DMSP and DMS dynamics during a mesoscale iron fertilization experiment in the Northeast Pacific—Part II: Biological cycling

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Received 14 March 2005; accepted 8 May 2006
Available online 2 October 2006

Abstract

Dimethylsulfiniopropionate (DMSP) and dimethylsulfide (DMS) biological cycling rates were determined during SERIES, a mesoscale iron-fertilization experiment conducted in the high-nutrient low-chlorophyll (HNLC) waters of the northeast subarctic Pacific. The iron fertilization resulted in the rapid development of a nanoplankton assemblage that persisted for 11 days before abruptly crashing. The nanoplankton bloom was followed by a diatom bloom, accompanied by an important increase in bacterial abundance and production. These iron-induced alterations of the plankton assemblage coincided with changes in the size and biological cycling of the DMSP and DMS pools. The initial nanoplankton bloom resulted in increases in particulate DMSP (DMSPp; 77–180 nmol L−1), dissolved DMSP (DMSPd; 1–24 nmol L−1), and biological gross (0.11–0.78 nmol L−1 h−1) and net (0.04–0.74 nmol L−1 h−1) DMS production rates. During the nanoplankton bloom, DMSPd consumption by bacteria exceeded their sulfur demand and the excess sulfur was probably released as DMS, consistent with the high gross DMS production rates observed during that period. The crash of the nanoplankton bloom was marked by the rapid decline of DMSPp, DMSPd, and gross DMS production to their initial values. Following the crash of the nanoplankton bloom, bacterial production and estimated sulfur demand reached transient maxima of 9.3 μg C L−1 d−1 and 14.2 nmol S L−1 d−1, respectively. During this period of high bacterial production, bacterial DMSPd consumption was also very high (6 nmol L−1 h−1), but none of the consumed DMSPd was converted into DMS and a net biological DMS consumption was measured. This transient period initiated a rapid decrease in DMS concentrations inside the iron-enriched patch, which persisted during the following diatom bloom due to low biological gross and net DMS production that prevented the replenishment of DMS. Our results show that the impact of Fe fertilization on DMS production in HNLC waters result from a complex interplay between the dynamics of the algal blooms and their influence on bacterial DMSP and DMS metabolism.
1. Introduction

Dimethylsulfide (DMS) produced by marine plankton represents the main natural source of sulfur emitted to the atmosphere (Andreae and Crutzen, 1997). In the atmosphere, DMS is oxidized into sulfate aerosols, which backscatter solar radiation through the formation of a sulfate haze and lead to the production of cloud condensation nuclei (CCN), which in turn increases cloud albedo. This combined effect can cool the atmosphere by decreasing the radiative flux, and thus mitigate global warming (Charlson et al., 1987).

Previous research in high-nutrient low-chlorophyll (HNLC) oceanic regions suggests that DMS accumulations in surface waters and emissions to the atmosphere may be limited by the availability of the trace nutrient iron (Turner et al., 1996, 2004; Watson and Liss, 1998). The low iron concentrations prevailing in HNLC waters limit the growth of large phytoplankton (mainly diatoms), while microzooplankton grazers control the smaller nanoflagellates, which are better adapted to grow under low iron conditions (Frost, 1991; Martin et al., 1991; Price et al., 1994). Mesoscale iron-enrichment studies in HNLC regions of the equatorial Pacific (IronEx II), Southern Ocean (SOIREE, EisenEx, SOFeX) and North Pacific (SEEDS, SERIES) resulted in increases in primary productivity and CO₂ uptake in surface waters (Coale et al., 1996, 2004; Boyd et al., 2000, 2004; Tsuda et al., 2003). IronEx II, SOIREE and EisenEx iron fertilization experiments also induced 1.6–6.5-fold increases in DMS (Turner et al., 2004), which led to the hypothesis that iron-induced CO₂ drawdown and DMS emission could act synergistically to moderate global warming (Turner et al., 1996).

During IronEx II, SOIREE and EisenEx, dimethylsulfoniopropionate (DMSP), the algal precursor of DMS, increased 2-fold and varied in parallel with the growth and decline of the DMSP-producing prymnesiophyte populations (Turner et al., 1996, 2004; Gall et al., 2001). The direct algal conversion of DMSP into DMS (Wolfe and Steinke, 1996; Wolfe et al., 2002) due to the grazing of the prymnesiophytes by heterotrophic ciliates was proposed as the most likely mechanism to explain the strong increase in DMS concentrations during SOIREE (Gall et al., 2001). However, the majority of DMS production is believed to occur indirectly, through the release of algal DMSP into seawater and its subsequent uptake and utilization by bacteria. Generally less than 10% of the DMSP consumed by bacteria is metabolized through the lyase cleavage pathway that produces DMS (Kiene et al., 2000), and DMSP is primarily demethylated and used as a source of carbon and reduced sulfur (Kiene et al., 1999). The relative importance of the bacterial DMSP demethylation and cleavage pathways is a major control of DMS production in marine waters and is dependent on the availability of DMSPd and on the sulfur requirement of the bacterial community (Kiene et al., 2000). Furthermore, bacteria also consume DMS (Kiene and Bates, 1990; Wolfe and Kiene, 1993; Zubkov et al., 2004), constituting an important sink for DMS in surface waters, along with photo-oxidation and ventilation (Simó and Pedró-Alió, 1999). Thus, the increase in DMS concentrations during the previous iron-enrichment experiments may also be explained by an alteration of the bacterial DMSP and DMS metabolism rather than grazing-induced direct algal DMS production.

In SERIES, the addition of iron also resulted in a DMSP-rich nanoplankton bloom, but did not generate a consistent response in DMS despite the two-fold increase in the DMSPp pool (Levasseur et al., 2006). Indeed, DMS concentrations followed the same pattern of increase and decrease inside and outside the Fe-enriched patch during the growth and decline of the nanoplankton bloom (first 14 days of the experiment). It is only during the subsequent diatom bloom that DMS concentrations diverged and became consistently lower (by a factor 10) inside the patch than in the surrounding area. In this article, we report on the variations in biological DMS(P) cycling rates that accompanied the evolution of the phytoplankton and bacterioplankton assemblages and DMS(P) pools during SERIES.

2. Material and methods

2.1. Creation, tracking and sampling of the iron-enriched patch

The SERIES iron-fertilization experiment was conducted near Ocean Station Papa (OSP; 50°N, 145°W) in a region of HNLC waters. The initial iron and sulfur hexafluoride (SF₆) infusion was carried out on July 9, 2002 (day 0), and a second iron infusion was conducted on day 7, following a rapid deepening of the wind-mixed layer (WML). The iron-enriched patch initially covered an area of 77 km² and expanded to 1000 km² on day 18.
Details of patch fertilization and tracking were presented by Boyd et al. (2004) and Law et al. (2006).

Sampling for biological DMS(P) cycling experiments was carried out from the research vessel B/O El Puma during days 1–19 of the study. Samples were collected between 9:00 and 14:00 (local time) everyday at the patch center (determined from the SF$_6$ distribution), and every 5 days outside the patch. Seawater for DMS(P) rate determination experiments was collected at one depth in the surface WML with a 10-L Go-Flo bottle and screened through 202-$\mu$m Nitex™ mesh to remove large grazers. The depth at which samples were collected varied between 1 and 14 m, depending on the water column structure. These discrete samples were representative of the WML, which varied from 8 to 32 m during the course of the experiment (Levasseur et al., 2006).

2.2. Nanophytoplankton and bacterial abundance

Seawater samples (2 ml) were preserved in 1% paraformaldehyde (final concentration), rapidly frozen in liquid nitrogen within an hour of collection, and stored at $-80^\circ$C until analysis. The abundances of nanophytoplankton and bacteria (stained with SYBR Green 1) were determined by flow cytometry, using a FACSort™ (Becton Dickinson, San Jose, USA) equipped with a 488-nm argon-ion laser (Hale et al., 2006).

2.3. Heterotrophic bacterial production and bacterial sulfur demand

Bacterial production was estimated from the incorporation of [3H]-thymidine. Samples were incubated in the dark for 4–6 h at in situ water temperatures and processed using standard protocols (Kirchman and Ducklow, 1993; Hale et al., 2006). Bacterial production rates were calculated assuming the standard conversion factor of $2 \times 10^{18}$ cells mol$^{-1}$ [3H]-thymidine incorporated (Fuhrman and Azam, 1982). Thymidine-based cell production rates were converted using bacterial cell carbon content calculated as a function of cell volume, determined from images of acridine orange stained cells (Norland, 1993; Hale et al., 2006).

The bacterial sulfur demand (Kiene and Linn, 2000b; Zubkov et al., 2001) was estimated by multiplying the bacterial production rates by a molar C:S ratio of 54.5 reported for marine bacteria associated with a bloom of *Emiliania huxleyi* (Fagerbakke et al., 1996). The molar C:S ratio of 54.5 specific to bacteria growing in an *E. huxleyi* bloom was selected since *E. huxleyi* was the most abundant phytoplankton species growing both inside and outside the patch during SERIES. Since the ‘bacterial sulfur demand’ is obtained by multiplying a carbon production rate by a molar C:S ratio, it should more appropriately be called ‘bacterial sulfur production’. For the sake of consistency, the term ‘sulfur demand’ will be used thereafter as in Kiene and Linn (2000b).

2.4. DMS(P) concentrations

To determine DMSP and DMS concentrations, seawater samples (71 ml) were gravity-filtered through 47 mm GF/F glass fiber filters (Whatman, 0.7 $\mu$m retention). For DMS, 24-ml serum bottles were filled with filtrate and sealed with a butyl stopper and aluminum crimp, leaving no headspace. DMS concentrations were determined within minutes of sampling. For DMSPd analyses, serum bottles were filled with 23 ml of filtrate and 1 ml of KOH (10 mol L$^{-1}$), and sealed. For DMSPp measurements, the filters were placed in serum bottles containing 23 ml of deionized water and 1 ml of KOH (10 mol L$^{-1}$), and sealed. All DMSP samples were stored at 4°C in the dark and analyzed within 3 weeks. Sulfur gas analyses were performed using purge and trap systems coupled to a Varian 3400cx or Varian 3800 gas chromatograph (GC) equipped with pulsed flame photometric detectors. DMSP samples were calibrated with a 5 ng DMSP mL$^{-1}$ standard prepared in 14-ml serum bottles containing 0.6 ml of KOH (10 mol L$^{-1}$). DMS samples were calibrated with injections of approximately 12 ng DMS mL$^{-1}$ diluted with He, prepared using a certified permeation tube (KinTek) (Scarratt et al., 2002).

2.5. Biological DMSPd and DMS cycling rates

The DMSP and DMS pools and biological cycling rates measured in SERIES, and a summary of the methods used, are presented in Fig. 1. To determine the biological (algal and bacterial) DMS production, four Tedlar gas-tight bags (1 l, Chromatographic Specialties Inc.), pre-cleaned with HCl and rinsed with deionized water, were filled with 600 ml of seawater, leaving no headspace. Two bags were used to determine the biological net DMS
production, and two bags were amended with methyl butyl ether (MBE, final concentration 30 μmol L⁻¹), an inhibitor of bacterial DMS consumption (Visscher and Taylor, 1993), to determine biological gross DMS production. The four bags were immediately sampled for initial DMSP and DMS concentrations, and incubated for 6 h in the dark. After 3 and 6 h, the bags were mixed gently, and sub-samples (71 ml) were gravity-filtered and analyzed for DMS(P) concentrations. The biological net DMS production rate was determined from the slope of the linear regression of the concentration of DMS vs. time in the incubations with no MBE. The biological gross DMS production rate was determined from the slope of the linear regression of DMS concentrations, and incubated for 6 h in the dark. After 3 and 6 h, the bags were mixed gently, and sub-samples (71 ml) were gravity-filtered and analyzed for DMS(P) concentrations. The biological net DMS production rate was determined from the slope of the linear regression of the concentration of DMS vs. time in the incubations with no MBE. The biological gross DMS production rate was determined from the slope of the linear regression of DMS concentration vs. time in incubations containing MBE. The bacterial DMS consumption rate was calculated by subtracting the biological net DMS production rate from the biological gross DMS production rate, only when the interaction term of analyses of covariance (ANCOVA) identified that the slopes were significantly different (p < 0.05). When slopes were not statistically different, bacterial DMS consumption was considered negligible.

Bacterial DMSPd consumption was determined in seawater samples during 3-h time course incubations in the dark at ambient surface water temperature. Seawater samples were amended with ³⁵S-DMSPd at tracer concentrations (<0.01 nmol L⁻¹; Kiene and Linn, 2000a) and 8 ml sub-samples were removed at four time points and preserved with 100 μl H₂SO₄ (3.6 mol L⁻¹). Volatile ³⁵S species (i.e. ³⁵S-DMS) were oxidized during storage while unconsumed ³⁵S-DMSPd remained stable at low pH. The unconsumed ³⁵S-DMSPd in each preserved sample was analyzed by pipetting 5 ml into 120-ml serum bottles sealed with a stopper holding a plastic cup that contained a filter (Gelman AE glass fiber) soaked with 3% H₂O₂. A 0.2 ml aliquot of NaOH (5 mol L⁻¹) was injected through the stopper to hydrolyze ³⁵S-DMSPd into ³⁵S-DMS and samples were shaken for more than 6 h, during which time ³⁵S-DMS was oxidized and trapped on the H₂O₂-soaked filters. Filters were removed and placed in 10 ml CytoScint (MP Biomedicals) and read on a scintillation counter (RackBeta Scintillation Counter, LKB Wallac). Bacterial DMSPd turnover rate constants were determined from the disappearance of ³⁵S-DMSPd during each incubation by computing the slope of the ln-transformed activity of ³⁵S-DMSPd vs. time (Kiene and Linn, 2000a). The bacterial DMSPd consumption rate was calculated by multiplying the DMSPd turnover rate constant by the initial DMSPd concentration.

The potential contribution of DMSP-sulfur to the bacterial sulfur demand was determined as the ratio of the bacterial incorporation of DMSP-sulfur and
the bacterial sulfur demand, assuming that 5% of the DMSPd consumed was assimilated into bacterial biomass. This sulfur assimilation efficiency is similar to the mean of $4.6 \pm 3.9\%$ reported for bacterioplankton associated with a coccolithophore bloom in the North Sea (Zubkov et al., 2001) and at the lower range of values reported for the oligotrophic waters of the Sargasso Sea (5–10%; Kiene and Linn, 2000a).

3. Results

3.1. Nanophytoplankton bloom, DMS(P) pools, and DMS production

The Fe addition resulted in a nanophytoplankton bloom that lasted for 11 days before rapidly declining back to initial abundance on day 12 (Fig. 2(A)). The nanoplankton bloom was followed by the full development of the diatom bloom (data not shown, see Levasseur et al., 2006). Outside the patch, nanoplankton abundance remained relatively low and stable.

Although DMSPp concentrations in the surface mixed layer showed some day-to-day variations inside the patch, there was a general increase from 76 nmol L$^{-1}$ to an average of $\sim 150$ nmol L$^{-1}$ (range 84–187 nmol L$^{-1}$) between days 3 and 8, and a decrease to 23–39 nmol L$^{-1}$ between days 12 and 19 (Fig. 2(B)). Outside the patch, DMSPp concentrations decreased from 75 nmol L$^{-1}$ on day 1, to less than 5 nmol L$^{-1}$ by days 16–19.

DMS concentrations inside the iron-enriched patch increased from $\sim 9$ nmol L$^{-1}$ on days 2–4 to a maximum of 22 nmol L$^{-1}$ on day 11, then decreased rapidly to low concentrations ($< 3$ nmol L$^{-1}$) at the end of the observation period (Fig. 2(C)). Outside the patch, DMS concentrations followed a similar trend, reaching a maximum of 19 nmol L$^{-1}$ on day 11 and decreasing to $\sim 7$ nmol L$^{-1}$ after day 11. Using a more complete dataset of out-patch DMS concentrations combining measurements by two ships, Levasseur et al. (2006) determined that in-patch and out-patch DMS concentrations were consistently different only after day 15, when concentrations inside the patch were up to 10-fold lower than outside.

Inside the patch, the biological (algal + bacterial) gross DMS production increased from 0.1 nmol L$^{-1}$ h$^{-1}$ to $> 0.4$ nmol L$^{-1}$ h$^{-1}$ between days 3 and 12, then decreased sharply to 0 nmol L$^{-1}$ h$^{-1}$ on day 13 (Fig. 2(D)). Afterward, biological gross DMS production rates ranged from 0.15 to 0.4 nmol L$^{-1}$ h$^{-1}$. Outside the patch, biological gross DMS production were highly variable ranging from a low 0.16 nmol L$^{-1}$ h$^{-1}$ on day 6 to rates $> 1.0$ nmol L$^{-1}$ h$^{-1}$ on days 1 and 16.

Biological net DMS production (gross DMS production–DMS consumption) was highly variable. Inside the patch, it increased from 0 to over 0.4 nmol L$^{-1}$ h$^{-1}$ between days 4 and 10, and declined to a net consumption of $- 0.2$ nmol L$^{-1}$ h$^{-1}$ on day 13 (Fig. 2(E)). Then, following a rapid increase to 0.3 nmol L$^{-1}$ h$^{-1}$ on day 14, the rates decreased again to 0 nmol L$^{-1}$ h$^{-1}$ on day 18. Outside the patch, biological net DMS production varied between the very high value of 1.5 nmol L$^{-1}$ h$^{-1}$ on day 1 to a net DMS consumption of $-0.2$ nmol L$^{-1}$ h$^{-1}$ on day 6.

3.2. Bacterial abundance, production and DMS(P) cycling

Inside the Fe patch, bacterial abundance in the surface mixed layer decreased from 0.5 to $10^9$ cells L$^{-1}$ between days 1 and 12, then sharply increased to a maximum of $1.2 \times 10^9$ cells L$^{-1}$ on day 17 (Fig. 3(A)). Outside the patch, bacterial abundance ranged from 0.2–0.5 $10^9$ cells L$^{-1}$, with the lowest abundance measured on day 11.

Bacterial production inside the patch was low and constant ($< 1.2$ $\mu$g CL$^{-1}$ d$^{-1}$) until day 8, then steadily increased to 6.4 $\mu$g CL$^{-1}$ d$^{-1}$ on day 19, with a transient peak of 6–9 $\mu$g CL$^{-1}$ d$^{-1}$ on days 12 and 13 (Fig. 3(B)). Outside the patch, bacterial production remained low ($< 2.0$ $\mu$g CL$^{-1}$ d$^{-1}$) throughout the study.

DMSPd concentrations inside the iron-enriched patch generally increased with time from an initial 1.8 nmol L$^{-1}$ to ca. 23 nmol L$^{-1}$ between days 8 and 13 (except for a transient decrease on day 9) and then declined to 3.9 nmol L$^{-1}$ between days 13 and 17 before increasing to 12.3 nmol L$^{-1}$ on day 19 (Fig. 3(C)). Outside the patch, DMSPd concentration showed considerable temporal variability, ranging from 2.8–19 nmol L$^{-1}$.

Except for three dates, the bacterial DMSPd turnover time inside the patch was generally ca. 7 h between days 1 and 11, after which the turnover times became lower than 4 h (Fig. 3(D)). Outside the patch, DMSPd turnover time decreased from 13.4 to 3.9 h during the course of the study. Bacterial DMSPd consumption rates inside the patch ranged from 0.2–5.9 nmol L$^{-1}$ h$^{-1}$, with a maximum rate on day 13 (Fig. 3(E)). Outside the patch, bacterial
DMSPd consumption ranged from 0.2–3.0 nmol L\(^{-1}\) h\(^{-1}\), with the highest rates measured on days 11 and 16.

Inside the patch, bacterial DMS consumption increased from 0 nmol L\(^{-1}\) h\(^{-1}\) to a maximum of ca. 0.40 nmol L\(^{-1}\) h\(^{-1}\) on days 5 and 6 before decreasing back to 0 nmol L\(^{-1}\) h\(^{-1}\) on days 9–11 (Fig. 3(F)). DMS consumption rates then peaked at 0.29 nmol L\(^{-1}\) h\(^{-1}\) on day 12 and remained below 0.14 nmol L\(^{-1}\) h\(^{-1}\) thereafter. Outside the patch, bacterial DMS consumption was high and relatively constant at 0.30–0.35 nmol L\(^{-1}\) h\(^{-1}\) until day 11, and was low (0.03 nmol L\(^{-1}\) h\(^{-1}\)) on day 19.

The estimated bacterial sulfur demand remained relatively constant inside the patch until day 8 (~1.5 nmol S L\(^{-1}\) d\(^{-1}\)) and increased to 9.7 nmol S L\(^{-1}\) d\(^{-1}\) on day 19, with a peak on days 12 and 13 (Fig. 4(A)). The estimated rates of DMSP-S incorporated by bacteria exceeded the bacterial sulfur demand between days 4 and 9, resulting in potential contribution of DMSP to the bacterial sulfur demand higher than 100% (Fig. 4(C)). After
day 10, the estimated bacterial DMSP-S incorporation was 1.9–5.6 times lower than bacterial sulfur demand (Fig. 4(A)), and the potential contribution of DMSP-S to the bacterial sulfur demand was consistently lower than 100% (Fig. 4(C)). In contrast, outside the patch, the bacterial sulfur demand remained below 1.9 nmol L\(^{-1}\) S d\(^{-1}\) and the estimated DMSP-S incorporated by the bacteria was 2–4 times higher (Fig. 4(B)); therefore the incorporation of DMSP-sulfur was sufficient to meet the bacterial sulfur demand (>100%; Fig. 4(D)) except on day 19.

4. Discussion

4.1. DMSP and DMS dynamics at Ocean Station Papa—the unperturbed HNLC conditions

DMSP and DMS rates measurements were only conducted on five occasions outside the patch during SERIES. These rates were highly variable, probably reflecting the presence of different water masses in the study region. For these reasons (low sampling frequency and regional small-scale heterogeneity), a statistical comparison between the rates...
measured inside and outside the patch was not conducted in this study. Nevertheless, the five out-patch rate measurements provide insights on the causes for the very high DMS concentrations characterizing HNLC waters around OSP (Wong et al., 2005).

DMS concentrations were remarkably high in the surface mixed layer at the beginning of SERIES (up to 15 nmol L$^{-1}$), and reached 26 nmol L$^{-1}$ 10 days later outside the patch (Levasseur et al., 2006). Our data show that these elevated DMS concentrations corresponded to high rates of biological gross DMS production as well. Outside the Fe patch, biological gross DMS production ranged from 0.1 to 1.8 nmol L$^{-1}$ h$^{-1}$ (Fig. 2(D)), values up to 20-fold higher than those previously measured in oligotrophic waters of the Sargasso Sea (<0.1 nmol L$^{-1}$ h$^{-1}$; Ledyard and Dacey, 1996; Levasseur et al., 2004), and in the upper range of DMS production rates measured for diverse coastal and open ocean environments (see review by Simó, 2004). Hence, our results show that the exceptionally high DMS concentrations prevailing in HNLC waters at OSP reflect high biological DMS production.

Levasseur et al. (2006) have suggested that the dominance of DMSP-rich prymnesiophytes *E. huxleyi* and *Phaeocystis* spp. at OSP was at least partly responsible for the high DMS concentrations measured outside the patch during SERIES. DMSP lyase, the enzyme responsible for the cleavage of DMSP into DMS, has been isolated from both *E. huxleyi* and *Phaeocystis* (Steinke et al., 1998; Stefels and Dijkhuizen, 1996). However, there are indications that healthy prymnesiophytes do not produce DMS, most production taking place when cells are grazed or attacked by viruses (Malin et al., 1998; Wolfe et al., 2002). It has been demonstrated in laboratory that zooplankton grazing induces the co-release of DMSP and DMSP lyase in *E. huxleyi* cultures, leading to DMS production (Wolfe and

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**Fig. 4.** Time course of bacterial sulfur demand (filled circles) and DMSP-sulfur incorporated into bacterial biomass (open circles) for (A) inside and (B) outside the iron-enriched patch, and the potential contribution of DMSP-sulfur to the bacterial sulfur demand for (C) inside and (D) outside the iron-enriched patch. Dotted line represents 100%.
At OSP, microzooplankton grazing is known to control the size of the nanoplanckton population (see review by Harrison, 2002). Hence, the high biological DMS production rates measured in the region may result from the grazing of the DMSP-rich prymnesiophyte population with a DMSP cleavage capacity.

Microzooplankton grazing may also indirectly increase the production of DMS by transferring algal DMSP to the dissolved pool, making it available for bacterial metabolism. Several bacteria can cleave DMSP (Visscher et al., 1992; Yoch et al., 1997; González et al., 1999), a pathway allowing them to use the carbon in the molecule (in the form of acrylate) while the sulfur moiety is released as DMS (Kiene et al., 2000; Yoch, 2002). The DMSP cleavage pathway is thought to be favored when sulfur in bacterial substrates is found in excess of the bacterial sulfur requirement (Kiene et al., 2000).

Outside the patch, bacterial production and sulfur demand were low, and bacterial DMSPd consumption was largely exceeding its sulfur demand (Figs. 3(B), 4(B) and (D)). These conditions (DMSPd consumption > sulfur demand) are believed to favor DMSP cleavage and the release of excess sulfur as DMS, and thus may partly explain the high DMS production rates observed at OSP.

HNLC waters at OSP thus bring together many conditions favoring high DMS production: a plankton community dominated by strong DMSP producers with a capacity for direct DMS production, a top-down control of the DMSP producers, and a bacterial community consuming DMSPd in excess of its sulfur demand.

4.2. DMSP and DMS dynamics during the Fe-induced bloom

The addition of iron stimulated the growth of all phytoplankton groups and induced a bloom that evolved in two phases (Marchetti et al., 2006). The initial nanophytoplankton (mostly E. huxleyi) responded rapidly, reaching four times out-patch abundances between days 3 and 10, and declining rapidly between days 10 and 12. Diatoms increased exponentially to reach maximum abundance and dominated the phytoplankton community on days 13–17. DMSPp concentrations varied in phase with the growth and decline of the nanoplanckton population (Fig. 2(A) and (B)), and more specifically with the strong DMSP-producing coccolithophore E. huxleyi (Levasseur et al., 2006). The temporal evolution of the Fe-induced bloom was paralleled by changes in bacterial productivity and DMS(P) cycling that can be divided in three successive periods: the nanoplanckton bloom, the transient period following the crash of the nanoplanckton bloom, and the diatom bloom. The characteristics of these three periods are presented in Table 1.

### 4.2.1. The nanoplanckton bloom period

The iron fertilization had no consistent effect on DMS concentrations during the initial nanoplanckton bloom (days 1–12; Fig. 2). This unexpected result suggests that the iron-induced bloom of DMSP-rich nanoplanckton did not significantly alter the biological cycling of DMSP and DMS. The nanoplanckton bloom was characterized by sustained high biological gross and net DMS production rates (averages of 0.4–0.5 nmol L⁻¹ h⁻¹; Fig. 2 and Table 1), but these rates were not consistently higher than the maximum rates measured outside the patch where lower nanoplanckton abundance was measured. Hence, although the biological gross DMS production was positively related to nanophytoplankton abundance inside the patch (r = 0.59; p < 0.05), direct algal DMSP cleavage was apparently not the sole process underlying this

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<th>Diatom bloom (days 14–19)</th>
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relationship. Our results suggest that bacterial DMS production may have been important during that period.

During this initial bloom, DMSPd concentrations were high (>10 nM), as well as the bacterial DMSPd consumption rates (Fig. 3). The bacterial DMSPd turnover times measured during that period (7–19 h) are in the range reported for the oligotrophic waters of the Sargasso Sea (11–28 h, Malmstrom et al., 2004), Gulf of Mexico (6–14 h, Kiene and Linn, 2000b), and the North Sea (9.6 h, Zubkov et al., 2002). As observed outside the patch, DMSPd was then generally consumed in excess of the bacterial sulfur demand (days 4–8; Fig. 4(A) and (C)). This excess consumption of DMSP-S indicates that during the nanoplankton bloom, the bacteria used DMSPd mostly as a source of carbon and the DMSP-S taken up was sufficient to meet their sulfur requirement. In the North Sea and the North Atlantic, DMSPd consumption also has been shown to satisfy 95% and 182% of the sulfur demand of the bacterial populations during blooms dominated by DMSP-rich nanoplankters (Zubkov et al., 2001; Simó et al., 2002). During the initial nanoplankton bloom, a large fraction of the DMSP-S taken up by the bacteria was probably released as DMS, contributing to the high DMS gross production measured during that period.

The nanoplankton bloom also was characterized by high bacterial DMS consumption rates (up to 0.44 nmol L\(^{-1}\) h\(^{-1}\)). Bacterial DMS consumption rates reported for the North Atlantic, North Sea and Sargasso Sea are generally less than 0.1 nmol L\(^{-1}\) h\(^{-1}\), with occasional peaks around 0.2 nmol L\(^{-1}\) h\(^{-1}\) (Simó and Pedrós-Alió, 1999; Levasseur et al., 2004; Wolfe et al., 1999; Zubkov et al., 2002).

Previous studies have reported a positive relationship between bacterial DMS consumption and DMS production (Simó et al., 1995; Simó, 2004; Wolfe et al., 1999) and/or DMS concentrations (van Duyl et al., 1998; Zubkov et al., 2002). During SERIES, the highest consumption rates were measured during the first 12 days of SERIES, when DMS production rates and concentrations were maximal. However, bacterial DMS consumption was not significantly correlated with DMS concentration, DMS production or heterotrophic bacterial production, suggesting that bacterial DMS consumption was not substrate-dependent and was restricted to a small sub-population not representative of the bulk of the bacterial community. Bacterial DMS metabolism is poorly known, but DMS is probably consumed by bacteria as a supplementary substrate (Zubkov et al., 2001, 2002) and, unlike DMSPd, its consumption satisfies only a small fraction of the bacterial sulfur demand (1–3%; Zubkov et al., 2002). The lower importance of DMS as a bacterial substrate may partly explain the high variability of bacterial DMS consumption rates measured during SERIES.

4.2.2. The transient period

The crash of the nanoplankton bloom and the following diatom bloom coincided with an important increase in bacterial production and an alteration of the bacterial DMSPd metabolism that led to a decrease in DMS levels inside the patch (Figs. 2 and 3). Shortly after the crash of the nanoplankton bloom, bacterial production and DMSPd consumption increased and reached transient maxima (Fig. 3(B) and (E)), indicating that bacteria may have benefited from dissolved organic matter (DOM, including DMSP) released by the collapse of the bloom. On day 13, the bacterial sulfur demand reached its highest values (14 nmol S L\(^{-1}\) d\(^{-1}\); Fig. 4(A)) while DMS gross production dropped to below our detection limit (Fig. 2(D)). These results show that a large quantity of DMSPd released during the crash of the DMSP-rich algae was rapidly consumed by bacteria and exclusively demethylated. The demethylation/demethiolation pathway is linked to sulfur assimilation and protein synthesis, but also yields a methyl group and three-carbon compound that can be used as carbon sources (Kiene and Linn, 2000a; Yoch, 2002). During the transient period of maximum bacterial production, DMSPd was thus demethylated and used as a source of both carbon and reduced sulfur by the highly productive bacterial population. Bacterial DMS consumption was also high during this transient period, and since there was no biological DMS production, the net DMS production was negative (net biological loss of DMS). During this transient period, all the sulfur contained in both DMSPd and DMS was thus used to satisfy the high bacterial sulfur demand, and bacterial processes represented a net sink of DMS. We hypothesize that these unusual transient conditions initiated the DMS deficit inside the Fe patch that persisted during the following diatom bloom.

4.2.3. The diatom bloom period

During the diatom bloom, DMSPd concentrations decreased by a factor of ca. 4, but bacterial
production kept increasing and DMSPd consumption rates remained as high as during the DMSP-rich nanoplankton bloom (Fig. 3). Bacteria were consuming the DMSPd pool twice faster during the diatom bloom (days 13–19; ca. 4 h) than during the nanoplankton bloom (ca. 8 h; Fig. 3(D)). The low DMSPd turnover times measured during the diatom bloom are similar to those reported for productive coastal waters of the Gulf of Mexico and Gulf of Maine (0.7–6.2 h; Kiene and Linn, 2000b; 1.7–6.2 h; Malmstrom et al., 2004). During this late phase of the bloom, the bacterial sulfur demand remained high and exceeded DMSP-S assimilation (Fig. 4(A) and (C)). Under these conditions, most of the DMSP-S was probably used to meet the high sulfur demand of the bacteria, resulting in lower DMS production rates (Fig. 2(D)). Our results thus suggest that the alleviation of DOC limitation and concurrent increase in bacterial sulfur demand induced a shift in bacterial DMSPd utilization from high DMS production during the nanoplankton bloom to demethylation in the diatom bloom. The shift in bacterial DMSPd metabolism was the likely mechanism that initiated and maintained the deficit in DMS measured in the Fe-enriched patch at the end of the experiment.

4.2.4. Bacterial productivity vs. DMSPd consumption

The relationship between bacterial DMSPd consumption and bacterial production may provide useful insights on the physiological status of the bacterial assemblage. Malmstrom et al. (2004) proposed that since DMSP assimilation can generally provide most of the bacterial sulfur for protein synthesis, it should better compare with leucine incorporation which is a proxy for protein synthesis rather than with thymidine incorporation, which is a better indicator of bacterial growth (division). In SERIES, bacterial DMSPd consumption was weakly but significantly \((r^2 = 0.34; P \leq 0.05)\) correlated with thymidine incorporation, and not with leucine incorporation. This suggests that throughout the experiment, DMSP was consumed primarily by dividing bacteria and mostly used as a carbon source rather than a source of reduced sulfur for protein synthesis. These results are consistent with the DOC-limited status of bacterial growth during SERIES (Hale et al., 2006). This scenario is not unique to SERIES. Positive relationships between DMSPd consumption and bacterial production as estimated by thymidine have been observed in the Gulf of Mexico (Kiene and Linn, 2000b), the North Atlantic (Malmstrom et al., 2004), and during an E. huxleyi bloom in the North Sea (Zubkov et al., 2001). This stresses the importance of DMSPd as a source of carbon for bacteria in a wide variety of marine environments.

4.3. Conclusions

Previous large-scale Fe-fertilization experiments consistently reported an initial nanoplankton bloom associated with increases in DMSPp and DMS concentrations (Turner et al., 1996; Watson and Liss, 1998). These observations led to the hypothesis that the Fe-induced increase in DMS emission in HNLC waters could act synergistically with CO₂ drawdown to moderate global warming. During SERIES, the addition of Fe also triggered an initial bloom of DMSP-rich nanoplankton, but no significant increase in DMS was measured. In addition, the crash of the nanoplankton bloom and the subsequent diatom bloom were characterized by a rapid decrease in DMS concentrations. Our DMSP and DMS cycling rates suggest that the DMS deficit resulted from a shift of the bacterial DMSPd metabolism from high DMS production in the nanoplankton bloom to demethylation in the diatom bloom. A comparison of previous Fe-enrichment studies suggests that the extremely strong increase in bacterial productivity and sulfur demand during SERIES was responsible for this unexpected DMS response. Bacterial production increased 10-fold during SERIES, compared to 2–3-fold increases observed during previous experiments (Hale et al., 2006). In addition, the maximum bacterial production rates reached during SERIES were 10 times higher than during the other experiments. The unique DMS response observed during SERIES may thus reflect the particularly strong bacterial response to Fe addition. Our results show that Fe fertilization of HNLC waters may generate contrasting DMS responses depending on the influence of iron on the bloom dynamics and bacterial DMSP metabolism.

Acknowledgements

The authors want to thank the captain and crew members of the research vessels El Puma J.P.Tully and Kaiyo Maru for their work and assistance during the cruise. A. Merzouk received a
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