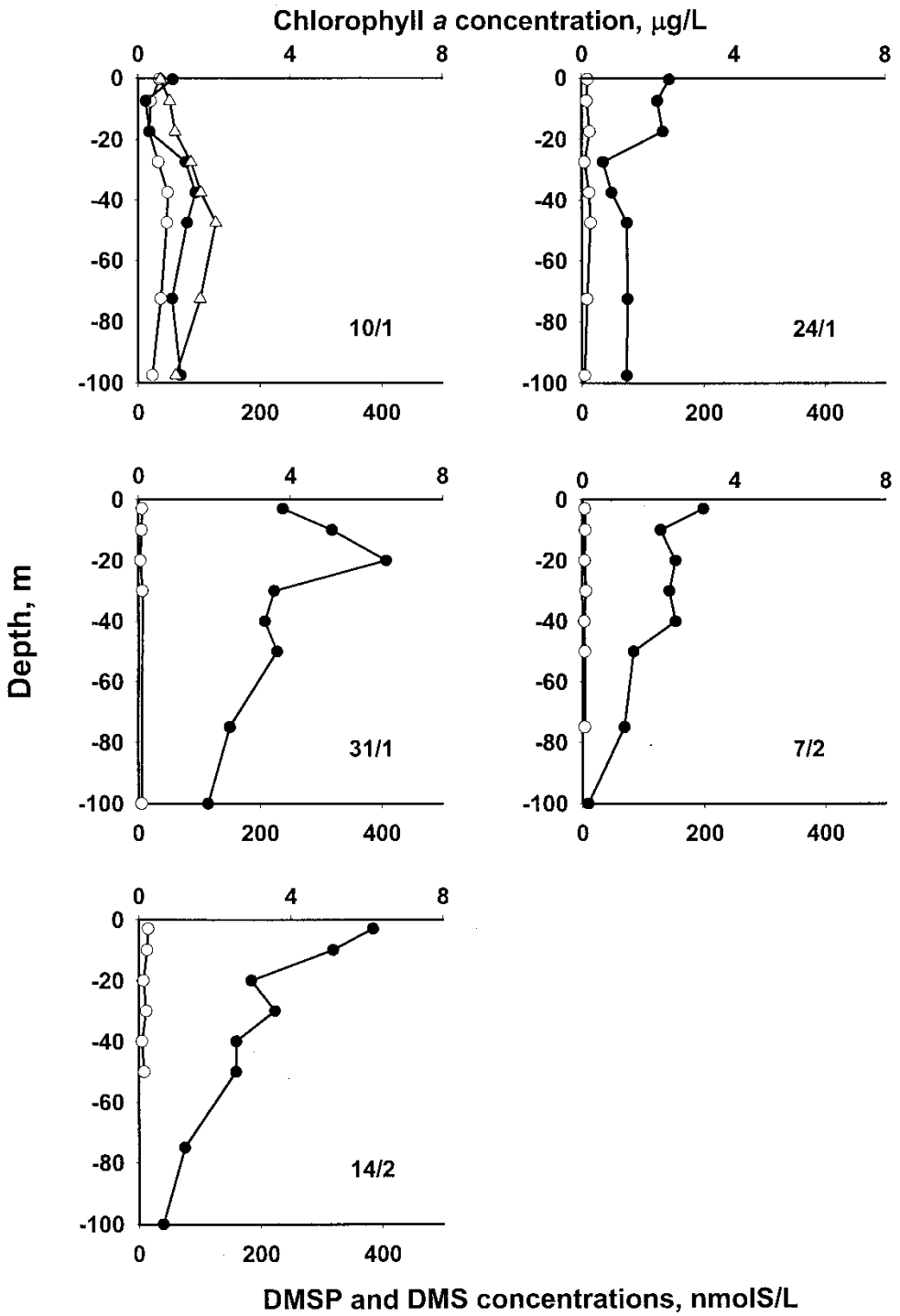

FIGURE 2 Continued.

TABLE I Mean and range of DMSP : chlorophyll *a* ratios (nmolS/μg) and phytoplankton community density (cells/L) in the first 30 m of the water column in samples collected in the Gerlache Inlet during the 2000–2001 Italian expedition

Date	*DMSP : chlorophyll a* (nmol S/μg)		
	Min	*Max*	*Mean*
28/11/2000	nd	nd	nd
06/12/2000	65	172	116
13/12/2000	13	55	28
19/12/2000	23	35	29
27/12/2000	16	18	17
02/01/2001	15	28	24
10/01/2001	27	104	57
24/01/2001	4	8	6
31/01/2001	0.6	1.9	1.3
07/02/2001	1.2	2.6	2.0
14/02/2001	2.5	3.4	2.8

Date	*Phytoplankton* (cells/L)	*Phaeocystis antarctica* (cells/L)	*Fragilariopsis spp.* (cells/L)
27/11/2000	159×10^3	158×10^3	320
13/12/2000	$51\,465 \times 10^3$	$48\,143 \times 10^3$	1×10^3
24/01/2001	1493×10^3	380×10^3	4×10^3
14/02/2001	5751×10^3	333	5732×10^3

Several authors have studied the phytoplanktonic community structure in the Ross Sea and concluded that diatoms and the prymnesiophyte *Phaeocystis* sp. both form major phytoplankton blooms during the spring and summer seasons [20,33]. Kirst *et al.* [34] found a clear correlation between chlorophyll, DMSP and DMS in the Weddell Sea, and concluded that *Phaeocystis* appears to be the major source of DMSP. The mean and range of DMSP : chlorophyll *a* ratios in the first 30 m of the water column are shown in Table I. The highest ratios ($\geq$17 nmolS/μgChl. *a*) were found during the phytoplankton bloom (from 6 December to 19 December) and the determinations on phytoplankton community present in the water samples collected on 13 December 2001 showed *Phaeocystis antarctica* to be the most abundant alga cells (Table I).

So, we can conclude that *Phaeocystis* spp. were the producers of DMSP and DMS in sea water under the sea ice in the Gerlache Inlet during the December period. After the phytoplankton bloom, the DMSP concentrations, like the chlorophyll *a* concentrations, quickly decreased in the first 30 m of the water column with the difference that the DMSP concentration remained low until the end of the study.

The simultaneous decrease in DMSP and chlorophyll *a* concentrations was not in contrast with the DMS maxima observed in the first 20 m on 27 December (see below) because this can be explained by DMS production during the senescence period of phytoplankton cells. High DMSP concentrations in deep water on 27 December suggest sedimentation of DMSP-containing algae. This already started on 19 December.

During the second peak in chlorophyll *a* concentration after the breakdown of the sea ice, DMSP concentrations stayed low at all depths until the end of the study. This could be due to the presence of phytoplankton species different from those present in the first bloom (December), which did not contain DMSP. The lowest

DMSP : chlorophyll *a* ratios (< 3 nmolS/μgChl. *a*) were found during the second peak in chlorophyll *a* concentration (from 31 January to 14 February), and the determinations on phytoplankton community present in the water samples collected on 14 February 2002 showed that the diatoms *Fragilariopsis* spp. were more abundant. The diatoms in fact are considered to be low DMSP producers, although several authors [35,36] have recently found a relation between the presence of diatoms and DMSP concentration.

DMS in Sea Water

The DMS concentration profiles within the water column from 27 November 2000 to 10 January 2001 at the sample site in the Gerlache Inlet (Antarctica) are shown in Fig. 2 (56 samples were collected).

The lack of DMS concentration profiles along the water column after 10 of January is due to the fact that we were unable to carry out DMS determinations within 6 h from the time of sampling.

Figure 2 shows a characteristic temporal evolution of DMS concentration at each depth. In particular, DMS concentrations of the samples collected on 27 November present values below the detection limit of our methodology (< 0.7 nmolS/L) at all depths. In the samples collected from 6 to 27 December 2000, the DMS concentrations in the water column increased from values only just within our detection limit to summer maxima (4.8×10^2 nmolS/L, surface water, 27 December 2000); the highest DMS concentrations were found in the first 40 m. From 2 to 10 January, the DMS concentrations decreased in the water column.

The range of DMS concentration levels along the water column obtained in this study (< 0.7–4.8×10^2 nmolS/L) are comparable with those found in other investigations in Antarctic areas [5,34,37]. However, the temporal evolution of DMS along the water column pictured in Fig. 2 is in agreement with that reported by Turner *et al*. [6]. Turner *et al*. [6] reported on the distribution of DMS and particulate and dissolved fractions of DMSP during two cruises through the Drake Passage to the Bellingshausen Sea, and found a vast range of DMS concentrations for open ocean areas, which probably integrates both seasonal and spatial variability. To visualize this, they plotted their data and literature data against the mid-points of the sampling periods, and attempted to fit a curve. The authors reported that this curve should be considered the upper limit for DMS concentration in Antarctic waters which showed the highest DMS values in November, December, January and February owing to the inclusion of several coastal and shelf data sets which have significantly higher DMS concentrations than most of the other records.

The DMS concentration profiles obtained in this study are also in agreement with those reported by DiTullio *et al*. [5] and Fogelqvist [37]. DiTullio *et al*. [5] reported DMS profiles showing subsurface maxima with low and constant DMS concentrations in deeper waters. Fogelqvist [37] also reported that the maximum concentrations of DMS were found at depths from 20 to 50 m, below which a steep gradient exists.

The DMS concentrations along the water column obtained in this work are very high, compared with the open oceans such as the Pacific Ocean (1.5–10.82 nmolS/L [38]), the Atlantic Ocean (1.0–93.8 nmolS/L [39]) and temperate coastal areas such as the Mediterranean Sea (0.1–4.3 nmolS/L [40]) and the Venice lagoon (0.8–15 nmolS/L [28]).

DMSP and Chlorophyll *a* in Sea Ice

Figure 3 shows the DMSP and chlorophyll *a* concentrations along the sea-ice cores carried out between 7 December 2000 and 11 January 2001 (88 samples were collected). Generally, the DMSP concentrations in sea-ice samples were higher than in the underlying water, as reported also by Turner *et al.* [6], who found DMS + DMSP concentration levels 20–500 times higher. Furthermore, the DMSP in our sea-ice cover showed a characteristic profile, with the highest concentrations in the bottom 30–40 cm of the ice cores. This ice layer also showed higher concentrations of chlorophyll *a* and the presence of a layer (a few tens of centimetres) of brown ice, both typical indicators of the presence of algae. On the basis of these observations, we can state that DMSP production in the landfast-ice cores was associated with the presence of phytoplankton. The DMSP ice concentrations found in this study (range: $4.4–4.5 \times 10^2$ nmol S/L) were comparable with those found in other Antarctic pack-ice studies [6,27,36].

During the austral summer, the DMSP concentration in the sea-ice decreased principally in the bottom layer, as did the chlorophyll *a* concentration. This may be due to an upward shifting of the porosity threshold increasing the layer in which exchange occurs with the underlying water.

The DMSP : chlorophyll *a* ratios in the bottommost 20 cm of the ice cores (range 1.5–7.6 nmol S/μg Chl. *a*) were lower than in the underlying water (Table I). This could be due to the presence in the ice cores of phytoplankton species different from those present in the underlying water. In particular, this ratio is comparable with that found in the first 30 m of water column during the second bloom when the diatoms

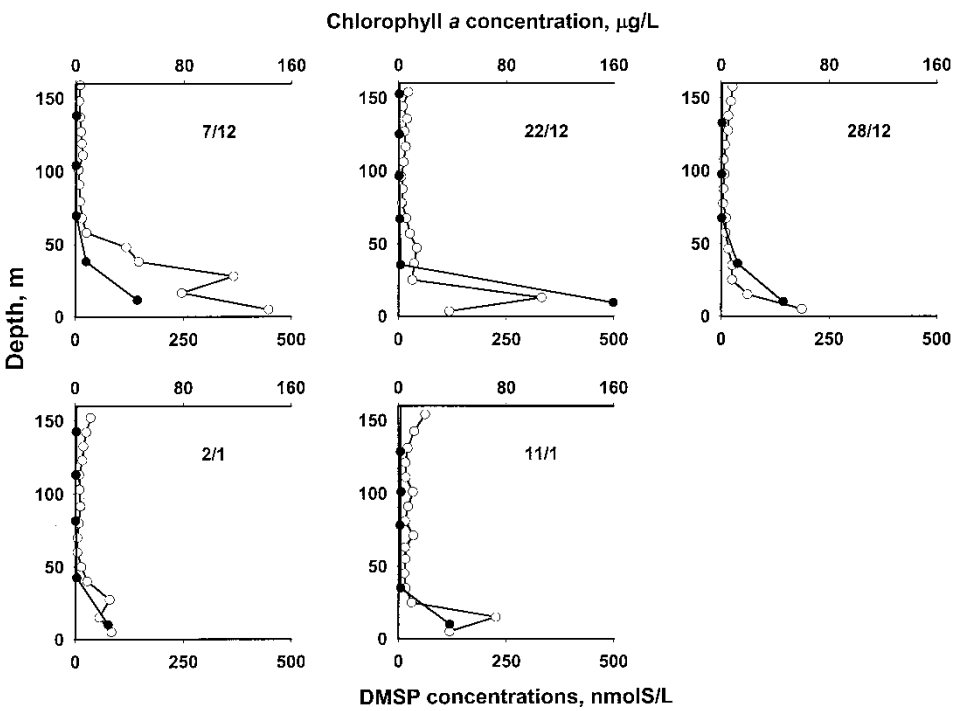

FIGURE 3 DMSP (○) and chlorophyll *a* (●) concentrations in the weekly collected samples along the sea-ice cores from 7 December 2000 to 11 January 2001.

(*Fragilariopsis* spp.) were more abundant. Thus we can conclude that in this period the diatoms may have been more abundant in the bottom ice.

CONCLUSION

The temporal evolution of DMS, DMSP and chlorophyll *a* concentrations along the water column in the coastal area of the Ross Sea (Gerlache Inlet) showed characteristic trends at each depth. The chlorophyll *a* trend indicated two principal phytoplankton blooms. The first was observed in about mid-December, when high DMS and DMSP concentrations were both present in the surface 40 m of water and in the ice (bottom 50 cm of the 2.5 m ice cover). The second was observed in late February, when the ice cover had disappeared, whilst the sea-water column showed small DMSP concentrations. *Phaeocystis* spp. were the most abundant species in the phytoplankton community in the water column during the first bloom, and they appear to be the producers of DMS and DMSP in the sea water underlying the ice pack during the Austral spring–summer period. Diatoms, however, were the more abundant species during the second phytoplankton bloom when there was no relation between chlorophyll *a* concentration and DMSP concentrations.

DMSP concentrations in the bottom ice layer were higher than in the underlying water by a factor of about 4, as was already shown for pack ice by Turner *et al*. [6].

The DMSP : chlorophyll *a* ratios in the bottommost of the ice cores were lower than in the underlying water during the first bloom when the *Phaeocystis antarctica* were the most abundant alga cells but similar to those found during the second bloom when the diatoms (*Fragilariopsis* spp.) were more abundant. Thus, we can conclude that the bloom underneath the ice could be due to advection of a bloom from open sea waters.

This study contributes new data on the temporal evolution of DMS and DMSP concentrations and on DMSP profile concentrations in landfast sea ice in the Antarctic ecosystem. Further progress is required to elucidate the role of the sea-ice cover on biogeochemical processes.

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