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Iron-induced alterations of bacterial DMSP metabolism in the western subarctic Pacific during SEEDS-II

Martine Lizotte [a,*], Maurice Levasseur [a], Isao Kudo [b], Koji Suzuki [c], Atsushi Tsuda [d], Ronald P. Kiene [e], Michael G. Scarratt [f]

[a] Québec-Océan, Département de Biologie, Université Laval, Québec, Canada
[b] Graduate School of Fisheries Sciences, Hokkaido University, Sapporo Hokkaido, Japan
[c] Faculty of Environmental Earth Science, Hokkaido University, Sapporo Hokkaido, Japan
[d] Ocean Research Institute, University of Tokyo, Tokyo, Japan
[e] Department of Marine Sciences, University of South Alabama, Mobile, AL, USA
[f] Maurice Lamontagne Institute, Fisheries and Oceans Canada, Mont-Joli, Canada

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ABSTRACT

The effect of added iron on bacterial cycling of the climate-active gas dimethylsulfide (DMS) and its precursor dimethylsulfoniopropionate (DMSP) was tested during the second Subarctic Pacific Iron Experiment for Ecosystem Dynamics Study (SEEDS II) from 19 July to 21 August 2004 aboard the R/V *Hakuho-Maru*. The study area in the northwest Pacific Ocean (48°N 165°E) was enriched with Fe and the conservative tracer, SF_6, allowing the fertilized patch to be tracked. Microbial DMSP cycling rates were determined in the surface mixed layer (5 m) during incubations using the ^{35}S-DMSP technique. The addition of iron resulted in a 4-fold increase in concentrations of chlorophyll *a* (chl *a*) within the surface mixed layer (5 m depth), and the length of the sampling period allowed the observation of both bloom and post-bloom conditions. Inside the fertilized patch, the alleviation of resource limitation gave rise to the concurrent increase in bacterial abundance and production. Changes in the phytoplankton community within the Fe-enriched patch translated into a sustained decrease in chl *a*-normalized particulate DMSP ($DMSP_p$) concentrations, suggesting a preferential stimulation of the growth of $DMSP_p$-poor phytoplankton species. Despite short-lived peaks of $DMSP_p$ within the Fe-enriched area, concentrations of $DMSP_p$ generally remained stable during the entire sampling period inside and outside the fertilized patch. During the Fe-induced bloom, microbial DMSP-sulfur (DMSP-S) assimilation efficiency increased 2.6-fold inside the Fe-enriched area, which indicated that as bacterial production increased, a greater proportion of DMSP-S was assimilated and possibly diverted away from the bacterial cleavage pathway (i.e. production of DMS). Our results suggest that iron-induced stimulation of weak $DMSP_p$-producers and DMSP-assimilating bacteria may diminish the potential production of DMS and thus limit its flux towards the atmosphere over the subarctic Pacific Ocean.

1. Introduction

Iron is essential for the growth of organisms, and iron derived from the atmosphere may be a limiting micronutrient for primary productivity in oceanic regions termed high-nutrient low-chlorophyll (HNLC) (Martin, 1990) which encompass ca. 25% of the World Ocean (de Baar et al., 1999). The persistence of low and constant phytoplankton stocks in these HNLC regions is thought to result from the growth limitation of large phytoplankton by weak iron supply, while top-down control by microzooplankton grazing constrains standing stocks of pico- and nano-phytoplankton which are better adapted to grow under conditions of low bio-available iron (Frost, 1991; Martin et al., 1991; Liu et al., 2004). Several mesoscale iron-enrichment experiments have been conducted in HNLC regions of the Southern Ocean, the equatorial Pacific, and the subarctic Pacific, and each has demonstrated that the addition of iron stimulates the growth of phytoplankton (see review by de Baar et al., 2005). Iron fertilization experiments have also resulted in shifts in floristic composition, increased CO_2 uptake in surface waters, and in modest increases in downward export of biogenic carbon (Boyd et al., 2004), which lends support to the suggestion that natural iron delivery to these oceanic regions could contribute to reduce the atmospheric CO_2 load and global warming (Martin, 1990).

Purposeful iron addition not only affects the capacity of the oceans to absorb CO_2 but also the production of the climate

* Corresponding author. Tel..: +1 418 656 2131x6274; fax.: +1 418 656 2339.
E-mail address: martine.lizotte@qo.ulaval.ca (M. Lizotte).

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relevant trace gas dimethylsulfide (DMS) and its precursor dimethylsulfoniopropionate (DMSP). Fe-enrichment experiments conducted in the Equatorial Pacific (IronEx II) and the Southern Ocean (SOIREE, EisenEx, SOFeX) have consistently reported increases in particulate DMSP ($DMSP_p$) by factors of 1.6 to 2.6 (Turner et al., 2004), as well as increases in DMS by factors of 1.6 to 6.8 (Turner et al., 2004, Wingenter et al., 2004). These results have led to the suggestion that Fe-induced CO_2 drawdown and DMS emission in these HNLC regions could act in conjunction to alleviate climate warming (Turner et al., 1996). However, results from recent mesoscale iron fertilisations conducted in the subarctic Pacific Ocean (SEEDS-I, -II, and SERIES) failed to show an increase in DMS levels (Takeda and Tsuda, 2005; Levasseur et al., 2006; Nagao et al., 2009), suggesting more complex iron-DMS dynamics.

DMS, which is produced by marine plankton, is by far the most abundant volatile sulfur compound in oceanic surface waters and sustains approximately half of the global biogenic sulfur flux to the atmosphere (Andreae, 1990). In the atmosphere, DMS influences climate through the formation of clouds and a sulfate haze, both of which cool the atmosphere by decreasing solar radiative flux (Charlson et al., 1987). Though phytoplankton appear to be the source of dimethylsulfoniopropionate, studies have shown that complex food web processes are involved in the degradation of DMSP into DMS (Simó, 2001; Kiene et al., 2000). Cleavage of DMSP via lyase enzymes yields DMS and acrylic acid (Cantoni and Anderson, 1956) and can occur through conversion by phytoplankton (Stefels and van Boekel, 1993; Wolfe and Steinke, 1996) and zooplankton (Dacey and Wakeham, 1986; Wolfe et al., 1994), although the majority of DMS production is thought to arise from bacteria (Kiene, 1990). However, recent studies indicate that commonly less than 10% of DMSP consumed by bacteria is metabolized through the cleavage pathway that produces DMS (Kiene et al., 2000), and DMSP is for the most part demethylated/demethiolated and used as a source of reduced sulfur and carbon which can ultimately be assimilated into bacterial proteins (Kiene et al., 1999). It has been hypothesized that the sulfur requirement of the bacterial assemblage (Kiene et al., 2000) coupled with the relative importance of DMSP to the overall labile sulfur compounds in the dissolved organic matter (DOM) pool control how efficiently bacteria assimilate DMSP-S through the demethylation pathway, and thereby potentially divert it from DMS production (Pinhassi et al., 2005). In addition to bacterial production of DMS, considerable bacterial consumption of DMS has been observed (Kiene and Bates, 1990; Wolfe and Kiene, 1993; Zubkov et al., 2004), which along with vertical mixing and photodegradation (Kieber et al., 1996; Simó and Pedrós-Alió, 1999), constitute removal processes that ultimately influence the rate of DMS emission to the atmosphere. Despite heterotrophic bacteria playing a fundamental role in the cycling of DMSP and DMS, the response of microheterotrophic communities to iron fertilization is not well understood.

During SERIES, in spite of a 2-fold increase in $DMSP_p$ (Levasseur et al., 2006), a strong increase in bacterial production and sulfur demand led to a shift in bacterial DMSP metabolism from high DMS production towards greater incorporation of sulfur from DMSP (Merzouk et al., 2006). Bacterial DMS(P) cycling experiments were not conducted during iron-enrichment studies in the Southern Ocean or in the equatorial Pacific, even though increases in DMS have been a common finding (Turner et al., 2004). Thus, possible bacterial mechanisms involved in the enhanced DMS production were not identified although changes in the magnitude of stocks and rate processes occurred within the microbial food web (Boyd, 2002). The aim of this study was to quantify the effects of an iron addition on the microbial cycling of DMSP in the Northwest Pacific Ocean during SEEDS II. Additionally, $DMSP_d$ enrichment experiments were conducted with deckboard incubations in order to determine how $DMSP_d$ bioavailability affected its assimilatory metabolism and its conversion to DMS.

2. Materials and methods

2.1. Study area and framework

The SEEDS II iron-fertilization experiment was conducted in the western subarctic gyre of the North Pacific Ocean (48°N, 166°E) in a region of HNLC waters. On 20 July 2004 (day 0), an 8×8 km patch of ocean was fertilized with iron and tracked using sulfur hexafluoride (SF_6) (Tsumune et al., 2005). A second infusion was performed on 26 July 2004 (day 6) following a dilution of the patch by vertical and horizontal mixing (Tsuda et al., 2007). Details of the experimental methodology of SEEDS II as well as patch behaviour and tracking are presented by Tsuda et al. (2007).

Sampling for the determination of DMS(P) concentrations and biological cycling experiments was carried out from the research vessel *Hakuho Maru* during days 2–12 (bloom phase) and days 23–32 (post-bloom phase) of the study. Samples were collected between 6:00 and 21:00 hours (local time) near the center of the patch (determined from the distributions of SF_6 and partial pressure of CO_2, pCO_2, in surface waters) as well as outside the fertilized patch. Seawater was collected at 5 m in the surface mixed layer (ca. 10–30 m) using acid-cleaned Niskin-X bottles mounted on a CTD-Carousel multi-sampling system secured to a titanium hydrowire. Additionally, seawater was prescreened through a 202-μm Nitex™ in order to remove large plankton (grazers).

2.2. DMSP and Chl a analyses

To determine chlorophyll *a* (chl *a*) concentrations, 115 ml of seawater were filtered on a glass-fiber filter (GF/F). The chl *a* content of the filters was determined by extraction with 6 ml of *N*,*N*-dimethylformamide (DMF) for >24 h (Suzuki and Ishimaru, 1990) and measured by fluorometry with a Turner Designs fluorometer using a non-acidification protocol (Welschmeyer, 1994). See Tsuda et al. (2007) for the complete presentation and discussion on chl *a* measurements.

Particulate DMSP ($DMSP_p$) was measured by gravity filtering 71 ml of seawater through 47-mm GF/F glass fiber filters (Whatman, 0.7 μm retention) and placing the filter in a serum vial containing 23 ml of deionized water and 1 ml of KOH solution (10 M). All DMSP samples were capped with rubber stoppers and aluminum seals, kept in the dark at 4 °C, and analyzed within five weeks of collection. Sulfur gas analyses were performed using a cryogenic purge-and-trap technique coupled to a Varian 3800 gas chromatograph (GC) equipped with a pulsed flame photometric detector (PFPD). DMSP samples were calibrated with a gravimetric standard (Research Plus Inc.) of DMSP (50 ng ml^{-1}) prepared in 14-ml serum bottles containing 0.6 ml of KOH (10 M) following methods described in detail by Scarratt et al. (2000). The analytical precision for DMSP was better than 7%.

Although samples of the dissolved fraction of the sulfur pool ($DMSP_d$+DMS) were taken and analyzed during SEEDS II, we chose not to present these data for the following reasons: (1) Recent evidence suggests that large-volume gravity filtration (>5 ml) can enhance the pool of dissolved DMSP ($DMSP_d$) when cells under pressure release their DMSP content (Kiene and Slezak, 2006); (2) The filtration method used (see description above) allows us to determine a dissolved sulfur pool (i.e. $DMSP_d$+DMS). In order