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PRODUCTION BIOLOGIQUE DU DIMÉTHYLSULFONIOPROPIONATE (DMSP) ET DU DIMÉTHYLSULFURE (DMS) EN FONCTION D'UN GRADIENT NATUREL EN FER DANS LE PACIFIQUE SUBARCTIQUE NORD-EST

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Résumé

Le diméthylsulfure (DMS) est le principal gaz biogénique sulfuré émis de l'océan vers l'atmosphère. Il peut exercer un effet refroidissant sur le climat en formant des aérosols sulfatés et en intensifiant l'albédo des nuages de basses altitudes, diminuant la quantité d'énergie radiative atteignant la surface de la Terre. Bien que le DMS puisse être produit directement par certaines espèces phytoplanctoniques, il provient principalement des bactéries hétérotrophes via la dégradation de son précurseur, le diméthylsulfoniopropionate (DMSP). Le DMSP est synthétisé par le phytoplancton en différentes concentrations selon les conditions environnementales, incluant la disponibilité du fer. La présente étude porte sur la dynamique microbienne du DMSP dans le Pacifique nord-est le long d'un gradient naturel en fer. Mes résultats montrent qu'une plus grande disponibilité en fer dans cette région océanique limitée en fer favorise la croissance des espèces productrices de DMSP et augmente le taux de conversion bactérien de DMSP en DMS. Ensemble, ces résultats indiquent que les apports en fer peuvent avoir un effet refroidissant sur le climat dans le Pacifique nord-est.

Abstract

Dimethylsulfide (DMS) is the main sulfur biogenic gas emitted from the ocean to the atmosphere. DMS may exert a cooling effect on climate through its oxidation to sulfate aerosols which both scatter sunlight and intensify the albedo of low clouds, thus decreasing the amount of solar radiation entering the atmosphere. Even though DMS can be produced by certain phytoplankton species, it is mainly produced by heterotrophic bacteria via the degradation of its precursor dimethylsulfoniopropionate (DMSP). DMSP is synthesized by phytoplankton at varying cellular quotas, depending on environmental conditions such as iron concentrations. This study has focused on DMSP microbial dynamics in the North East Pacific along a natural iron gradient. My results show that an increase in iron availability favors a DMSP-rich algal community and increases the bacterial conversion of DMSP into DMS. Together, these results suggest that increases in iron availability may have a cooling effect on climate in the North East Pacific.

Avant-Propos

Ce mémoire de maîtrise a été réalisé sous la supervision du Professeur Maurice Levasseur. Le corps de ce mémoire a été rédigé en anglais sous forme d'article scientifique, article dont je suis l'auteure principale. Au printemps 2007, j'ai participé à une mission en mer qui m'a permis de récolter les données nécessaires à la réalisation de cette étude. J'ai réalisé la majeure partie des travaux de terrain et de laboratoire ainsi que l'analyse des résultats et la rédaction du mémoire. À des étapes clés de ma rédaction, les conseils judicieux de mon directeur ainsi que ceux de ma collègue Martine m'ont aidé à orienter mon travail. Maurice Levasseur, Michael Scarratt, Connie Lovejoy, Ronald Kiene, Chi Shing Wong ainsi que Martine Lizotte, Michael Arychuk, Keith Johnson, Marie Robert, Angelica Peña et Sonia Michaud sont co-auteurs de l'article scientifique qui sera soumis prochainement pour publication dans une revue scientifique de niveau international. J'ai eu l'occasion de présenter mes résultats lors de l'école d'été Surface Ocean Lower Atmosphere Study (SOLAS) en Corse à l'automne 2007 et sous forme d'affiche et de présentation orale au cours des assemblées générales de Québec-Océan en novembre 2007 et 2008.

Le mémoire comprend trois chapitres:

Chapitre 1 - Introduction générale

Chapitre 2 - Microbial cycling of DMSP along a natural iron gradient in the North East Subarctic Pacific.

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Chapitre 3 - Conclusion

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« *Fais de ta vie un rêve, et d'un rêve, une réalité.* »

Antoine de Saint-Exupéry

À ma mère

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Chapitre 1 : Introduction générale

Le DMS et le climat

Le climat planétaire est influencé en grande partie par des interactions complexes entre l'océan et l'atmosphère. Ces deux systèmes interdépendants occupent un rôle central dans le système climatique global non seulement par le transport de chaleur et les échanges d'eau qu'ils induisent, mais aussi du fait de leur importance dans le cycle général de plusieurs éléments dont le soufre. Les émissions océaniques de soufre sont dominées par un gaz produit par le plancton marin, le diméthylsulfure (DMS) (Haas 1935). Le DMS est le principal gaz biogénique sulfuré émis de l'océan vers l'atmosphère. Il représente plus de 90 % du soufre naturel gazeux émis et 25 % des émissions totales de soufre, biogéniques et anthropiques (Simó 2001; Brimblecombe 2004). Le flux de DMS se propage toujours de l'océan vers l'atmosphère et varie en fonction de la concentration en DMS dans les eaux de surface, de la vitesse du vent et de la température de l'eau (Liss et Slater 1974; Liss et Merlivat 1986; Nightingale et al. 2000). Dans l'atmosphère, le DMS subit une photo-oxydation chimique qui mène à la formation de divers composés, principalement l'acide méthanosulfonique (MSA), le dioxyde de soufre (SO_2) et le sulfate (SO_4^{2-}). Ces produits d'oxydation altèrent le budget radiatif de l'atmosphère terrestre via la formation d'aérosols de sulfate (Charlson et al. 1987; Andreae et Crutzen 1997). Ces derniers régulent de façon directe le climat en absorbant et en dispersant les radiations solaires et, de manière indirecte, en contribuant à la formation de noyaux de condensation des nuages (NCN) au-dessus des régions océaniques (Charlson et al. 1987; Andreae et Crutzen 1997; Liss et al. 1997) (Figure 1.1). Une densité élevée de NCN augmente l'albédo des nuages et favorise ainsi la réflectivité des rayons lumineux vers l'atmosphère. Charlson, Lovelock, Andreae et Warren ont proposé en 1987 l'hypothèse CLAW (Figure 1.1). Selon cette hypothèse, une augmentation des émissions de DMS due au

réchauffement résulterait en une augmentation de l'albédo des nuages et en une réduction de la quantité de lumière atteignant la surface des océans, créant ainsi une boucle de rétroaction contribuant à stabiliser le climat. Cette hypothèse demeure toutefois à vérifier étant donné le peu de connaissances sur l'impact d'une augmentation des radiations solaires sur la production planctonique de DMS (Schwartz 1988; Rijssel et Gieskes 2002).

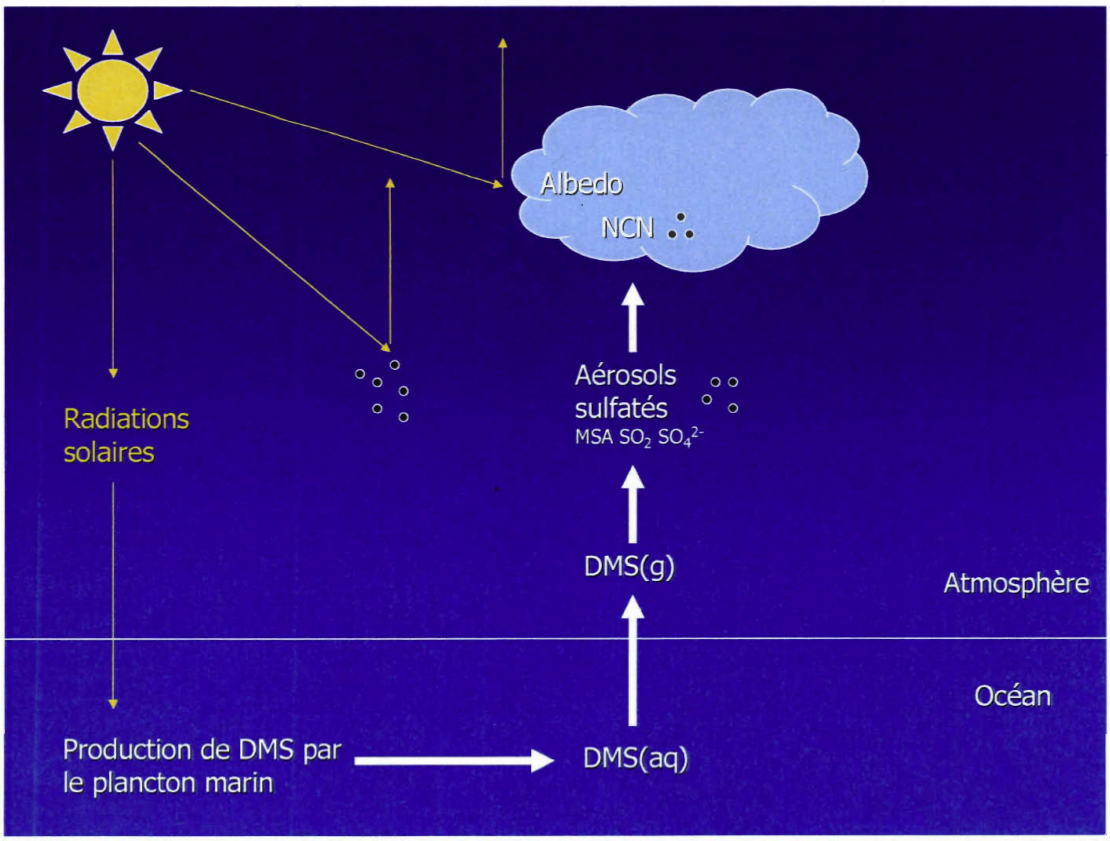

Figure 1.1: Représentation schématique de l'hypothèse CLAW selon laquelle le DMS synthétisé par le plancton marin influence le bilan radiatif de la Terre, régulant ainsi le climat (Figure traduite et adaptée de Simó (2001)).

La production biologique du DMSP : ses rôles et mécanismes de régulation

Dans les océans, le DMS provient de la dégradation enzymatique de son précurseur, le diméthylsulfonioproprionate (DMSP) (Challenger et Simpson 1948; Cantoni et Anderson 1956). Il semble que la synthèse du DMSP soit exclusive au règne végétal et plus particulièrement aux algues eucaryotes (Keller et al. 1989), ce qui explique son caractère ubiquiste dans tous les océans (Cooper et Matrai 1989). La capacité à synthétiser le DMSP est présente chez un vaste éventail de taxons algaux et ce à travers divers écosystèmes allant des eaux tropicales jusqu'aux eaux polaires (Malin et Kirst 1997). Cependant les concentrations intracellulaires de DMSP varient fortement en fonction des groupes présents (Keller et al. 1989; Malin et Kirst 1997). Certains groupes, comme les dinoflagellés et les prymnésiophycées, sont d'importants producteurs de DMSP (Keller et al. 1989; Matrai et Keller 1993; Burkill et al. 2002), tandis que d'autres tels les diatomées possèdent des quotas cellulaires faibles en DMSP (Keller et al. 1989; Yoch 2002).

Le DMSP chez le phytoplancton occuperait plusieurs fonctions physiologiques et écologiques. Le DMSP jouerait un rôle d'osmolyte chez un vaste éventail d'espèces phytoplanctoniques. Ce rôle favoriserait la protection des protéines et la stabilisation des membranes lors de chocs osmotiques et thermiques (Stefels 2000). En plus de ses propriétés osmolytiques, le DMSP aurait des fonctions de cryoprotection en stabilisant l'activité enzymatique à basses températures (Karsten et al. 1996), augmentant ainsi la compatibilité pour les protéines (Kirst et al. 1991). Le DMSP ainsi que ses produits de dégradation (DMS et acrylate) posséderaient aussi des propriétés antioxydantes permettant de détruire les radicaux libres présents chez le phytoplancton (Sunda et al. 2002). L'action antioxydante du DMSP et de ses composés dérivés protégerait les cellules contre les stress causés par le rayonnement ultraviolet ou par les carences en fer et en azote (Sunda et al. 2002; Bucciarelli et Sunda 2003). Le DMSP participerait également à un mécanisme de soupape

permettant aux cellules de dissiper l'excès de soufre ou de carbone lors de périodes d'instabilité ou de perturbations environnementales (Stefels 2000).

Finalement, un rôle de défense contre la prédation a aussi été suggéré pour le DMSP, le DMS et l'acrylate (Strom et al. 2003a). Les producteurs de DMSP et ses produits dérivés dissuaderaient chimiquement les brouteurs zooplanctoniques (Wolfe et al. 1997; Strom et al. 2003a; Strom et al. 2003b) et les macroinvertébrés (Van Alstyne et Houser 2003). Cette défense anti-brouteurs serait déclenchée lors du clivage du DMSP en DMS et en acrylate grâce à l'enzyme DMSP-lyase. L'acrylate est un composé répulsif pour le zooplancton et possède une activité anti-microbienne (Wolfe et Steinke 1996). Cette constatation a donc suggéré aux scientifiques la participation indirecte du phytoplancton possédant la DMSP-lyase à un mécanisme de défense tri-phasique (Steinke et al. 2002).

Certaines espèces phytoplanctoniques, telle qu'*Emiliania huxleyi*, possèdent l'enzyme DMSP-lyase responsable du clivage du DMSP en DMS (Holligan et al. 1983; Barnard et al. 1984; Turner et al. 1988; Malin et al. 1993). Chez les cellules phytoplanctoniques saines, le DMSP est isolé de la DMSP-lyase dans le cytosol. Cette barrière physique limite le clivage et se traduit par une faible production de DMS (Stefels et van Boekel 1993; Wolfe et Steinke 1996). La rencontre du substrat et de son enzyme est possible lors de l'exsudation et de la lyse des cellules phytoplanctoniques; ce bris cellulaire pouvant résulter du broutage (Wolfe et al. 1997), d'un stress, de la mort cellulaire ou d'attaques virales (Hill et al. 1998; Malin et al. 1998). Bien que certaines espèces phytoplanctoniques possèdent la DMSP-lyase et puissent ainsi contribuer à la production de DMS, la principale voie de production du DMS serait bactérienne (González et Simó 2000). Le clivage enzymatique bactérien nécessite la libération du DMSP particulaire ($DMSP_p$) puis la prise en charge et la dégradation du DMSP dissout ($DMSP_d$) par les bactéries possédant la DMSP-lyase (Yoch 2002).

Le rôle des bactéries dans le cycle du DMS

Les communautés bactériennes associées aux floraisons phytoplanctoniques riches en espèces productrices de DMSP jouent un rôle important dans le cycle du soufre (González et Simó 2000). Le $DMSP_d$ représente un substrat important pour le bactérioplancton océanique, pouvant combler jusqu'à 95 % de leurs besoins en soufre et jusqu'à 15 % de leurs besoins en carbone selon les milieux (Kiene et al. 2000; Zubkov et al. 2001). Chez les bactéries, le DMSP emprunte majoritairement la voie de déméthylation et la voie de clivage enzymatique (Figure 1.2) (Kiene 1996; Yoch 2002). La déméthylation se produit dans les sédiments anoxiques et dans les eaux libres et ne libère pas de DMS (Kiene et Taylor 1988; Kiene 1996; Yoch 2002). Elle prédomine lorsque la demande en soufre des bactéries est importante et conduit à la production de méthanethiol (MeSH), précurseur de la synthèse des acides aminés sulfurés méthionine et cystéine (Kiene et al. 1999; Yoch 2002; Pinhassi et al. 2005). Seul le clivage enzymatique via la DMSP-lyase conduit à la formation de DMS et d'acrylate (équation 1) (Cantoni et Anderson 1956; de Souza et Yoch 1995). Cette voie métabolique est empruntée lorsque les besoins bactériens en soufre sont comblés. Les cellules bactériennes utilisent l'acrylate comme source de carbone pour supporter leur croissance hétérotrophe et relâchent le DMS dans le milieu (de Souza et Yoch 1995). Le DMS représente généralement moins de 10 % du $DMSP_d$ consommé par les bactéries (Kiene et Linn 2000b; Kiene et al. 2000; Vila-Costa et al. 2006). Ce taux de conversion peut toutefois atteindre 50 % sous certaines conditions (voir revue par Kiene et al. 2000).

$$(CH_3)_2S^+CH_2CH_2COO^- \xrightarrow{\text{DMSP-lyase}} CH_3SCH_3 + CH_2=CHCOO^- + H^+ \qquad (1)$$

$$\text{DMSP} \rightarrow \text{DMS} + \text{Acrylate} + H^+$$

En plus de la ventilation vers l'atmosphère, deux autres mécanismes retirent le DMS de la colonne d'eau : la dégradation par les bactéries et la photo-oxydation par les radiations solaires (Figure 1.2) (voir revue par Simó 2001). La consommation bactérienne de DMS représente un puits important pour le DMS et augmenterait en fonction des concentrations ambiantes de DMS (Kiene et Bates 1990; Wolfe et al. 1999). Une forte production de DMS résulterait en une augmentation de l'abondance ou de l'activité des bactéries consommatrices de DMS (Kiene et Service 1991; Levasseur et al. 1996). De plus, une partie non négligeable du DMS est photo-oxydée en sulfoxyde de diméthyle (DMSO) via une oxydation photochimique (Kieber et al. 1996; Toole et al. 2003) ou une photo-oxydation biologique sous le contrôle des bactéries phototrophes (Zeyer et al. 1987; Liss et al. 1997). Les océans sont toujours supersaturés en DMS et représentent donc une source continue de ce gaz pour l'atmosphère. Moins de 10 % du DMS produit est éventuellement émis dans l'atmosphère (Bates et al. 1994; Ledyard et Dacey 1996). La dynamique du DMSP et du DMS est activement contrôlée par le métabolisme microbien et varie en fonction des différentes voies métaboliques empruntées (Malmstrom et al. 2004). Malgré des avancées importantes dans le domaine, on connaît encore mal les facteurs contrôlant la production bactérienne de DMS. Des études récentes démontrent que la structure des assemblages bactériens (Gonzalez et al. 2000; Zubkov et al. 2001; Malmstrom et al. 2004; Pinhassi et al. 2005; Howard et al. 2006) de même que leurs conditions physiologiques (Kiene et al. 2000) affectent les taux de production de DMS dans le milieu océanique.

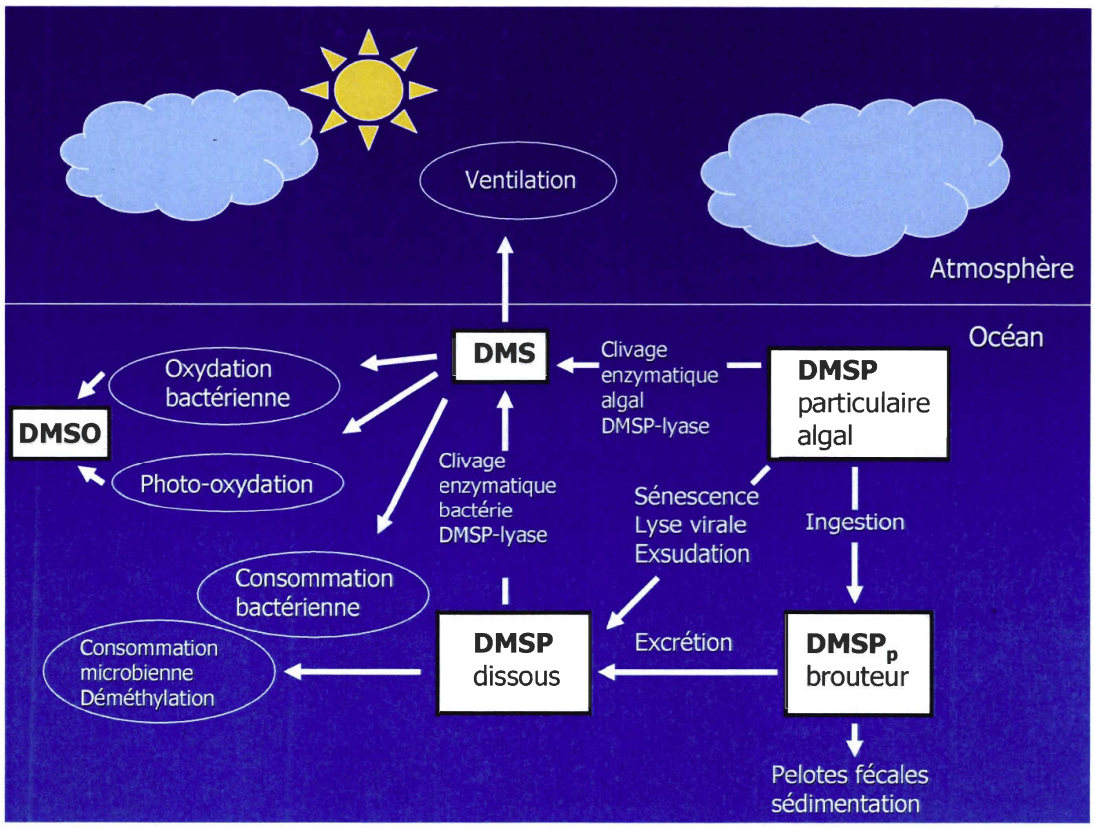

Figure 1.2: Représentation schématique du cycle du DMS dans l'océan (Figure adaptée de Kiene (1992) et de Dacey et al. (1998)).

Les régions HNLC et le DMS

La croissance du phytoplancton marin est influencée par les conditions physicochimiques du milieu. Les principaux macronutriments qui contrôlent la croissance des algues marines sont le nitrate et le phosphate et, à un moindre degré, le silicate. La biodisponibilité du fer, un micronutriment nécessaire à la synthèse de protéines chez le plancton végétal est aussi un facteur limitant pour la croissance du phytoplancton. Plus de 25 % de l'océan global est limité en fer (Martin et al. 1994). Ces étendues océaniques, qualifiées de « High-Nutrient, Low-Chlorophyll » (HNLC),

sont caractérisées par de faibles biomasses algales en dépit de la présence de fortes concentrations en macronutriments inorganiques. Les régions HNLC sont situées dans l'océan Austral, le Pacifique équatorial et subarctique (Martin et al. 1989; Boyd et al. 1996).

Expériences d'enrichissement en fer

Afin de mieux caractériser l'influence des limitations en fer sur les écosystèmes planctoniques, douze expériences d'enrichissement en fer à grande échelle furent réalisées jusqu'à maintenant (Boyd et al. 2007), ainsi que plusieurs expériences en microcosme (Boyd et al. 1999). Les expériences à grande échelle impliquent l'ajout de fer, sous forme de $FeSO_4$, sur une surface d'environ 100 km^2 et le suivi des propriétés chimiques et biologiques de cette parcelle sur des périodes variant de quelques jours à plusieurs semaines. Bien que les recherches lors des enrichissements en fer aient été davantage concentrées sur la capacité de la masse d'eau enrichie à séquestrer le CO_2 atmosphérique via la séquestration en profondeur du carbone nouvellement fixé (pompe biologique), l'impact du fer sur la production d'autres gaz affectant le climat, dont le DMS, a également attiré l'attention des chercheurs.

Lors des premières expériences réalisées dans l'océan Austral et équatorial, l'ajout de fer a entraîné une augmentation des teneurs en DMS. Les niveaux de DMS ont triplé lors des expériences IronEx II (Turner et al. 1996) et SOIREE (Turner et al. 2004) et quintuplé lors de SOFeX (Wingenter et al. 2004). Toutefois, tel que discuté ci-après, une toute autre réponse a été observée lors de l'expérience *Subarctic Ecosystem Response to Iron Enrichment* (SERIES) menée en 2002 dans le Pacifique nord-est.

L'expérience SERIES et le Pacifique nord-est

Lors de SERIES, l'ajout de fer a résulté en une augmentation de l'abondance et de la production du phytoplancton et des bactéries hétérotrophes (Agawin et al. 2006; Hale et al. 2006) mais en une diminution inattendue des concentrations de DMS (Levasseur et al. 2006). Une augmentation de la capacité bactérienne à consommer le DMSP suite à la floraison des diatomées induite par l'enrichissement en fer a aussi été observée, mais le DMSP a été majoritairement utilisé par les bactéries comme source de soufre via la voie de déméthylation (Merzouk et al. 2006). Les résultats de SERIES ont démontré que les effets du fer sur la production nette de DMS pouvaient être très variables, variabilité imputée aux changements de la biomasse et de la composition des communautés phytoplanctoniques, de même qu'aux variations rapides (jour) du métabolisme bactérien. Les résultats obtenus lors de SERIES ont mis en évidence l'importance des liens entre les apports en fer, la structure du réseau microbien et la production du DMS.

Les expériences d'enrichissement en fer à grande échelle représentent probablement une simulation réaliste des évènements sporadiques de dépôts de poussières éoliennes qui enrichissent les régions limitées en fer. Toutefois, la capacité de ces expériences à reproduire les apports en fer résultant d'autres mécanismes, dont le mélange vertical, est moins certaine (Boyd et al. 2007). Les écosystèmes et les cycles biogéochimiques peuvent répondre différemment face à des ajouts de fer localisés et sporadiques, tels que reproduits lors d'expériences d'enrichissement artificiel, comparativement à des additions lentes et continues de fer par mélange vertical ou latéral. Les résultats du programme KEOPS réalisé sur le Plateau de Kerguelen dans l'océan Austral représentent un bon exemple de cette différence. Lors de cette expérience, les apports en fer par mélange n'ont pas résulté en une augmentation des concentrations de DMS telle qu'observée lors des expériences d'enrichissement à grande échelle réalisées

dans la même région (Bopp et al. 2008). Les évènements d'approvisionnement naturel en fer sont toutefois difficiles à observer, ainsi très peu d'études ont évalué leur impact sur les écosystèmes et les cycles biogéochimiques.

Le Pacifique nord, principalement sa portion ouest, est approvisionné épisodiquement en fer via les grands vents provenant des régions désertiques asiatiques (Moore et al. 2002; Han et al. 2008). Ces évènements coïncident avec des augmentations de la biomasse phytoplanctonique ainsi que des augmentations du flux du matériel biogénique vers les profondeurs (Young et al. 1991; Yuan et Zhang 2006). Plusieurs études ont montré que les poussières atmosphériques provenant de l'Asie représentaient une source importante de fer pour la gyre d'Alaska (Moore et al. 2002; Moore et Braucher 2007). Des travaux récents ont toutefois démontré que le mélange vertical et l'advection de tourbillons (*eddies*) formés au niveau des marges continentales du golfe d'Alaska (Johnson et al. 2005) représentent d'importantes sources de fer pour cette région (Hongo et al. 2005; Lam et al. 2006; Crawford et al. 2007; Cullen et al. 2007; Lam et Bishop 2008). L'impact de ces modes d'apports en fer sur la dynamique du DMS dans le Pacifique subarctique nord-est n'est pas connu.

L'objectif de mon étude est de déterminer l'influence d'un gradient naturel en fer sur la dynamique microbienne du DMSP et du DMS dans les eaux HNLC du Pacifique subarctique nord-est. Mon étude a été réalisée dans le cadre des missions *Line P* de Pêches et Océans Canada. Cette radiale s'étend de l'Île de Vancouver à la station Papa et couvrent un gradient en fer, de la zone côtière riche en fer aux conditions HNLC caractérisant la gyre d'Alaska.

Chapitre 2 : Microbial cycling of DMSP along a natural iron gradient in the North East Subarctic Pacific

Abstract

The Alaskan Gyre is a High Nutrient Low Chlorophyll region (HNLC) characterized in summer by exceptionally high concentrations of dimethylsulfide (DMS), a biogenic gas with a potential cooling effect on climate. Surface waters in this region are replenished with Fe by sporadic aeolian dust deposition, and on a more regular basis, by vertical mixing and advection of coastal eddies. Results from a mesoscale Fe fertilization experiment conducted in 2002 in the Gyre showed a stimulation of all components of the plankton food web but no net impact on DMS concentrations and sea-to-air flux. In this study, we report on the impact of natural Fe fertilization through mixing on microbial dimethylsulfoniopropionate (DMSP) metabolism and DMS production during a cruise conducted between May 21 and June 19, 2007, along the Line P transect extending from the southern tip of Vancouver Island to Ocean Station Papa (OSP) in the Alaskan Gyre. The impact of Fe supply was evidenced at two spatial scales: 1) between the Fe-rich coastal stations and the Fe-poor HNLC stations, and 2) within the Fe-poor HNLC stations per se. First, the HNLC stations were characterized by significantly higher $DMSP_p$: chl *a* ratio (mean of 84 nmol μg^{-1}) and higher volatile ^{35}S yields (mean of 8 %) compared to the coastal stations (mean of 26 nmol μg^{-1}, and mean of 4 %, respectively), indicating a dominance of strong phytoplankton $DMSP_p$ producers and a more efficient bacterial conversion of DMSP into DMS under Fe-limiting conditions. Secondly, increases in Fe concentrations from mixing within the HNLC waters resulted in significantly higher $DMSP_p$ concentrations ($r^2 = 0.79$), $DMSP_p$: chl *a* ratios ($r^2 = 0.86$), and

volatile ^{35}S yields ($r^2 = 0.77$). These results show that, in the HNLC waters of the North East Pacific, increases in Fe availability can lead to a more productive system in terms of DMSP and DMS with a potential effect on cloud formation, leading in a cooling effect on climate.

Introduction

The productivity of more than 25 % of the world's oceans is limited by Fe (de Baar et al. 1999; de Baar et al. 2005). These areas, referred to as High-Nutrient, Low-Chlorophyll (HNLC) regions, are found in the Southern Ocean, the Equatorial Pacific, and the North East (NE) Subarctic Pacific. HNLC regions are supplied with Fe via different mechanisms: sporadically via the deposition of aeolian dust (an allochtonous source), by mixing/diffusion and lateral advection (autochthonous sources) (Jickells et al. 2005). The relative contribution of these natural sources of Fe varies in time and space, with aeolian deposition dominating in regions adjacent to and downwind of the dust sources during windy periods, and mixing/advection further away from these sources. Geological records suggest that higher Fe deposition took place over the Southern Ocean HNLC region during the last glaciation (Legrand 1997; Petit et al. 1999), while direct observations show that vertical mixing and lateral advection may represent the dominant source of Fe around islands and over shallow plateaus (Belviso et al. 2008). The impact of artificial Fe supply on the dynamics of plankton blooms in HNLC regions has been well documented, but our understanding of how natural Fe supply impacts biogeochemical processes and in particular the production of climate active trace gases remains limited.

The potential impact of Fe aeolian deposition on biogeochemical cycles has been studied in different HNLC regions by artificially fertilizing large (ca. 100 km^2) surfaces of the ocean (see reviews by de Barr et al. 2005; Boyd et al. 2007). Although primarily focused on the carbon cycle, several of these Ocean Iron Fertilisations (IOFs) reported increases in the concentration of the biogenic anti-greenhouse gas dimethylsulfide (DMS) following Fe addition (Turner et al. 2004). These earlier results suggested that Fe could potentially increase both carbon sequestration and DMS emissions with a cumulated cooling effect on climate. These IOFs are

considered valuable simulations of large sporadic aeolian Fe dust deposition events, but their relevance to non-aeolian Fe delivery processes such as mixing has been questioned (Boyd et al. 2007). Ecosystems and biogeochemical cycles may respond differently to short artificial pulses of Fe, as simulated by IOFs, as compared with continuous slow addition of Fe through natural autochthonous sources. For example, it was recently shown that natural Fe fertilization through mixing above the Kerguelen plateau in the Southern Ocean HNLC region has no stimulating effect on DMS concentrations in contrast to increases in DMS measured during the IOFs conducted in the same region (Bopp et al. 2008). However, natural Fe supply events are difficult to monitor and very few studies have examined their effects on ecosystems and biogeochemical cycles.

DMS is the most important biogenic sulfur compound emitted from the ocean into the atmosphere. Oceanic emissions of DMS influence the climate directly through their oxidation into sulfate aerosols by hydroxyl radicals (OH), and indirectly by the impact of sulfate aerosols on cloud condensation nuclei (CCN) formation with further effects on cloud albedo (Charlson et al. 1987; Andreae 1990). As a consequence, DMS emissions reduce the radiative flux to the Earth's surface (Charlson et al. 1987) with a resulting cooling effect of the climate. The oceanic production of DMS results from a suite of interrelated biotic processes involving most components of the food web, from viruses to zooplankton (review by Simó 2001). DMS is produced by the algal and bacterial cleavage of dimethylsulfoniopropionate (DMSP), an osmolyte found in different concentrations in a wide variety of phytoplankton groups (Keller et al. 1989). The composition of the plankton assemblage ultimately governs the production rate of DMSP, the release of algal DMSP into the water via exudation, grazing or viral attack, and the bacterial metabolism of DMSP and its biological transformation into DMS (Hill et al. 1998; Malin et al. 1998). Fe supply can influence several of these processes either directly through physiological responses, or indirectly through changes in biomass, community structure and dissolved organic

matter. The response of the ocean to Fe supply may thus vary widely depending on initial conditions.

The North Pacific is sporadically supplied with Fe during seasonal eastward dust transport from Asia (Moore et al. 2002; Han et al. 2008). These events often coincide with increases in surface biomass and biogenic material flux at depth (Young et al. 1991; Yuan and Zhang 2006), indicating the stimulating effect of Fe on primary production. Past studies have also identified Asian dust as the main source of Fe to the Alaskan Gyre (Moore et al. 2002; Moore and Braucher 2007). However, recent studies have shown that mixing and the offshore advection of eddies from the continental margin of the Gulf of Alaska (Johnson et al. 2005), two autochthonous supply mechanisms, also represent non-negligible sources of Fe (Hongo et al. 2005; Lam et al. 2006; Crawford et al. 2007; Cullen et al. 2007; Lam and Bishop 2008). In 2002, a large scale Fe fertilization was conducted around Ocean Station Papa (OSP) (50° N, 145° W; Subarctic Ecosystem Response to Iron Enrichment Study - SERIES) in order to explore the potential effect of Fe on the ecosystem and biogeochemical fluxes in the NE Pacific (Boyd et al. 2004). One of the unexpected results of this experiment was the decrease in DMS concentrations (Levasseur et al. 2006) in spite of strong stimulation of the growth of the DMSP producers. This response was attributed to a shift in the bacterial assimilation of DMSP-derived sulfur (DMSP-S) coinciding with a sharp increase in bacterial growth and sulfur demand resulting in little DMS production (Merzouk et al. 2006). Whether these results can be extrapolated to other modes of Fe supply such as mixing still needs to be determined.

The aim of this study was to assess the impact of natural Fe fertilization of the upper mixed layer in the NE Pacific on DMSP and DMS cycling, with a particular focus on the microbial metabolism of DMSP using radio-labelled ^{35}S-DMSP.

Materials and methods

Study area and sampling scheme

The study was conducted in the HNLC waters of the Gulf of Alaska in the NE Subarctic Pacific Ocean, a region that has been monitored over the last 50 years by various research vessels belonging to the Government of Canada, see Freeland (2007) for a review of the Line P cruise program.

From May 21 to June 19, 2007, water samples were collected aboard the CCGS *John P. Tully* at 11 stations located along the Line P Transect beginning at the southern tip of Vancouver Island (station P1) and ending at OSP (station P26, Figure 2.1). Water samples for nutrients and chlorophyll *a* (chl *a*) measurements were collected at 10 m using a General Oceanics rosette equipped with 10 L Niskin PVC bottles coupled to a CTD probe (conductivity, temperature, depth) system model SBE 11 plus (Seabird Electronics, Seattle, Washington, USA). For Total Dissolved Fe (TDFe), bacteria and DMSP/DMS measurements, water samples were collected at 10 m using trace metal clean techniques (Johnson et al. 2005) with a 10 L Go-Flo bottle (General Oceanics) at the two coastal stations and with a 12 L Niskin-X bottle (General Oceanics) at open ocean stations using a Kevlar line. Stations P1 (114 m) and P4 (1320 m) were located on the continental margin and on the continental slope, respectively. The other stations, P8 to P26, were located in the open ocean with a mean water depth of 3630 m.

Nutrients, chl a, and Fe analyses

Concentrations of nitrate + nitrite ($NO_3^- + NO_2^-$), silicic acid (H_4SiO_4) and phosphate (PO_4^{3-}) were determined on board with a Technicon AAII autoanalyzer following the

methods described in Barwell-Clarke and Whitney (1996). For chl *a* determination, 330 mL of seawater was filtered through a glass fiber 25 mm MFS GF-75 filter (nominal rating 0.3μm) at < 70 mm Hg vacuum, the pigments collected on the filter were extracted with 90 % acetone, and quantified with a Turner 10 AU fluorometer as described in Strickland and Parsons (1972). For TDFe, water was collected in 125 mL low density polyethylene bottles and then acidified with 1.0 mL of 6 M ultra pure hydrochloric acid (HCl; 1:1 Seastar Baseline) per 125 mL, to get a final concentration of 0.05 M HCl (pH 1.6). The samples were stored for approximately 3 months prior to subsequent analysis following the Obata et al. (1993, 1997) analytical method.

In the laboratory, Fe samples were processed in a clean tent with high efficiency particulate air filter providing positive pressure. The samples were prepared for analysis by adding 600 μL NH_4OH per 125 mL sample to neutralize at pH 1.5 and then increased back for analysis at pH 3.2 by adding pH 3.2 Ammonium formate buffer (625 μL per 125 mL sample). Samples were delivered to the system using an 8-port valve (Hamilton MVP 8) and a peristaltic pump. Approximately 2 to 16 mL (0.5 – 4 minutes load time) were passed through an 8-hydroxyquinoline resin column and immobilized on silica gel at a flow rate of 4 mL min^{-1}. The iron was removed from the column using dilute HCL (0.3 M). The resulting eluent was then mixed with 0.74 mM luminol, 0.6 M aqueous ammonia (to give a final pH of approximately 9.5), and 0.7 M hydrogen peroxide prior to entering the cell. A Hamamatsu photomultiplier tube measured the light emitted by the chemiluminescent reaction of the iron and the luminol as the eluent passed through the cell, resulting signal was recorded on a computer. Standards were made by diluting commercial atomic absorption standards down to 10-100 ppb using 0.05 M Seastar double-distilled HCl. These working standards were added to low-iron open ocean seawater prepared just prior each analysis (i.e. 114 mL of a 100 ppb standard in 250 mL seawater gives a 0.8 nM iron standard). A set of standards was run at the beginning and at the end of each set of samples. The curve was non-linear, and therefore a quadratic equation was

used to describe the curve and calculate sample concentrations. The data were blank-corrected using low iron seawater that was loaded for a brief period of 5 s.

Heterotrophic bacterial abundance and Card-FISH identification

Water samples for bacterioplankton abundance and identification were preserved 24 hours at 4°C with borate-buffered formaldehyde (2 % final concentration), filtered onto 0.2 μm pore size, 25 mm diameter polycarbonate membranes, and frozen at -20°C until analysis. Cell identification for specific prokaryotic groups was made by fluorescence *in situ* hybridization (FISH) using horseradish peroxidase (HRP) labeled oligonucleotide probes (www.biomers.net.) combined with signal amplification by tyramide labeled with carboxyfluorescein. This catalyzed reporter deposition (Card) approach has the advantage of providing enhanced fluorescence intensities (Pernthaler et al. 2002) compared to the standard FISH assay. Sections were cut from each filter and hybridized with the HRP probes specific to Bacteria (Eub338) and 3 major phylogenetic lineages of this latter domain: beta (β; Bet42a), gamma subclasses of the Proteobacteria (γ; Gam42a) and the Roseobacter clade (Ros536), a clade within alpha proteobacteria.

Bacterial abundance and identification following DAPI staining (Porter and Feig 1980) and Card-FISH (Pernthaler et al. 2002) procedures were then determined with an epifluorescence microscope. A minimum of 400 and 100 positive cells per field for DAPI staining and Card-FISH technique respectively were counted in a minimum of 10 fields per sample.

DMSP and DMS concentration analysis

DMSP is found in two major operational pools in seawater, a filterable particulate fraction and a dissolved fraction, referred to as $DMSP_p$ and $DMSP_d$ respectively. Fractionation of DMSP within the particulate and dissolved phases was determined using the Small-Volume gravity Drip Filtration (SVDF) technique (Kiene and Slezak 2006). This technique reduces cell breakage and the release of DMSP from phytoplankton cells. Water was gently collected directly from the 10 L Go-Flo bottle or the 12 L Niskin-X bottle and poured into a polysulfone magnetic filter tower through a 47 mm Whatman GF/F filter (0.7 μm retention). For $DMSP_d$ determination, between 20-50 mL was allowed to fill the filter tower and 3.5 mL of filtrate was collected into a 15 mL sterile falcon tube in which 50 μL of 50 % H_2SO_4 was added to eliminate the DMS. For total DMSP ($DMSP_t$) determination ($DMSP_t = DMSP_p + DMSP_d$), an unfiltered volume of 3.5 mL was collected and 50 μL of 50 % H_2SO_4 was added. The DMSP samples were then stored at 4 °C for at least 24 h. After this reaction period, 25 mL serum bottles were filled with 21 mL of deionized water (milli-Q water), 3 mL of the stored filtrates, and 1 mL of 5 M NaOH. These bottles were then quickly sealed with a butyl stopper and aluminum crimp, leaving no headspace. All DMSP samples were stored at 4 °C in the dark and analyzed within 6 weeks. Sulfur gas analysis was performed using a purge and trap system coupled to a Varian 3800 gas chromatograph equipped with a pulsed flame photometric detector (PFPD). DMSP samples were calibrated with a 5 ng mL^{-1} DMSP standard prepared in 14 mL serum bottles containing 0.6 mL of KOH 10 M. The DMSP concentrations in seawater samples were determined by a comparison of a standard curve established with DMSP standard samples. The $DMSP_p$ was obtained by subtracting $DMSP_d$ from $DMSP_t$.

DMS concentrations were collected using completely filled 150 mL serum bottles and were subsequently analysed using a Hewlett-Packard 5880A gas chromatograph equipped with FPD and a Chromasil 330 column (Sulpelco 1-1496). Summarily, the samples were loaded onto the stripper and purged with ultra-high-purity nitrogen for 10 minutes at ~100 mL min^{-1}. The DMS was extracted from the water and absorbed onto a Tenax TA trap kept at -80°C. The trap was subsequently desorbed at 100°C onto the column which eluted into the FPD. Standards were run in the same manner as samples and were prepared in deionized water from a pure stock DMS solution and covered a linear range of 0.5 nM to 20 nM.

^{35}S-DMSP incubations for the determination of microbial DMSP cycling

For the determination of the microbial uptake and metabolism of DMSP, unfiltered seawater was collected at 10 m with ultra-clean techniques and transferred gently into 71 mL brown polyethylene bottles. The bottles were then processed in accordance with the method established by Kiene and Linn (2000a). Briefly, these samples were amended with ^{35}S-$DMSP_d$ at trace level (final concentration < 0.1 nM $DMSP_d$), shaken gently for an equal mixture and settled for 5 minutes. The total amount of added isotope was determined by pipetting 1 mL (out of the 71 mL volume) into a 20 mL scintillation vial containing 10 mL of scintillation cocktail (CytoScint). The remaining samples were then incubated in the dark for 3 hours at *in situ* water temperature and sub-sampled after 0, 30, 60, and 180 minutes of incubation. At each time point, the incubation bottles were gently shaken and 5 mL was pipetted into 120 mL serum vials containing 0.5 mL sodium dodecyl sulfate (SDS, 0.2 % final concentration) and 1 mL of $DMSP_d$ (100 µM final concentration). The addition of SDS and $DMSP_d$ stopped further bacterial uptake and metabolism of ^{35}S-$DMSP_d$ (Kiene and Linn 2000a). The serum bottles were sealed with a rubber stopper fitted with a plastic cup holding an H_2O_2 soaked filter (Gelman AE glass fiber) in the headspace.

Serum bottle samples were shaken for at least 6 hours during which volatile ^{35}S (i.e. ^{35}S-DMS and ^{35}S-methanethiol (MeSH)) degassed into the headspace and were oxidized on the H_2O_2 soaked filters. The filters were placed in 10 mL of scintillation cocktail and the radioactivity on the filters was measured with a scintillation counter to determine the amount of volatile ^{35}S produced from bacterial $DMSP_d$ degradation. A new H_2O_2-soaked filter was then placed in the plastic cup and the serum bottles were resealed. A 0.2 mL aliquot of NaOH 5 M was injected with a syringe into the remaining sample through the rubber septum to hydrolyze unreacted ^{35}S-$DMSP_d$ into ^{35}S-DMS. Samples were again shaken for at least 6 hours, after which the filters were removed and placed in 10 mL of scintillation cocktail and used to determine the amount of unconsumed ^{35}S-$DMSP_d$ at each time point. The amount of isotope in each sample was read on a RackBeta scintillation counter with a count time of 20 minutes per sample.

This incubation protocol allowed the determination of five parameters: 1) the microbial $DMSP_d$ loss rate constant (k_{DMSPd}), calculated as the slope of the ln-transformed activity of unconsumed ^{35}S-$DMSP_d$ during the 3 hour time course; 2) the microbial $DMSP_d$ consumption rate, calculated by multiplying the loss rate constant by the *in situ* concentration of $DMSP_d$; 3) the $DMSP_d$ turnover time ($1/k_{DMSPd}$); 4) the bacterial volatile ^{35}S yield, expressed as a percentage which was taken as the fraction of ^{35}S-$DMSP_d$ consumed by bacteria that was recovered as ^{35}S-DMS at the end of the 3 hour incubations; and 5) the bacterial DMSP-S assimilation efficiency, also expressed as a percentage, calculated as the proportion of ^{35}S-$DMSP_d$ consumed by bacteria and recovered into TCA-insoluble macromolecules. The bacterial volatile ^{35}S yield is mainly DMS, but small amount of the volatile MeSH could also be produced and persist during the 3 hour incubations (R. Kiene *pers. comm.*). Hence, we will use the term volatile ^{35}S yield instead of DMS yield in this manuscript.

Based on the recent discovery that some diatoms can take up and accumulate $DMSP_d$ (Vila-Costa et al. 2006), the $DMSP_d$ loss rate constant, consumption rates, and turnover rates as measured with this protocol are considered to be microbial (bacterioplankton and phytoplankton), while the volatile ^{35}S and DMSP-S assimilation efficiencies are assumed to be strictly bacterial.

Results

Oceanographic setting

The physical and biochemical characteristics of the water column during the study were typical of spring and summer conditions for the NE Subarctic Pacific. Temperature at 10 m depth was relatively uniform at 11.2 °C at the coastal stations (P1 and P4), and decreased more or less regularly towards the oceanic stations to reach 7.1 °C at P26 (Figure 2.2A). Salinity at 10 m depth was ca. 31.5 at P1 and P4, remained relatively uniform at 32.4 from P8 to P16, and then gradually increased to reach 32.6 at P26 (Figure 2.2A). The temperature/salinity (T/S) diagram (Figure 2.3) indicates the presence of three water masses at 10 m: a coastal water mass characterized by low salinity and high temperature (P1 and P4), the Alaskan Gyre water mass characterized by high salinity and low temperature (P18 to P26), and a transition zone from P8 to P16 characterized by salinity slightly lower than the Alaskan Gyre (32.4) and warmer temperatures (9-11 °C) representative of the mixing between NE Subarctic Pacific HNLC waters and Alaskan current waters.

The three water masses exhibited distinct macro- and micronutrients signatures. $NO_3^- + NO_2^-$, H_4SiO_4 and PO_4^{3-} concentrations were high at P1 (8.9, 22.7 and 1.0 μM, respectively) and reached extreme minima at P4 ($NO_3^- + NO_2^-$: 0.1 μM; H_4SiO_4: 2.1 μM; PO_4^{3-}: 0.27 μM; Figure 2.2B). $NO_3^- + NO_2^-$, H_4SiO_4) and PO_4^{3-} concentrations were relatively high at P8 (5.8, 9.4 and 0.91 μM, respectively) and then increased between P8 and P26 (Figure 2.2B). TDFe concentrations were maximum at stations P1 and P4 with a mean value of 3.41 nM, decreased sharply to 1.78 nM at station P8, remained close to 1 nM from stations P14 to P18, and exhibited values below 0.79 nM for the rest of the transect (Figure 2.2C). Between P8

and P26, TDFe concentrations decreased linearly with water density (σt: data not shown). There is no TDFe value at P12 due to contamination during the sampling.

Chl *a* concentrations were maximal (8.4 μg L^{-1}) at P1, decreased sharply to 1.6 μg L^{-1} at P4, and remained below 0.5 μg L^{-1} for the rest of the transect (Figure 2.2D). Bacterial abundance (estimated with DAPI) was high at P1 (2.1 x 10^9 cells L^{-1}) and P4 (3.9 x 10^9 cells L^{-1}), decreased gradually between P8 and P18, and remained below 0.7 x 10^9 cells L^{-1} for the rest of the transect (Figure 2.2D).

Heterotrophic bacterial community composition

The abundance of bacteria detected with the general eubacterial probe (Eub338; Figure 2.4) followed the same general pattern as total bacterial abundance (Figure 2.6) with maxima close to the coast (P1: 0.65 x 10^9 cells L^{-1} and P4: 2.1 x 10^9 cells L^{-1}) and minima in the open ocean (mean of 0.24 x 10^9 cells L^{-1}) (Figure 2.4). The abundance of the Roseobacter clade (Ros536 probe) was maximum close to the coast with a peak at P4 (4.4 x 10^8 cells L^{-1}) and decreased to lower values at the offshore stations (mean of 8.3 x 10^7 cells L^{-1}). The abundance of Gammaproteobacteria (Gam42a probe) was variable along the transect with maxima at P4 and P16 (2.1 x 10^8 cells L^{-1} and 2.7 x 10^8 cells L^{-1} respectively) and concentrations lower than 2.0 x 10^8 cells L^{-1} for the rest of the transect. Betaproteobacteria (Bet42a probe) abundance ranged from 7.1 x 10^6 cells L^{-1} to 7.1 x 10^7 cells L^{-1} with a similar pattern to the abundance of the Roseobacter clade.

Concentrations of dimethylated sulfur compounds

Concentrations of $DMSP_p$ exhibited a regular inshore-offshore decline with maximum and mininum concentrations of 102.1 nM and 17.8 nM measured at P1 and

P26, respectively (Figure 2.5A). $DMSP_p$: chl *a* ratios showed a different pattern, with values below 30 nmol μg^{-1} at the coastal stations (P1 and P4), a peak value of 171 nmol μg^{-1} at P8, followed by a gradual decrease towards the offshore stations (Figure 2.5A). $DMSP_d$ concentrations ranged between 1.3 nM and 3.6 nM with no consistent pattern related to the $DMSP_p$ pool or the different water masses described above (Figure 2.5B). DMS concentrations exhibited considerable variations, with peak values of 4.4 nM and 3.6 nM measured at P8 and P22, respectively, and a minimum of 1.1 nM at P14 (Figure 2.5C). DMS concentrations showed no correlation with the particulate and dissolved DMSP pools. DMS concentrations normalized to chl *a* (DMS : chl *a* ratio, see Table 1) exhibited a mean of 0.9 ± 0.9 nmol μg^{-1} for stations P1 and P4, and of 6.2 ± 3.8 nmol μg^{-1} for the rest of the transect (P8-P26).

DMS(P) microbial metabolism

Microbial $DMSP_d$ consumption rates closely followed the variations in bacterial abundance (Figures 2.6A and 7; $r^2 = 0.85$). Rates were high near the coast with values of 26.3 nmol L^{-1} d^{-1} at P1 and 58.0 nmol L^{-1} d^{-1} at P4, and lower offshore with an average of 8.6 nmol L^{-1} d^{-1} from P8 to P26 (Figure 2.6A, Table 1). Accordingly, the microbial turnover time of the $DMSP_d$ pool ranged from a rapid 1.3 h at P4 to a much longer 11.9 h at P26 (Figure 2.6B). The volatile ^{35}S yields, our estimate of the DMS yields, ranged between 3 % and 13 % along the transect, with values higher in the HNLC region (8 ± 2 %) and lower at the two coastal stations (4 ± 2 %) (Figure 2.6C, Table 1). The bacterial DMSP-S assimilation efficiency, which represents the proportion of ^{35}S-DMSP assimilated into macromolecules, was 26 ± 4 % at the Fe-rich coastal stations and 14 ± 7 % at the offshore stations (Figure 2.6C, Table 1).

Discussion

The physical, chemical and biological conditions during our study were typical of the NE Subarctic Pacific during springtime (Crawford et al. 2007; Peña and Varela 2007). The general inshore-offshore decrease in near-surface temperature, and increase in salinity along the transect are common features of this region at this time of the year. The low salinity at the coastal stations reflects freshwater supply from land. As expected, inshore waters were Fe-rich and exhibited moderate (1.6 $\mu g\ L^{-1}$) to high (8.4 $\mu g\ L^{-1}$) chl *a* concentrations. Macronutrient concentrations were high at P1 but were almost exhausted at P4, a condition previously reported (Sherry et al. 2002) for this station at this time of the year and reflecting a declining phytoplankton bloom (Boyd and Harrison 1999). Salinity increased steeply from P4 to P8 to reach values more typical of the Alaskan Current and Gyre. TDFe concentrations were ca. 1.8 nM in this warm water mass, and gradually decreased thereafter to reach a minimum of 0.9 nM at P18, a value closer to the expected concentrations in the HNLC waters of the Gulf of Alaska. In spite of the relatively high TDFe concentration at P8 (1.78 nM), phytoplankton biomass was low and macronutrient concentrations high at this station, consistent with HNLC conditions. Phytoplankton biomass and macronutrient concentrations remained respectively low and high for the rest of the transect, indicating HNLC conditions (Harrison et al. 1999).

Based on these physical, chemical and biological properties, stations along the transect were subdivided into two categories exhibiting distinct Fe levels and supply mode: the Fe-rich coastal waters (P1 and P4) where TDFe concentrations were high and primarily delivered through riverine input, and the HNLC waters (P8 to P26) with waters from the Alaskan Gyre and the transition zone where TDFe concentrations were generally low and primarily delivered through mixing. As we will discuss next, these different Fe regimes exerted an important influence on

biological processes within the microbial food web which in turn shaped the microbial cycling of the dimethylated sulfur compounds.

Microbial DMSP/DMS cycling: Fe-rich coastal waters versus HNLC waters

Variations in Fe availability along the transect influenced the abundance and composition of the phytoplankton assemblage which in turn directly affected the size of the $DMSP_p$ pool. Maximal concentrations of $DMSP_p$ were detected in the Fe-rich coastal stations (mean of 82 ± 29 nM) whereas the lowest values were from the HNLC stations (mean of 31 ± 11 nM) (Table 1). Few $DMSP_p$ measurements have been reported so far from the open waters of the NE Pacific, and none in coastal waters. The only data available are from the July 2002 SERIES experiment where Levasseur et al. (2006) estimated $DMSP_p$ concentrations between 5 and 75 nM around P26 outside the Fe-enriched patch. In the present study, $DMSP_p$ levels varied between 17 and 51 nM in the HNLC waters, suggesting that similar conditions prevailed during the two studies. The impact of Fe availability on the distribution of $DMSP_p$ could be seen across the transect, irrespective of supply mode (riverine versus mixing) and type of phytoplankton assemblage (coastal versus oceanic). Indeed, our results show a significant positive relationship between $DMSP_p$ concentrations and TDFe concentrations when all stations (except for P12 due to contamination) were pooled (Figure 2.8; $r^2 = 0.74$, $p < 0.01$). This relationship reflects the stimulating effect of Fe on total phytoplankton biomass and, as discussed below, the biomass-specific algal DMSP synthesis.

In addition to the effect of Fe on the size of the $DMSP_p$ reservoir, TDFe availability also affected the structure of the plankton assemblage with resulting changes in DMSP concentrations per unit of chl *a* (Figure 2.5A). The Fe-rich coastal waters exhibited a mean $DMSP_p$: chl *a* ratio of 26 ± 19 nmol μg^{-1}, while waters from the HNLC portion of the transect displayed an average value of 84 ± 36 nmol μg^{-1}

(Table 1). The difference in the ratio between the two regions was consistent with contrasting phytoplankton communities dominated by species with different $DMSP_p$ quotas. Low ratios measured at the coastal biomass-rich stations reflect the dominance of DMSP-poor diatoms in these waters (data not shown; Keller et al. 1989; Boyd et al. 1996; Boyd and Harrison 1999) and a similarly low ratio was reported in the NE Atlantic during the spring diatom bloom (33 ± 18 nmol μg^{-1}; Andreae et al. 2003). In contrast, the high ratios in the Fe-poor offshore waters reflect the dominance of Prymnesiophytes (data not shown). As observed during this study, the phytoplankton assemblage around OSP (P26) is generally dominated by the Prymnesiophyceae *Emiliania huxleyi* and *Phaeocystis* spp. (Boyd and Harrison 1999; Levasseur et al. 2006), two strong DMSP producers (Keller et al. 1989). The dominance of these small algal cells is attributed to their capacity to compete under low Fe conditions due to their high surface-to-volume ratios and their ability to implement low Fe-demand metabolic pathways (Martin et al. 1989; Sunda et al. 1991; Sunda and Huntsman 1997). Low Fe availability may thus favour the development of strong DMSP producers (Malin and Kirst 1997) hence explaining the higher ratios of $DMSP_p$: chl *a* observed in the Fe-poor offshore waters (Figure 2.5A).

In spite of the large variations in the size of the $DMSP_p$ pool, concentrations of $DMSP_d$ remained low and relatively uniform along the transect reflecting the labile nature and rapid bacterial turnover rate of this compound. Average concentrations of $DMSP_d$ in Fe-rich waters and HNLC waters were similar with means of 3.1 ± 0.7 nM and 2.1 ± 0.6 nM, respectively (Figure 2.5B; Table 1). These concentrations were within the range previously reported by Kiene and Slezak (2006) in contrasting oceanic environments using the SVDF technique (from 0.4 to 2.8 nM). Our results suggest that low $DMSP_d$ (< 3 nM) may be typical of oceanic conditions (Kiene and Slezak 2006), irrespective of the size of the $DMSP_p$ reservoir and Fe availability. Our estimates of the concentrations and turnover rates of $DMSP_d$ along the transect provided further evidence of the importance of this substrate for a broad spectrum of

bacterial clades (Kiene and Linn 2000a; Malmstrom et al. 2004). Microbial consumption of $DMSP_d$ varied by a factor of 14 (from 4 to 58 nmol L^{-1} d^{-1}), closely following the bacterial abundance ($r^2 = 0.85$, $p < 0.01$; Figures. 2.6A and 2.7). $DMSP_d$ consumption was also strongly correlated with Eubacteria, that are known to be mainly heterotrophic bacteria ($r^2 = 0.83$, $p < 0.01$; results not shown). The highest microbial $DMSP_d$ consumption rates were measured in the Fe-rich coastal waters (mean of 42 ± 22 nmol L^{-1} d^{-1}), and the lowest rates in the HNLC waters (mean of 9 ± 5 nmol L^{-1} d^{-1}) (Table 1). These mean values were comparable as those reported for the biomass-rich coastal waters of the Gulf of Mexico (39 nmol L^{-1} d^{-1}) and for the oligotrophic waters of the Sargasso Sea (3.8 nmol L^{-1} d^{-1}; Kiene et al. 2000).

Due to the relative stability of the $DMSP_d$ pool size, the changes in microbial $DMSP_d$ consumption rates were accompanied by similar changes in $DMSP_d$ turnover times, with faster turnover times estimated at the Fe-rich coastal stations (mean of 2.5 ± 1.7 h) and slower ones at the Fe-poor stations (mean of 7.7 ± 3.0 h) (Figure 2.6B; Table 1). The mean $DMSP_d$ turnover times measured during this study for the two regions (inshore versus offshore) were remarkably similar to values reported from environments with similar biological productivities. For example, Kiene and Linn (2000a) reported $DMSP_d$ turnover times of 3 h in shelf waters and of 10 h in oceanic waters, while Malmstrom et al. (2004) and Zubkov et al. (2002) measured $DMSP_d$ turnover times of 11-28 h and 9.6 h for the Sargasso Sea and the North Sea, respectively. These results confirm the importance of $DMSP_d$ as a substrate for bacteria and, when considering the full transect which encompasses the two Fe regimes, suggest that bacterial $DMSP_d$ consumption was generally not limited by $DMSP_d$ availability.

In addition to the differences in $DMSP_d$ consumption rates mentioned above, the dominant metabolic pathway of DMSP also differed between the coastal and HNLC waters. The proportion of $DMSP_d$ consumed by bacteria cleaved into DMS (volatile

^{35}S yield, see Table 1) was twice as high in the HNLC waters (8 ± 2 %) than in the Fe-rich coastal waters (4 ± 2 %). The range of volatile ^{35}S yields along the transect (3-14 %, Figure 2.6C) was comparable to the range of values (2-21 %) reported earlier in a study of coastal, shelf and oceanic waters (Kiene and Linn 2000b), as well as with the range of values (7-13 %) reported for an HNLC region of the North West (NW) Subarctic Pacific (Lizotte et al., in press). Our results agree with mounting evidence suggesting that most of the $DMSP_d$ consumed by the microbial community (> 86 % in our study) is processed through the demethylation pathway without the formation of DMS (Kiene and Linn 2000b). The bacterial DMSP-S assimilation efficiency showed an inverse pattern to the one observed for volatile ^{35}S yield, with values higher in the Fe-rich coastal waters (26 ± 4 %) than in the HNLC waters (14 ± 7 %). In Fe-poor waters where the production of labile dissolved carbon by phytoplankton is thought to be weak (Kirchman 1990), bacteria are generally limited by the availability of organic carbon. Hale et al. (2006) demonstrated that this condition prevailed around OSP during the SERIES experiment in Fe-poor waters. In these conditions, bacteria may use DMSP mostly as a carbon source through the cleavage pathway, which would lead to higher volatile ^{35}S yields. DMSP-S assimilation efficiency increased sharply as bacterial abundance increased and reached a maximum value of ca. 25 % when bacterial abundance exceeded ca. 1.5×10^9 cells L^{-1} (Figure 2.6C). These results indicate that the higher bacterial abundance in the Fe-rich coastal waters led to a greater fraction of DMSP-S being assimilated into bacterial proteins and a lower fraction being lost as DMS. Conversely, our results suggest that bacterial communities in Fe-limited HNLC waters exhibited a lower S demand leading to lower assimilation of DMSP-S and higher volatile ^{35}S yield. These results agree with the findings of Lizotte et al. (in press) who observed an increase in bacterial DMSP-S assimilation efficiency following Fe-induced increases in bacterial abundance and productivity during the Fe-enrichment experiment SEEDS II in the NW Subarctic Pacific. Furthermore a similar pattern has been reported by Kiene and Linn (2000b) where highest bacterial DMSP-S assimilation into macromolecules occurred in coastal waters (mean of

44 ± 21 %) while lower DMSP-S assimilation efficiencies were observed in oceanic waters (mean of 12 ± 7 %).

Concentrations of DMS varied between 1.1 and 4.4 nM along the transect with no obvious effect of the supply of Fe. The mean DMS concentrations (2.4 ± 0.1 nM and 2.2 ± 1.2 nM) were similar in the Fe-rich and the Fe-poor waters respectively (Table 1). These similar results are not unexpected given the numerous and diverse abiotic and biotic factors controlling the concentrations of DMS in surface waters (see review by Simó 2001). There are few values of DMS concentrations reported for this region at this time of year. Wong et al. (2005) reported DMS concentrations of ca. 3 nM at P20 and ca. 2 nM at P26 which are similar to values in our study at the same site (2.9 nM at P20, and 1.5 nM at P26). In July 2002, Levasseur et al. (2006) measured DMS concentrations as high as 15 nM around P26, indicating that DMS could accumulate in the water column under certain conditions. However, as was observed for $DMSP_p$, concentrations of DMS normalized to chl *a* (DMS : chl *a* ratio, see Table 1) were divergent for Fe-rich coastal waters and Fe-poor offshore waters with means of 0.9 ± 0.9 nmol μg^{-1} and 6.2 ± 3.8 nmol μg^{-1}, respectively. The dominance of DMSP-rich phytoplankton groups within the HNLC waters, as discussed earlier, seems to enhance the biomass-specific capacity of the plankton community to produce DMS.

The differences in DMSP microbial metabolic pathway evidenced between the two regions further suggest the existence of different sulfur cycling systems in these contrasting environments characterised by different algal community structure and productivity, labile carbon availability and bacterial biomass and growth.

Impact of Fe availability on DMSP/DMS microbial cycling within HNLC waters

The offshore region of the transect (P8 to P26) was physically characterized by the gradual mixing of the relatively Fe-rich warm water mass found at P8 with the Fe-impoverished waters from the Alaskan Gyre (Figures. 2.2A and 2.3). As a consequence, TDFe concentrations of 1.8 nM at P8, decreased to 0.9 nM between P8 and P18 due to mixing, and remained fairly low and uniform further offshore (0.7 to 1.1 nM).

$DMSP_p$ concentrations increased linearly with TDFe concentrations from stations P8 to P26 within the HNLC region (Figure. 2.9A; $r^2 = 0.79$; $p < 0.01$). In contrast, the Fe addition had no effect on chl *a* concentrations in this portion of the transect and, consequently, the $DMSP_p$: chl *a* ratios increased linearly with TDFe concentrations ($r^2 = 0.86$; $p < 0.01$; Figure 2.9B). Since concentrations of chl *a* did not increase with TDFe, this relationship suggests that Fe stimulated the synthesis of DMSP by the DMSP-rich algal assemblage thriving at these low Fe offshore stations. These results suggest that the high $DMSP_p$: chl *a* ratios characterizing the planktonic assemblage in the HNLC region reflected the abundance of strong DMSP producers but that their DMSP quota was still limited by the availability of Fe. This explanation is not consistent with the current consensus that high $DMSP_p$: chl *a* ratios reflect the Fe-stressed conditions of the phytoplankton assemblages. If this was the case, relieving Fe limitation should have resulted in a decrease in the $DMSP_p$: chl *a* ratio. The increase of the DMSP:chl *a* ratio with Fe that we found could also reflect an accumulation of DMSP in the micrograzers community, which may contain up to 73 % of the particulate DMSP pool in the Alaskan Gyre (Levasseur et al. 2006). Finally, the absence of trend of chl *a* with Fe in this region suggests that diatoms did not respond to Fe, or that grazers kept the diatom population low, thus preventing a decrease in the $DMSP_p$: chl *a* ratio.

The Fe fertilization observed at our Fe-poor offshore stations also influenced the activity of the bacterial community. At those stations, the increase in bacterial abundance did not lead to an increase in microbial $DMSP_d$ consumption, suggesting the presence and use of other substrates by the community. However, the metabolism of the $DMSP_d$ taken up by bacteria and its conversion into DMS was affected by TDFe availability and volatile ^{35}S yields increased linearly with TDFe in this portion of the transect (Figure 2.9C). These results show that within the HNLC waters, the stimulation of the DMSP producers by TDFe led to a more efficient bacterial cleavage of $DMSP_d$ into DMS. This finding contrasts with results from Lizotte et al. (in press) who observed a long-term (> 10 days) decrease in volatile ^{35}S yields following the stimulation of $DMSP_p$-poor phytoplankton during the Fe-experiment SEEDS II in the NW Subarctic Pacific. Our interpretation is reinforced by the strong positive relationship found between the DMS bacterial yields and the $DMSP_p$: chl *a* ratio in this region ($r^2 = 0.83$, $p < 0.01$, Figure 2.10). Thus, the bacterial uptake of $DMSP_d$ remained uniform while its importance as a carbon source increased, resulting in a higher volatile ^{35}S yield.

The response of the Alaskan Gyre phytoplankton assemblage to natural Fe fertilization was similar to the responses reported over the first days of most large scale Fe fertilization experiments where rapid increases in $DMSP_p$ due to a stimulation of the Prymnesiophyceae were observed (Turner et al. 2004; Levasseur et al. 2006). Our results show that this Fe-induced stimulation of DMSP production is not specific to single concentrated Fe pulses but may be generated by other modes of Fe supply. The higher volatile ^{35}S yields observed at high TDFe stations within the HNLC waters during our study was not observed during the IOFs SERIES (Merzouk et al. 2006) and SEEDS II (Lizotte et al., in press), indicating that different modes of Fe delivery may generate specific responses in term of DMS net production.

Summary and conclusions

The Line P transect in the NE Subarctic Pacific offered a unique opportunity to study DMSP/DMS microbial cycling over a range of changing environmental conditions, from Fe-rich coastal waters seasonally nitrogen-depleted and influenced by coastal hydrodynamics to Fe-poor offshore waters where macronutrients are plentiful and primary productivity is limited by the availability of Fe.

Two major systems characterized by different Fe supply rates were sampled along the transect: the permanently Fe-rich coastal waters and the occasionally Fe-poor HNLC offshore waters. Characteristic conditions of DMSP and DMS microbial dynamics were observed in each regime. The coastal stations were dominated by high phytoplankton biomass and $DMSP_p$ concentrations, but with a low $DMSP_p$: chl *a* ratio reflecting the dominance of weak DMSP producers such as diatoms. By contrast, the offshore stations were characterized by low phytoplankton biomass, low $DMSP_p$ concentrations, but a high $DMSP_p$: chl *a* ratio reflecting the prevalence of a community dominated by DMSP-rich Prymnesiophyceae as previously reported in the same region (Levasseur et al. 2006). Bacterial abundances also differed in the two regions with the biomass-rich coastal waters having higher bacterial concentrations. The differences in TDFe availability and biomass were accompanied by substantial variations in DMSP/DMS pool size and microbial cycling.

Microbial $DMSP_d$ consumption closely followed the abundance of bacteria along the transect, reflecting the importance of this substrate for most bacteria. However, the dominant metabolic pathway of the DMSP uptake by the microbial community differed between the two regimes, with a lower fraction of the DMSP-S being assimilated and a larger fraction ending up as DMS (higher volatile ^{35}S yield) in the HNLC waters compared to the coastal stations. This particular metabolic pattern

suggests a preferential use of DMSP as a carbon source rather than as a sulfur source under HNLC conditions, probably resulting from the carbon-limited status of the bacteria in this system. In contrast, bacteria used DMSP mostly as a sulfur source in the biomass-rich coastal waters where labile dissolved organic carbon is probably plentiful.

Our work offered a rare opportunity to assess the impact of a natural addition of Fe within an HNLC region. As our sampling progressed from the coast toward the center of the Alaskan Gyre, we measured a gradual decrease in Fe levels due to mixing while other biochemical parameters were still reflecting HNLC conditions. This natural Fe gradient was accompanied by increases in DMSP concentrations and $DMSP_p$: chl *a* ratios showing a stimulation of the DMSP producers and possibly an accumulation of DMSP into microzooplankton. Bacteria were also affected by these natural Fe inputs, exhibiting an increase of their efficiency to convert DMSP into DMS. Together, these results suggest that natural input of Fe in the NE Subarctic Pacific HNLC waters initially stimulates the production of DMSP and improves its bacterial conversion into DMS with an overall potential stimulation effect on DMS ventilation. The increase in $DMSP_p$ measured during this study and most large scale Fe fertilization experiments, including SERIES, suggests that the stimulation of the DMSP dynamics will take place whatever the Fe supply mode: atmospheric dust deposition or vertical mixing.

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Chapitre 3 : Conclusion

Le fer limite la production primaire dans plus de 25 % des océans. L'impact des limitations en fer sur les écosystèmes planctoniques a été caractérisé grâce à douze expériences d'enrichissement artificiel en fer réalisées dans les différentes régions HNLC de l'océan global (Boyd et al. 2007). Ces expériences à grande échelle représentent une simulation réaliste des évènements sporadiques de dépôts de poussières éoliennes qui enrichissent les régions limitées en fer. Toutefois, leur capacité à reproduire l'approvisionnement en fer par d'autres mécanismes dont le mélange vertical est mise en doute. L'objectif de ce mémoire était d'élucider l'impact d'un gradient naturel en fer lié au mélange sur la dynamique microbienne du DMSP/DMS dans le Pacifique subarctique nord-est. Les résultats de ce mémoire montrent pour la première fois qu'une plus grande disponibilité du fer par mélange dans les régions HNLC pourrait stimuler la croissance des producteurs phytoplanctoniques riches en $DMSP_p$ et augmenter le rendement bactérien en DMS. L'ensemble de ces résultats suggère que les apports en fer par mélange peuvent contribuer à refroidir le climat dans cette région océanique.

Deux systèmes hydrodynamiques caractérisés par des conditions physicochimiques et des sources d'approvisionnement en fer distinctes ont été échantillonnés lors de mon étude : les eaux côtières riches en fer et les eaux de la gyre et du courant d'Alaska pauvres en fer (HNLC). Les caractéristiques physicochimiques propres à ces deux systèmes ont exercé une influence importante sur les processus biologiques et sur le cycle microbien du DMSP.

Tel qu'attendu, les stations côtières riches en fer étaient caractérisées par une forte biomasse phytoplanctonique ainsi que des concentrations en $DMSP_p$ élevées. Ces eaux exhibaient cependant des ratios $DMSP_p$: chl *a* faibles, suggérant la dominance

de diatomées pauvres en DMSP. Inversement, les stations échantillonnées en eaux HNLC étaient caractérisées par une biomasse phytoplanctonique et des concentrations en $DMSP_p$ faibles, mais un ratio $DMSP_p$: chl *a* élevé, reflétant une communauté phytoplanctonique riche en $DMSP_p$. Les deux grandes régions étaient aussi caractérisées par des abondances bactériennes distinctes : élevées dans les eaux côtières riches en fer et faibles dans les eaux HNLC. Mes mesures du métabolisme bactérien du DMSP ont permis de déterminer l'impact du fer sur la composante microbienne du cycle du DMS. La consommation microbienne du $DMSP_d$ variait d'un facteur 14 entre les deux systèmes, suivant de près l'abondance bactérienne, indiquant l'importance de ce substrat pour la communauté bactérienne. Les changements dans la consommation microbienne du $DMSP_d$ étaient accompagnés par des variations similaires des taux de recyclage bactérien du $DMSP_d$ avec des taux rapides en eaux côtières et des taux plus lents en conditions HNLC. Finalement, la proportion de DMSP consommé par les bactéries et clivé en DMS était deux fois plus élevée en milieu limité en fer qu'en milieu riche en fer. La dominance de la voie métabolique par clivage enzymatique en conditions HNLC suggère une limitation en carbone des bactéries. Au contraire, les bactéries utilisaient le DMSP principalement comme source de soufre dans les eaux côtières riche en fer où le carbone organique dissout est probablement abondant. Ces métabolismes bactériens distincts entre les deux régions montrent que le rendement bactérien en DMS est influencé par la composition spécifique de l'assemblage phytoplanctonique qui est elle-même influencée par la disponibilité du fer.

Mon étude a permis pour la première fois l'évaluation de l'impact d'un approvisionnement naturel en fer sur le cycle du DMSP/DMS dans une région HNLC. Mes résultats démontrent qu'une augmentation de la disponibilité en fer en marge de la gyre d'Alaska peut être accompagnée d'une stimulation de la croissance des producteurs de DMSP se traduisant par une augmentation des concentrations en $DMSP_p$ et du ratio $DMSP_p$: chl *a*. De plus, mes résultats montrent que ces apports en fer peuvent également résulter en une augmentation des taux de conversion

bactérienne du DMSP en DMS. L'ensemble de ces résultats suggère qu'un enrichissement naturel en fer dans la région HNLC du Pacifique subarctique nord-est résultera en une stimulation de la production phytoplanctonique de DMSP et de sa conversion bactérienne en DMS. L'effet stimulant du fer sur la production de DMSP (et le rapport DMSP : chl *a*) observé lors de mon étude et de l'expérience SERIES suggère que la stimulation du cycle du DMSP/DMS prendra place indépendamment du mode d'approvisionnement : déposition de poussières atmosphériques ou mélange vertical.

Dans ce contexte, des expériences futures menées dans les différentes régions HNLC mesurant l'impact d'enrichissement naturel en fer par mélange permettraient d'évaluer l'influence des modes d'approvisionnement sur la dynamique microbienne du DMSP. Ces études, jumelées aux expériences d'enrichissement artificiel passées, permettraient d'estimer de façon plus précise l'influence des différents modes d'approvisionnement en fer sur la dynamique du DMSP/DMS et sur le climat.

Oceanographic variables measured	Fe-rich coastal waters		Fe-poor offshore waters	
	mean n = 2	stdev	mean n = 9	stdev
$DMSP_p$ (nM)	82	29	31	11
$DMSP_d$ (nM)	3.1	0.7	2.1	0.6
DMS (nM)	2.4	0.1	2.2	1.2
$DMSP_p$:chl *a* ratio (nmol μg^{-1})	26	19	84	36
DMS:chl *a* ratio (nmol μg^{-1})	0.9	0.9	6.2	3.8
Microbial $DMSP_d$ consumption rate (nM d^{-1})	42	22	8.6	5.1
Bacterial $DMSP_d$ turnover time (h)	2.5	1.7	7.7	3.0
DMSP-S assimilation efficiency (%)	26	4	14	7
Volatile ^{35}S yield (%)	4	2	8	2

Table 2.1. Means and standard deviations for different variables measured in Fe-rich coastal waters (2 stations) and Fe-poor offshore waters (9 stations) along Line P within the NE Subarctic Pacific Ocean.

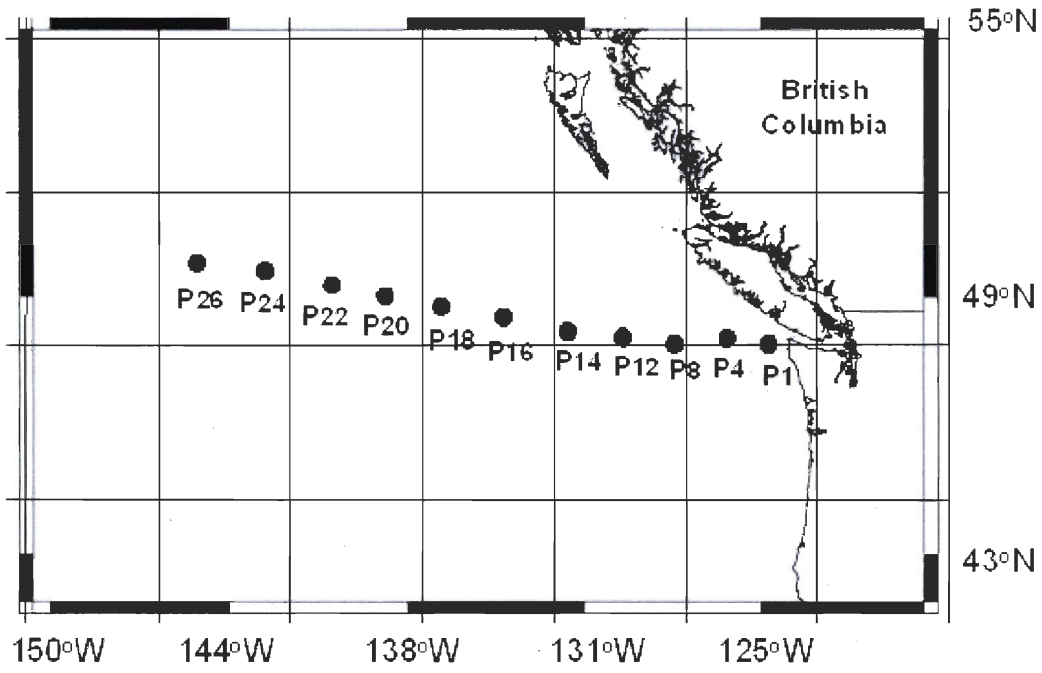

Figure 2.1: Study site showing the 11 stations investigated along a transect (Line P) in the NE Subarctic Pacific Ocean. Station P26 is Ocean Station Papa. The cruise took place from May 21 to June 19, 2007.

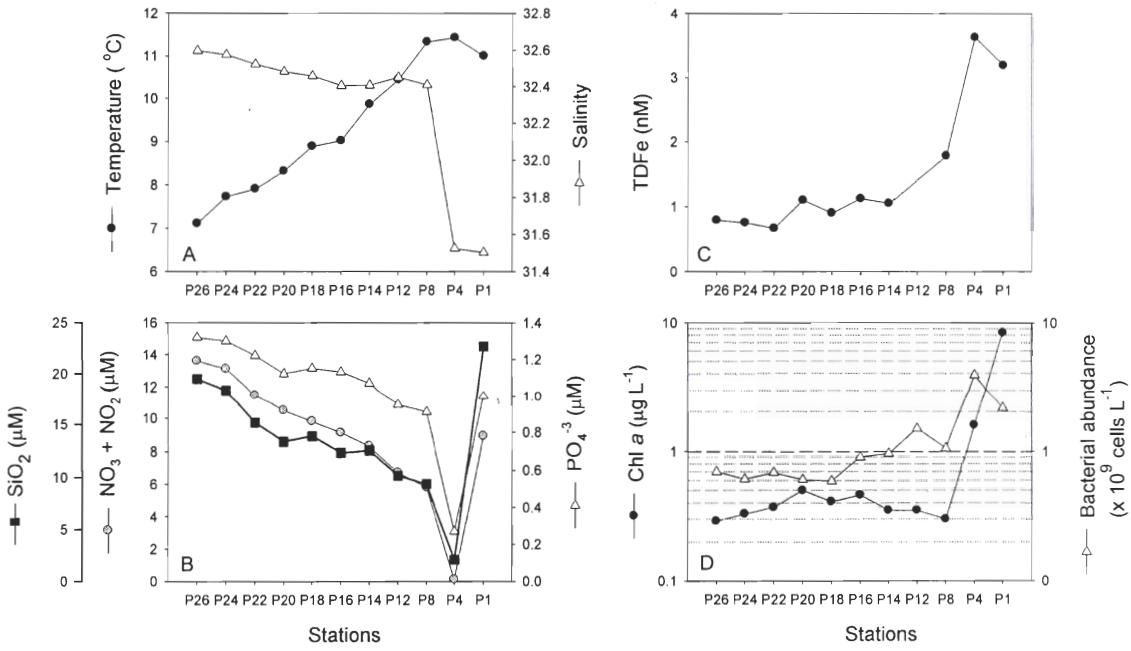

Figure 2.2: Spatial variations in (A) temperature and salinity; (B) macronutrient concentrations; (C) TDFe concentrations (station P12 is missing due to contamination); and (D) chlorophyll *a* concentrations and bacterial abundance along a transect in the NE Subarctic Pacific Ocean. Please note the log scale.

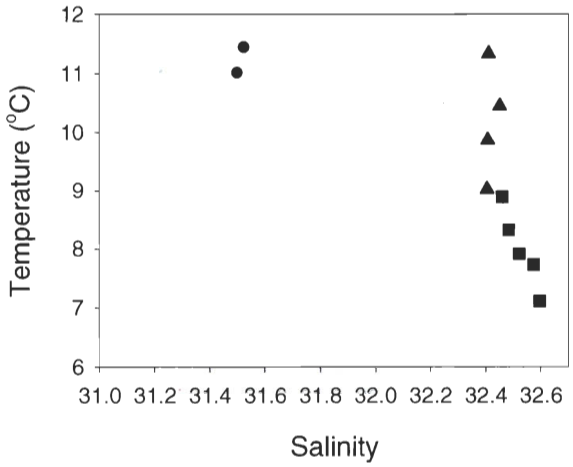

Figure 2.3: Temperature/salinity diagram at 10 m for P1 and P4 (circles), P8-P16 (triangles) and P18-P26 (squares) in the NE Subarctic Pacific Ocean.

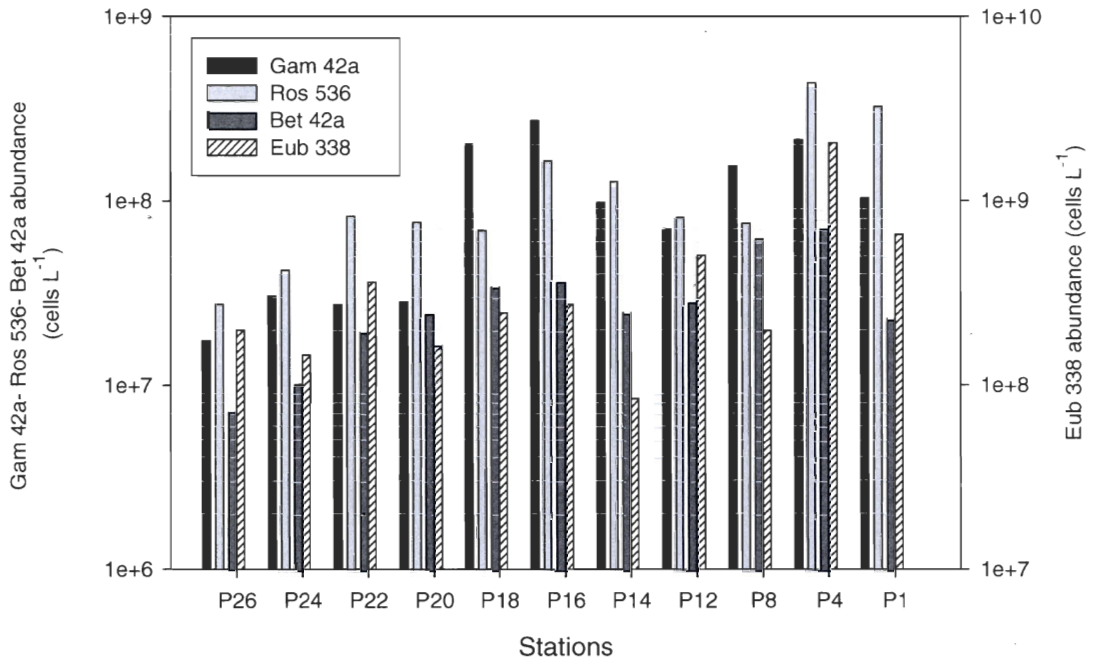

Figure 2.4: Spatial variations along Line P within the NE Subarctic Pacific Ocean in abundance of heterotrophic bacteria (Eubacteria, Eub338); Betaproteobacteria (β, Bet42a), Gammaproteobacteria (γ, Gam42a) and the Roseobacter clade (Ros536) using the Card-FISH technique. Please note the log scale.

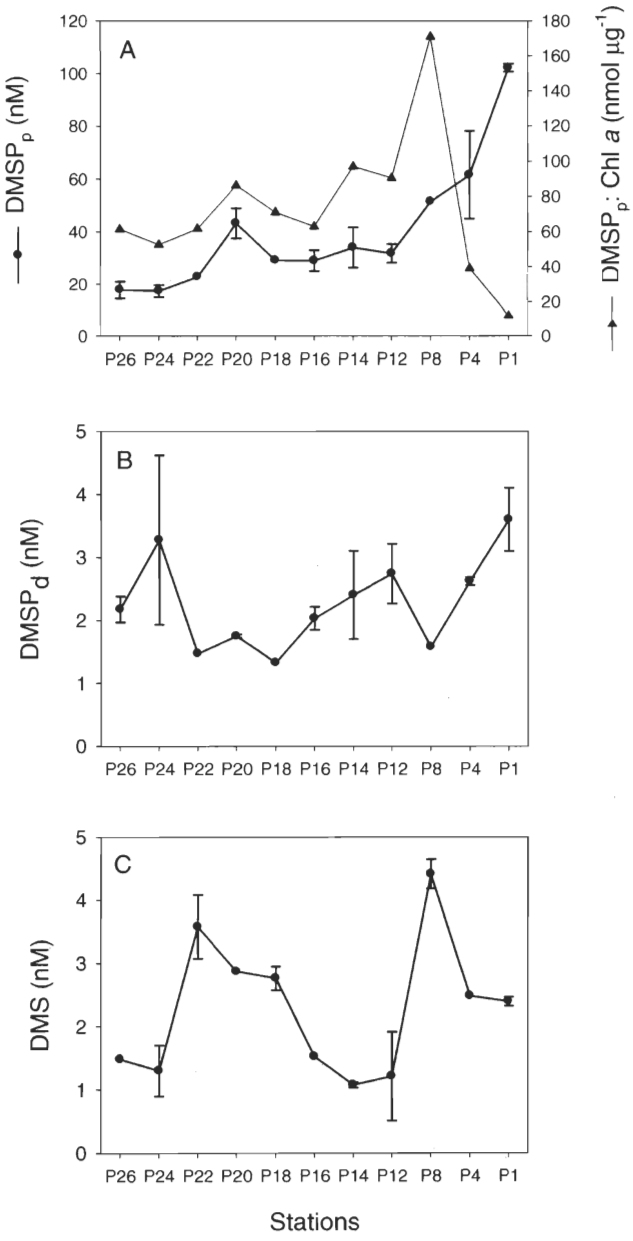

Figure 2.5: Spatial variations in (A) $DMSP_p$ concentrations and $DMSP_p$: chl *a* ratio; (B) $DMSP_d$ concentrations; and (C) DMS concentrations along the transect in the NE Subarctic Pacific Ocean. The error bars indicate the standard deviation.

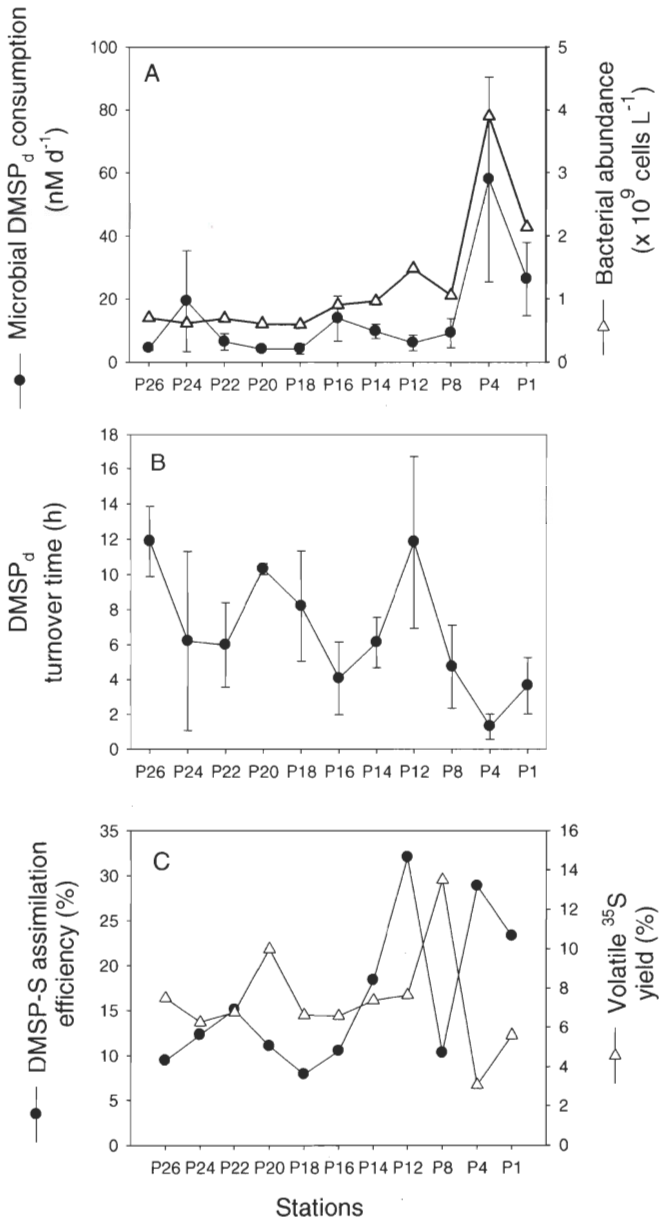

Figure 2.6: Spatial variations in (A) microbial $DMSP_d$ consumption and bacterial abundance; (B) $DMSP_d$ turnover time; and (C) bacterial DMSP-S assimilation efficiency and volatile ^{35}S yield along a transect in the NE Subarctic Pacific Ocean. The error bars indicate the standard deviation.

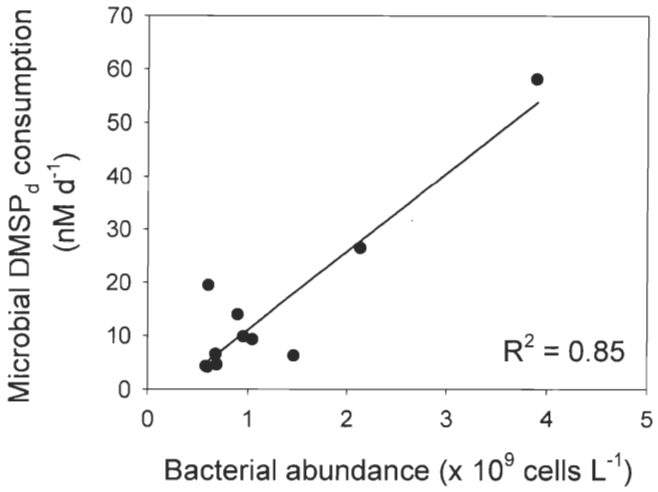

Figure 2.7: Linear regression between microbial $DMSP_d$ consumption and bacterial abundance ($r^2 = 0.85$; $p < 0.01$) at 11 stations within the NE Subarctic Pacific Ocean.

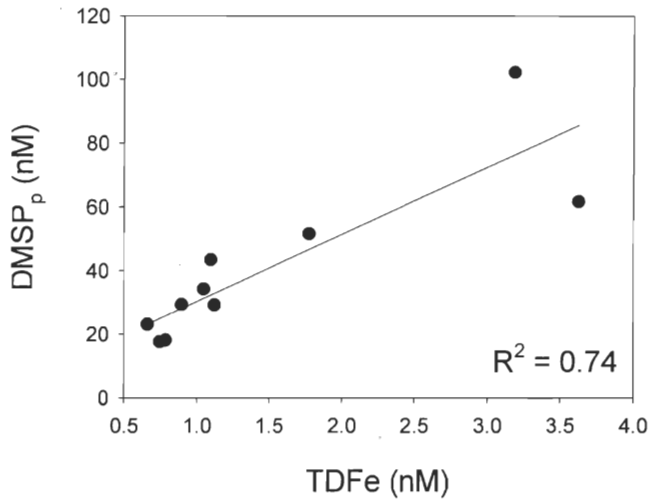

Figure 2.8: Linear regression between $DMSP_p$ and TDFe concentrations ($r^2 = 0.74$; $p < 0.01$) at 10 stations (P1 - P26; excluding P12 due to contamination) within the NE Subarctic Pacific Ocean.

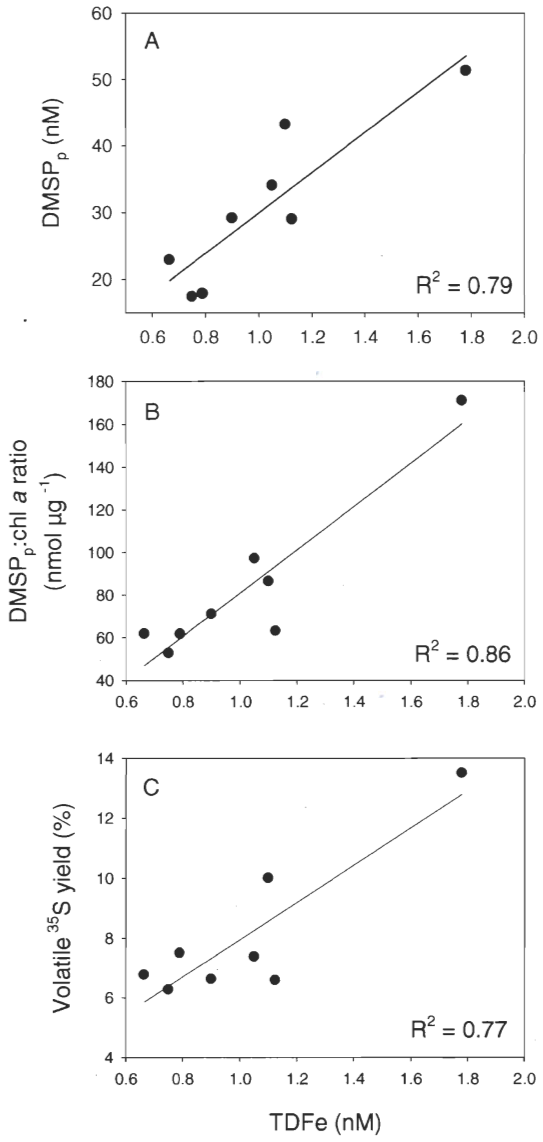

Figure 2.9: Linear regressions between TDFe concentrations and (A) $DMSP_p$ concentrations ($r^2 = 0.79$; $p < 0.01$); (B) $DMSP_p$: chl *a* ratio ($r^2 = 0.86$; $p < 0.01$); and (C) the volatile ^{35}S yield ($r^2 = 0.77$; $p < 0.01$) at 8 stations (P8 –P26; excluding P12 due to contamination) within the HNLC region in the NE Subarctic Pacific Ocean.

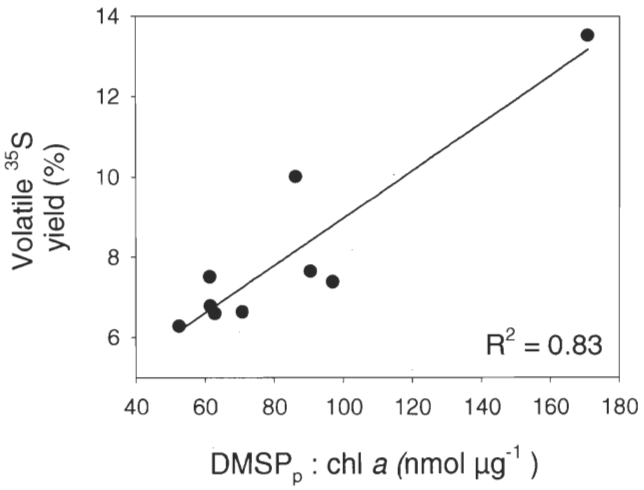

Figure 2.10: Linear regression between volatile ^{35}S yield and $DMSP_p$: chl *a* ratio ($r^2 = 0.83$; $p < 0.01$) at 9 stations (P8-P26) within the HNLC region in the NE Subarctic Pacific Ocean.

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