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Effect of natural iron fertilisation on the distribution of DMS and DMSP in the Indian sector of the Southern Ocean

Sauveur Belviso[a,*], Laurent Bopp[a], Julie Mosseri[b], Marc Tedetti[c], Nicole Garcia[b], Brian Griffiths[d], Fabien Joux[e], Ingrid Obernosterer[e], Julia Uitz[f], Marcel J.W. Veldhuis[g]

[a]*Laboratoire des Sciences du Climat et de l'Environnement, UMR CEA-CNRS-UVSQ 1572, CEN-Saclay, Bât 701 L'Orme des Merisiers, 91191 Gif-sur-Yvette, France*
[b]*Laboratoire d'Océanographie et de Biogéochimie, Centre d'Océanologie de Marseille, UMR CNRS 6535, Case 901, Campus de Luminy, 13288 Marseille Cedex 9, France*
[c]*Laboratoire de Microbiologie, Géochimie Ecologie Marines, Centre d'Océanologie de Marseille, UMR CNRS 6117, Case 901, Campus de Luminy, 13288 Marseille Cedex 9, France*
[d]*CSIRO, Antarctic Climate and Ecosystems Cooperative Research Centre, GPO Box 1538, Hobart, Tasmania 7001, Australia*
[e]*Laboratoire d'Océanologie Biologique de Banyuls, Université Paris 6, UMR CNRS 7621, BP 44, 66651 Banyuls-sur-Mer, France*
[f]*Laboratoire d'Océanographie de Villefranche, Quai de La Darse, B.P. 8, 06238 Villefranche-sur-Mer, France*
[g]*Department of Biological Oceanography, Royal Netherlands Institute for Sea Research, P-Box 59, NL-1790 AB Den Burg, Texel, The Netherlands*

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Abstract

Understanding the processes controlling the distribution and fate of dimethylsulphide (DMS) in marine surface waters is critical to quantifying the flux of DMS to the atmosphere. All fertilisation experiments in the Southern Ocean trying to mimic a short-term (several weeks) atmospheric, dust-related, iron supply so far have shown that DMS concentrations increase when iron is added artificially in small patches to iron-limited regions. During the Kerguelen Ocean and Plateau compared Study (KEOPS), we have investigated the impact on surface concentrations of DMS and its precursor, particulate dimethylsulphoniopropionate (DMSPp), of iron supplied by mixing from below. We found that the massive summer phytoplanktonic bloom sustained by naturally enhanced vertical mixing of deep iron-rich seawater above the Kerguelen Plateau is not a substantially larger source of DMS than the surrounding low-primary productivity waters. The sustained enrichment of iron over the Kerguelen Plateau does not translate into an increase in DMS concentration because: (1) the nano-phytoplankton, which is the main producer of DMSPp in the area, is not favoured by the continuous supply of iron in surface waters, (2) the transfer efficiency of DMSP to DMS is probably low due to the higher levels of bacterial production measured over the plateau, which, likely, also stimulate the bacterial removal of DMS, and (3) nitrates and fresh chromophoric dissolved organic matter, supplied in surface waters from enhanced mixing of deep water over the plateau, increase the photodegradation rates of DMS. Thus, artificial short-term iron supplies from above and naturally sustained ones show fundamental differences in their impacts on the distribution and net production of DMS.
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Keywords: Southern Ocean; Kerguelen Island; Dimethylsulphide; DMS; DMSP; Iron

1. Introduction

Understanding the biogeochemistry of dimethylsulphide (DMS) is of global significance since atmospheric DMS indirectly influences climate regulation (Charlson et al., 1987). The emissions of DMS from the vast Southern Ocean might have a particularly strong influence on the atmosphere because of the lack of other sources of volatile sulphur in this region (Bates et al., 1992). In the Southern Ocean, the role of iron in controlling both biological productivity and nutrient utilisation is pivotal. Previous studies report increased plankton biomass and DMS concentrations upon short-term iron fertilisation (Turner et al.,

*Corresponding author. Tel.: +33 1 69 08 81 45; fax: +33 1 69 08 77 16.
E-mail address: sauveur.belviso@lsce.ipsl.fr (S. Belviso).

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2004; Wingenter et al., 2004). Thus, adding iron stimulates short-term net DMS production. However, it is not known if net DMS production would continue to be stimulated on time scales longer than a few weeks. Iron can be supplied in surface waters also from below since iron levels increase with increasing depth as most micronutrients do.

The question of how the ecosystem and DMS production would respond to iron delivered from below as opposed to from above (atmospheric deposition) has never been investigated in the field. During the Kerguelen Ocean and Plateau compared Study (KEOPS) it was demonstrated that iron-rich deep water over the Kerguelen Plateau (Indian sector of the Southern Ocean) fuelled the surface layer with iron and major nutrients that sustained a massive plankton bloom (Blain et al., 2007, 2008). Here we report on the effect of sustained natural iron fertilisation on the distribution of DMS and particulate dimethylsulphoniopropionate (DMSPp) in the same area. To characterize the organisms responsible for the production of DMSPp, concentrations of DMSPp were measured during a series of *in vitro* experiments and *in situ* surveys where the composition and the biomass of the phytoplankton community were investigated using HPLC and flow cytometry. It is well known that DMS production is not only controlled by DMSP producers but also by many other biological mechanisms (grazing, bacterial and viral activities, etc.). Those activities were documented extensively during KEOPS but, due to time constrains, the specific production rates of DMS could not be measured. According to Toole et al. (2004), the indirect photodegradation of DMS is a very important sink for this compound in the cold and nutrient-rich waters of the Southern Ocean. Hence, in the present study specific experiments were designed to determine the role of photodegradation for the DMS cycling in the Kerguelen area. The pseudo first-order rate coefficients for DMS photodegradation (DMS-PFORC) were measured in surface and deep waters of the area.

Our results are compared with those obtained during short-term artificial iron addition experiments in order to shed new light on the potential impact of iron supply over a longer period in the Southern Ocean.

2. Material and methods

2.1. Spatio-temporal distribution of DMSPp and DMS

To study the effect of sustained iron fertilisation on the concentrations of DMSPp and DMS, seawater was collected during the KEOPS (19 January–13 February 2005) at 18 stations on three transects (A, B and C; Fig. 1) and at the KERFIX station (Fig. 1). Samples were collected with General Oceanics 12-dm^3 Niskin bottles mounted on a rosette equipped with a SeaBird SBE19+ CTD. Seawater samples were transferred to Pyrex glass BOD bottles (0.5 dm^3) and stored in the fridge near *in situ* surface temperatures ($3.0 \pm 1.0\,^{\circ}C$) until gas chromatographic (GC) analysis aboard (see Section 2.4).

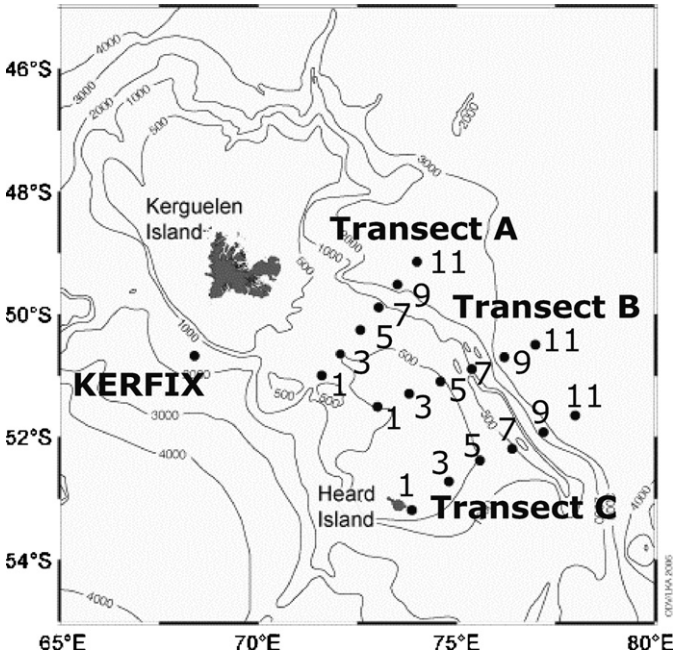

Fig. 1. Location of the study sites. Stations A3 and C11 are on and off plateau, respectively.

2.2. DMSPp production during bottle incubation experiments

Bottle incubation experiments were performed at Stations A3 (inside the bloom) and C11 (outside the Kerguelen Plateau and the bloom, Fig. 1). Seawater was collected at 30 m using GO-FLO bottles and transferred to a clean laboratory. Unfiltered seawater was subsequently distributed to 4-dm^3 polycarbonate (PC) bottles and amended with $FeCl_3$ (1 nM final concentration calculated from the amount added). This concentration was about six times the dissolved iron (DFe) concentration measured at the depth of the deep temperature minimum characterising the remnant winter water, and 2–5 times the DFe concentrations measured over the plateau at 500 m depth near the bottom (Blain et al., 2007). In surface waters, DFe concentrations were about 0.1 nM and were typical of surface waters of the open Southern Ocean (Blain et al., 2007). Unamended seawater incubations served as control. The seawater samples were placed in an outdoor incubator at 50% surface solar radiation. The incubations were kept at surface water temperature by a running seawater system. The duration of the incubation was 9 d, and every 3 d concentrations of chlorophyll *a* (Chl *a*) and DMSPp were determined in duplicate PC bottles of each the DFe and the control treatments.

2.3. Photochemical experiments

2.3.1. Photodegradation of DMS

The experimental protocol employed during KEOPS to measure DMS-PFORC was tested extensively in June 2004

during a workshop carried out in the Mediterranean Sea (UVECO) where the water samples received extra nutrients and chromophoric dissolved organic matter (CDOM) to mimic expected conditions in the Southern Ocean. For the KEOPS DMS photodegradation experiments, seawater was collected at 35 and 400 m (Stations A3 and B5, inside the bloom), and at 35 m at Station C11 (Fig. 1) using GO-FLO bottles mounted on a Kevlar line. Sampling was usually done late at night in order to start the incubations at dawn. Seawater was immediately filtered through clean Sartroban cartridges (0.2 μm with 0.4-μm prefilter, Sartorius) and subsequently treated as follows. To determine DMS-PFORC we added DMS from a freshly prepared aqueous DMS (Sigma-Aldrich) stock solution to a 0.5-dm^3 Pyrex-glass bottle containing 0.2-μm filtered seawater (final concentration of 10–20 nM). After DMS addition, the bottle was rotated by hand at least 20 times and its content was poured slowly in triplicate 60-cm^3 clean quartz and Pyrex tubes that were sealed with clean screw caps with PTFE/Silicone liners, with very small headspace. For dark treatments, the Pyrex tubes were covered with aluminium foil. Exposure to natural solar radiation was done in an on-the deck recirculating water bath (0.1-m depth) maintained at *in situ* surface temperature, for 10–12 h. DMS-PFORC was calculated as in Hatton (2002).

2.3.2. Irradiance

A profiling ultraviolet radiometer (Biospherical PUV-510) was used to measure surface irradiance at four wavelengths in the UV region (305, 320, 340, and 380 nm; 8–10 nm bandwidths) as well as broadband photosynthetically active radiation (PAR; 400–700 nm).

2.3.3. CDOM

The CDOM concentration was evaluated by the fluorescence measurement on 0.2-μm filtered water samples at an excitation wavelength of 350 nm and an emission wavelength of 450 nm using a 1-cm quartz cuvette. The CDOM fluorescence was determined on a Turner fluorometer. It was standardized with a quinine sulphate solution (1 QSU = 1 ppb quinine sulphate in 0.05 M H_2SO_4).

2.3.4. Nutrients

Samples for nitrate and nitrite concentrations were collected in 60-cm^3 polyethylene flasks and immediately poisoned after sampling with 0.1 cm^3 $HgCl_2$ (6 g dm^{-3}; Kirkwood, 1992) and stored at 4 °C until analysis. The samples were then processed in the laboratory with the standard colorimetric method (Tréguer and Le Corre, 1975), using a Technicon Autoanalyser II.

2.4. GC analysis of DMSP–DMS

Unfiltered seawater, 10-μm and Whatman GF/F filtered water (see below) were used for the analysis of total DMSPp, size-fractionated DMSPp (DMSPp < 10 μm) and dissolved DMSP (DMSPd < GF/F), respectively. An 8-cm^3 aliquot of whole or filtered water was transferred to glass tubes, treated with cold alkali, sealed with a Teflon faced septum, and allowed to sit at room temperature for at least 12 h. The content of a sample tube was drawn into plastic or glass syringes and immediately injected into the sparging device. Samples sparged with helium for 10 min at 70 cm^3 min^{-1} were cryotrapped on liquid nitrogen in a 0.16-mm diameter FEP-Teflon loop. The trap was heated to 95 °C, and its content was immediately injected onto the Innowax capillary column (Hewlett-Packard). Water vapour had been previously removed using a Permapure mini-dryer (model MD050-72F). For DMS analysis we used 25-mm diameter Whatman GF/F glass-fiber filters mounted on Teflon cylinders that were allowed to sink slowly through seawater contained in a clean 0.3-dm^3 Teflon beaker, thus producing GF/F filtrates by reverse filtration. Then, a 5- to 20-cm^3 aliquot of the filtrate was immediately sparged with helium. DMSP and DMS samples were analysed onboard R/V *Marion Dufresne* using a Varian 3800 gas chromatograph equipped with a Pulsed Flame Photometric Detector. DMS was calibrated from DMSP standards (Kiadis BV, The Netherlands) prepared in 8-cm^3 glass tubes sealed with Teflon faced septa. DMSPp was obtained by subtracting the DMSP + DMS content of the GF/F filtrate from the total DMSP + DMS content of unfractionated whole water.

2.5. High-performance liquid chromatography (HPLC) analysis of pigments

Seawater samples (1.5–2.8 dm^3) were filtered through 25-mm Whatman GF/F filters. The filter pads were placed in cryotubes and stored in liquid nitrogen until laboratory analysis. Phytoplankton pigments were extracted from the filters in 3-cm^3 HPLC-grade methanol for 30 min minimum time. The extracts were then sonicated, and, 30 min later, clarified by vacuum filtration on GF/F filters. The extracts were injected (within 24 h) onto a reversed-phase C8 Zorbax Eclipse column. Instrumentation comprises an Agilent Technologies 1100 series HPLC system with diode array detection at 450, 667 and 770 nm. It allowed the determination of the Chl *a* (universal indicator of the phytoplankton biomass), and of a suite of accessory pigments (carotenoids and chlorophylls) used as biomarkers of diverse phytoplankton taxa or groups. The diatoms-to-phytoplankton ratio was calculated using equations described in Uitz et al. (2006).

2.6. Enumeration of small phytoplankton by flow cytometry

Freshly collected CTD bottle samples were routinely analysed for their phytoplankton community composition with a bench-top flow cytometer (COULTER XL-MCL) within 1 h after sampling. Prior to analysis the samples were stored on ice in the dark. Chl *a* autofluorescence (emission > 630 nm) and phycoerythrin autofluorescence (PE, emission 575 ± 20 nm) were measured along with the

forward scatter (an indicator of cell size). The machine drift was tested using calibration beads with known size (3 and 10 μm) and fluorescence properties on a day-to-day basis, and cell sizes and fluorescence properties were corrected when necessary. Furthermore, additional tests showed that the total measuring time should not exceed 30 min. After this period the sample temperature increased $>10\,^{\circ}C$ resulting in a disintegration of the phytoplankton community.

The phytoplankton community showed a continuous range of cell size versus cellular Chl *a* autofluorescence but in general 3–5 major groups could be distinguished with a cell size <20 μm. Phytoplankton groups included picophytoplankton (<2 μm), small-sized eukaryotes (3–5 μm), and single cells of *Phaeocystis antarctica* (4–6 μm). The identity of the latter group was confirmed microscopically.

3. Results

3.1. Vertical and horizontal distribution of Chl a, DMSPp and DMS

Concentrations of Chl *a*, DMSPp and DMS were homogenously distributed in the upper 80 m of the water column at Stations A3 and C11 (on and off plateau, respectively; Fig. 2). Measurements of Chl *a* revealed that phytoplankton biomass in surface waters (0–150 m) was several fold higher above than outside the Kerguelen plateau (Figs. 2A and 3A). In contrast, there was no significant difference in concentrations of DMSPp and DMS between stations A3 and C11 (Figs. 2B, C and 3B, C).

The massive bloom at station A3 results almost entirely from the accumulation of diatoms, which represented 70–90% of the Chl *a* pool, in contrast to their relative contribution of 30% in the surrounding HNLC waters. There was no significant correlation between the levels of fucoxanthin (diatoms) and DMSPp, with most of the DMSPp being found in the size fraction lower than 10 μm (DMSPp <10 μm). Conversely, there was a significant linear correlation ($r^2 = 0.53$, $p<0.01$, $n = 101$) between the amount of DMSPp in this size fraction and the number of nano-phytoplankton (Fig. 4). Hence the survey of DMSPp levels suggests that small photosynthetic eukaryotes were the major producers of DMSPp, with diatoms producing only marginal amounts.

3.2. DMSPp production during bottle incubation experiments

Addition of DFe to unfiltered seawater collected in surface waters at C11 (off plateau) had no effect on DMSPp and Chl *a* during the first 3 d of incubation at 50% surface solar radiation (Fig. 5A). At day 9 of the incubation, however, mean concentrations of DMSPp and Chl *a* were both higher by a factor of 1.5 in the DFe-treatment as compared to the unamended control. Concentrations of DMSPp were similar at the beginning and the end of the incubation period whereas Chl *a* levels were by factors of 6–9 higher at day 9 as compared to day 0. DMSPp-to-Chl *a* ratios decreased by about a factor of 6 in nine days both in the DFe-treatment and the control (Fig. 5B). Temporal trends in Chl *a* and DMSPp concentrations very much resembled those in cell numbers of diatoms and autotrophic nano-flagellates, respectively (data not shown).

Concentrations of Chl *a* and DMSPp were 2.5- and 1.3-fold higher in the DFe-treatment as compared to the unamended control after 9 d of incubation of seawater collected in surface waters at A3, respectively (Fig. 5C). DMSPp-to-Chl *a* ratios decreased in nine days by about a factor of 2 in the control and by about a factor of 3 in the DFe-treatment (Fig. 5D). Cell numbers of autotrophic nano-flagellates (U. Christaki, pers. comm.) and DMSPp concentrations displayed similar trends.

3.3. Photodegradation of DMS

Above the Kerguelen Plateau, the DMS-PFORC of surface and deep waters was determined twice at station A3 (24 January and 13 February) and once at station B5

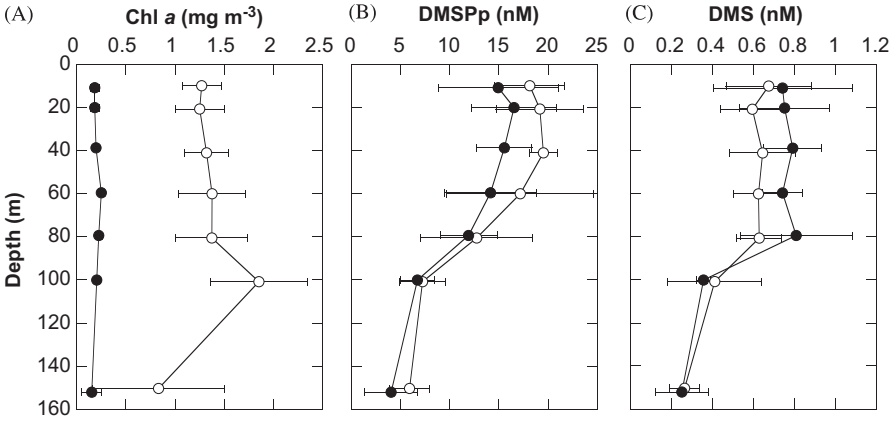

Fig. 2. Mean profiles ($n = 3$) of Chl *a*, DMSPp and DMS concentrations at A3 (circles) and C11 (black dots). The error bar is ± one standard deviation.

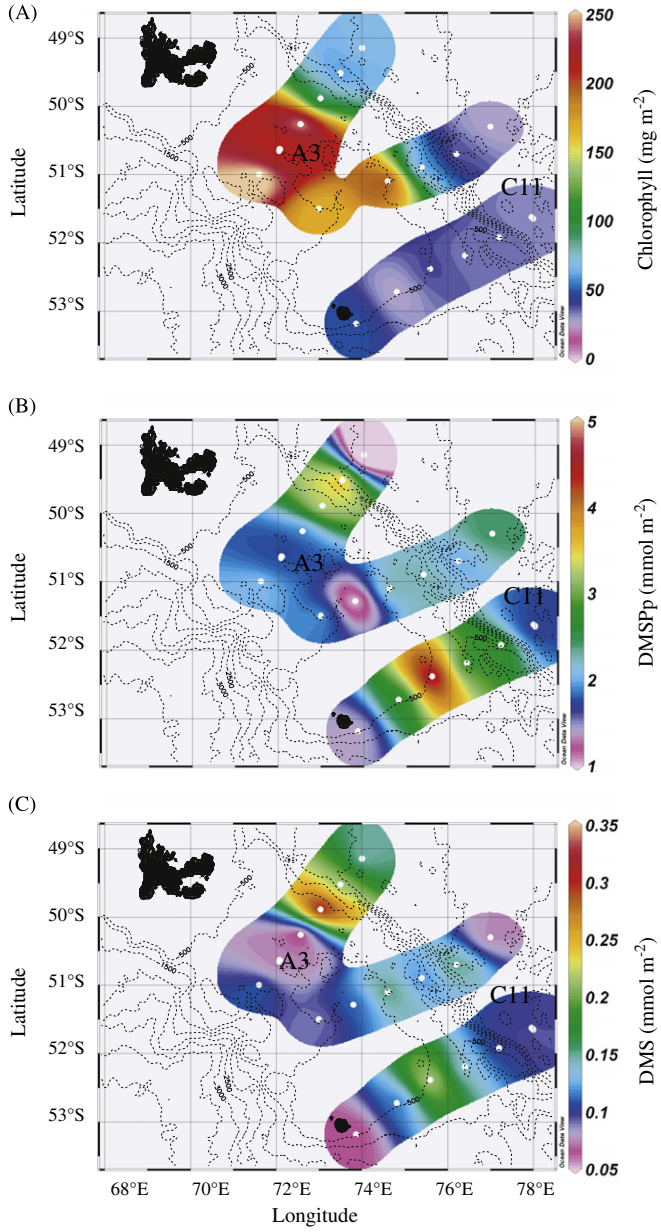

Fig. 3. Spatial distribution of Chl *a*, DMSPp and DMS standing stocks in the KEOPS investigation area: (A) Chl *a*, (B) DMSPp, and (C) DMS standing stocks each obtained from vertical profiles integrated between 150 m and the surface. Each vertical profile was constructed from samples collected at seven different depths.

(4 February; Fig. 6). Samples were incubated at almost similar UV-B and UV-A irradiance conditions ($9.0 \pm 1.2\,kJ\,m^{-2}$ at 340 nm, $0.6 \pm 0.1\,kJ\,m^{-2}$ at 305 nm). DMS-PFORC in all three experiments was significantly higher at 400 m ($0.30 \pm 0.09\,h^{-1}$ ($n = 3$)) than at 35 m ($0.10 \pm 0.03\,h^{-1}$ ($n = 3$), $p = 0.01$). The highest DMS-PFORC measured in surface and deep waters were $0.12\,h^{-1}$ (4 February) and $0.4\,h^{-1}$ (13 February), respectively (Fig. 6). Deep waters of the Kerguelen Plateau were enriched (by about a factor of 2) in CDOM and nitrates compared to surface waters (e.g. 21.5 μM and 0.3 QSU at 35 m depth, and 38.1 μM and 0.6 QSU at 400 m depth, station A3, 24 January 2005).

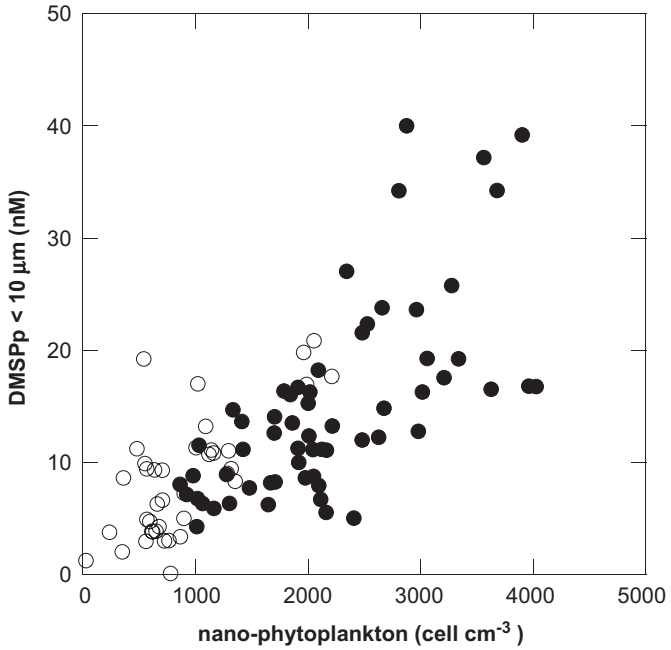

Fig. 4. Scatter plot of DMSPp concentration in the size fraction <10 μm and cell number of nano-phytoplankton made of small sized eukaryotes (3–5 μm) and single cells of *Phaeocystis antarctica* (4–6 μm). Data points were sorted according to Chl *a* levels (0.1 < low Chl *a* < 0.8 mg m^{-3} (black dots), 1 < high Chl *a* < 3.4 mg m^{-3} (white dots)).

UV-B and UV-A doses experienced in HNLC waters on 28 January (station C11, 3.3 kJ m^{-2} at 340 nm, 0.15 kJ m^{-2} at 305 nm) were about a third of that above the Plateau. Nitrate concentration and DMS-PFORC in the water sample taken at 35 m were equal to 27.8 μM and 0.016 h^{-1}, respectively.

4. Discussion

DMSPp did not exhibit higher concentrations or standing stocks above the highly productive Kerguelen Plateau than outside (Figs. 2 and 3). As a consequence, the DMSPp-to-Chl *a* ratio was considerably lower inside than outside of the bloom (e.g. 8 ± 2 mmol g^{-1} in B5, 10 ± 3 mmol g^{-1} in A3, 51 ± 10 mmol g^{-1} in C11). During bottle incubation experiments, DMSPp concentration was not stimulated by DFe addition as much as the Chl *a* concentration did (Fig. 5). The temporal trends were in all cases towards a marked decrease of the DMSPp-to-Chl *a* ratio (Fig. 5). Our findings differ from those of DiTullio et al. (2001) where the response to iron addition resulted in a marked increase of the DMSPp-to-Chl *a* ratio during a shipboard bottle incubation experiment carried out in the subantarctic zone south of Tasmania. Within the area investigated during KEOPS, there was a significant linear correlation between the amount of DMSPp <10 μm and the number of nano-phytoplankton (Fig. 4). Nano-phytoplankton had lower or similar numerical abundance above the Kerguelen Plateau as they did offshore. Cell numbers of nano-phytoplankton and DMSPp concentrations

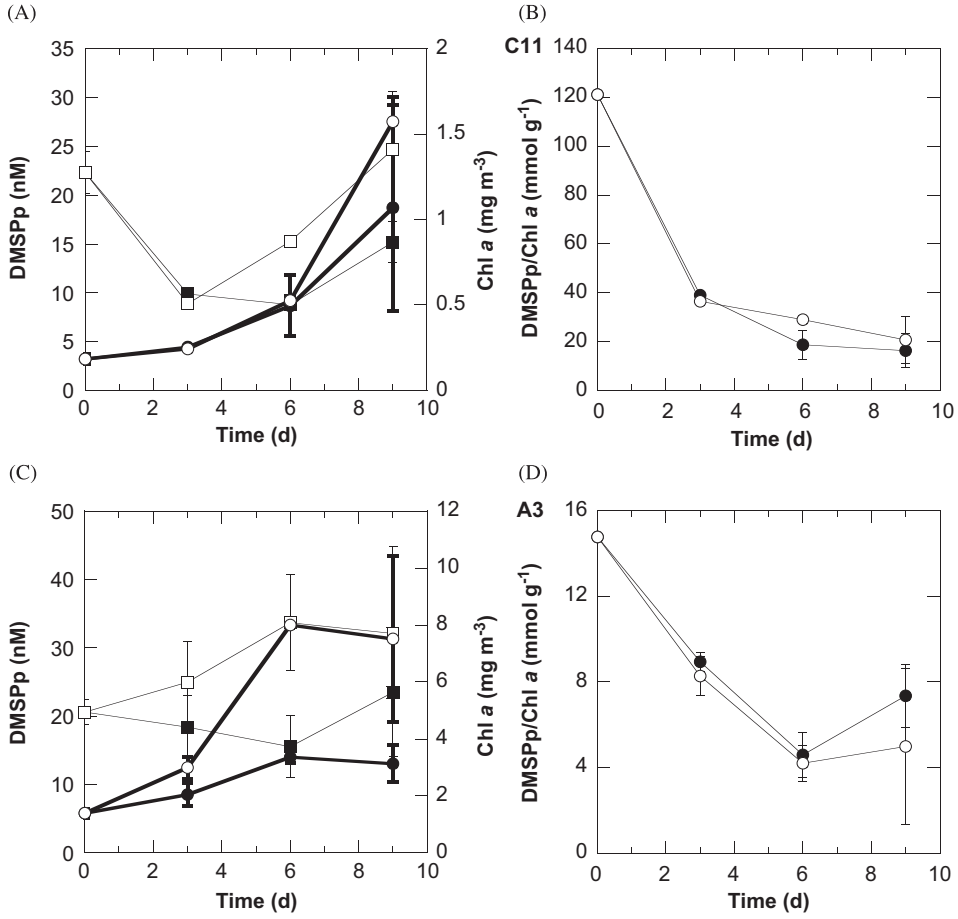

Fig. 5. Temporal variability of DMSPp and Chl *a* concentrations, and the ratio of both parameters, measured during on-deck bottle incubation experiments with or without dissolved iron added. Controls (dark symbols). With dissolved iron added (white symbols): (A) DMSPp (squares, thin lines) and Chl *a* (dots, thick lines), and (B) DMSPp vs. Chl *a* at station C11, (C) DMSPp and Chl *a*, and (D) DMSPp vs. Chl *a* at station A3. Median values are displayed and the error bar is the range of duplicated samples (i.e. two bottles per treatment were sampled at each time interval).

displayed also similar trends during bottle incubation experiments (data not shown). Hence, there was no DMSPp accumulation in the naturally and artificially fertilised blooms because the nano-phytoplankton (including *Phaeocystis*) was likely the major producer of DMSPp, with diatoms producing marginal amounts. Our findings also differ with those of the artificial iron-addition experiment SOIREE (Turner et al., 2004). In this experiment both diatoms and nano-phytoplankton bloomed simultaneously. In SOIREE, diatoms accounted for 30–60% of the Chl *a* pool in the fertilised area whereas the massive bloom above the Kerguelen Plateau resulted almost entirely (70–90% of the Chl *a* pool) from the accumulation of diatoms.

Neither DMSPp nor DMS had higher concentrations or standing stocks above the highly productive Kerguelen Plateau (Figs. 2 and 3). Since DMSP is the main precursor of DMS, it is possible that DMS concentrations also were controlled there by the abundance of nano-phytoplankton. However, we can provide a series of observations to indicate that the low levels of DMS in the naturally fertilised area were not due solely to the low abundances of nano-phytoplankton.

First, the photodegradation of DMS represents an important contribution to the temporal and spatial variability of DMS concentrations in the surface ocean (Kieber et al., 1996). It has recently been suggested that hydroxyl (OH) radicals, produced from photolysis of nitrates and CDOM, could be indirectly (e.g. through the production of bromine and carbonate-derived radicals) involved in the photochemical loss processes of DMS in the surface ocean (Bouillon and Miller, 2004, 2005). Above the Kerguelen Plateau, the massive diatom bloom was sustained by vertical supply of iron coming from deep iron-rich waters (Blain et al., 2007). These deep waters were also substantially enriched in inorganic nutrients and CDOM compared to surface waters. The highest potential for DMS photodegradation determined in the present study ($0.22–0.40\,h^{-1}$) was observed for deep waters above the Kerguelen Plateau (Fig. 6). So, the sustained injection of material of deep-water origin would enhance the photoproduction of radicals and the photochemical sink of DMS above the Kerguelen Plateau.

DMS photodegradation rates in surface waters above the Kerguelen Plateau ($0.07–0.12\,h^{-1}$) were $\approx 50\%$ lower than those measured in the Southern Ocean north of the

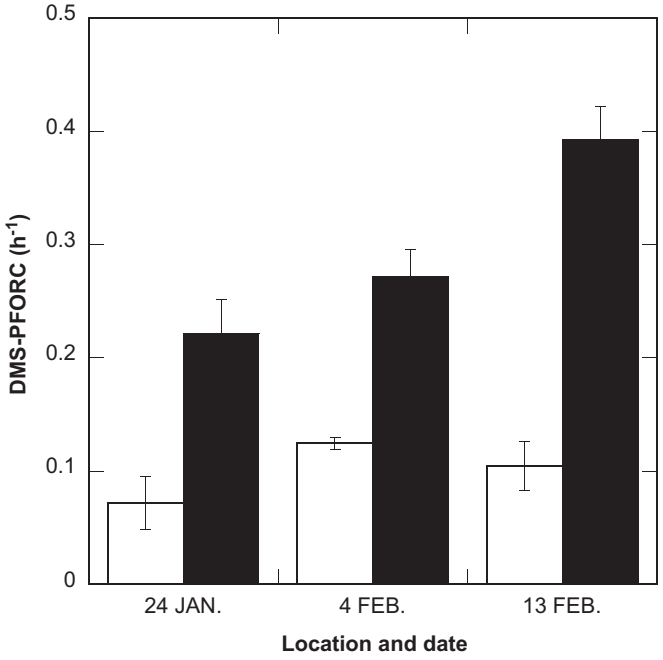

Fig. 6. Histogram showing three independent determinations of the DMS pseudo first-order rate coefficient for photodegradation (DMS-PFORC) in surface (white bar) and deep water (dark bar) samples of the Kerguelen plateau. The error bar is a 95% confidence interval of DMS-PFORC. It was calculated from the slope of the regression line when the natural logarithm of the DMS concentrations for dark and light treatments is plotted against time.

Ross Sea (0.16–0.23 h^{-1}, Toole et al., 2004). A much lower rate was measured in the HNLC waters (Station C11), but these samples received only about a third and a fifth of the UV-A and the UV-B doses received during the experiments performed above the Kerguelen Plateau. Nevertheless, it is suggested that in upwelling areas, such as the Antarctic Divergence zone (Toole et al., 2004), and in area with enhanced vertical mixing, such as above the Kerguelen Plateau (this study), the DMS photodegradation rates would be more important than in HNLC waters. Moreover, using an approach similar to that described by Kieber et al. (1996), it can be shown that photodegradation likely plays an important role in the loss of DMS in the bloom area. DMS column burdens for several depth intervals (0–1 m for example or for the whole mixed layer, 70 m in average at A3) were calculated from the vertical profiles of DMS. Piston velocities and sea-air fluxes of DMS were calculated using wind speed, sea-surface temperature and DMS data collected aboard R.V. *Marion Dufresne*. The flux-to-burden ratio is the sea-air turnover rate constant that can be compared to the DMS-PFORC measured during KEOPS. The sea-air turnover rate constant was about 0.1 h^{-1} in the depth interval 0–1 m and about 0.001 h^{-1} in the mixed layer. DMS-PFORC in the bloom area was, on average, $0.10 \pm 0.03\ h^{-1}$ ($n = 3$). Hence, when the smallest depth interval is considered, it appears that photodegradation is as important as atmospheric ventilation in the removal of DMS in the bloom area. In contrast, photodegradation of DMS in the Equatorial Pacific was of minor importance in the 0–1 m interval (Kieber et al., 1996).

Secondly, grazing of nano-phytoplankton by microzooplankton is an important pathway for DMS production (Simó, 2001). Unfortunately, those grazing rates were not determined during the cruise. Nevertheless, the potential of ciliates as primary production consumers is discussed by Christaki et al. (2008). They have estimated that the fraction of the primary production that transits through the ciliates at Station A3 (on plateau) and C11 (off plateau), was at the most 8.7% and 4.3%, respectively. Moreover, the efficient top-down control by mesozooplankton grazing probably prevented the biomass build-up of ciliates in the bloom area (Christaki et al., 2008). Hence, it is likely that the potential to transfer DMSPp to the dissolved pool by microzooplankton grazing was not markedly higher in the bloom area than outside.

Thirdly, it has been shown that actively growing bacteria metabolise DMSP for assimilatory purposes rather than cleaving it to DMS (Kiene et al., 2000). The abundance of heterotrophic bacteria at station A3 was roughly twice that observed at C11 (Christaki et al., 2008). Rates of bacterial production in surface waters at Station A3 ($3\ \mu g\ C\ l^{-1}\ d^{-1}$) were 6-fold higher than at the HNLC site C11 ($0.5\ \mu g\ C\ l^{-1}\ d^{-1}$) (Obernosterer et al., 2008). This suggests that the potential for bacterial DMS production in the natural bloom was lower than in HNLC waters. The high rates of bacterial production on plateau would also likely result in higher DMS losses than off plateau. So lower DMS production and higher DMS consumption would prevent the accumulation of this gas on the Kerguelen Plateau.

Thus, the sustained enrichment of iron over the Kerguelen Plateau did not translate into an increase in DMS concentration likely for three main reasons: (1) growth of nano-phytoplankton was not favoured by the continuous supply of iron in surface waters, (2) due to the higher levels of bacterial production measured over the plateau than outside, the transfer efficiency of DMSP to DMS (i.e. the DMS yield *sensu* Kiene et al., 2000) was probably lower and the bacterial removal of DMS higher on than off the plateau, and (3) nitrates and fresh CDOM supplied in surface waters from enhanced mixing of deep water over the plateau increased the photodegradation rates of DMS.

The continuous supply of low quantities of iron from below over a relatively long time period (months) represents the major difference between KEOPS and artificial iron-enrichment experiments of shorter duration (weeks) intending to mimic the consequences of a dust deposition event. Blain et al. (2007) showed that during the survey of the third month of the bloom over the Kerguelen Plateau its ecosystem structure differed from those observed during short-term iron addition experiments in terms of autotrophic and heterotrophic community activities, but also in terms of the efficiency of the fertilisation on carbon sequestration. During the KEOPS cruise we

surveyed during one month an ecosystem that had evolved over roughly 2 months. In that sense the ecosystem reached a higher degree of maturation than a transient ecosystem generated by artificial iron fertilisation, which is mainly studied from the pre-bloom until the bloom phase. We here shed new light on the consequences of sustained nutrient and iron fertilisation from below on DMS emissions to the atmosphere. Our results clearly demonstrate that, on the long term, there is no positive effect of natural iron fertilisation on the distribution of DMSPp and DMS in the Indian sector of the Southern Ocean. For further insights into the potential large-scale and long-term impact of iron fertilisation on DMS emissions, the reader is referred to the modelling work performed by Bopp et al. (2008), where a biogeochemical model is used that explicitly represents the oceanic iron and sulphur cycles.

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