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## Distributions of atmospheric non-sea-salt sulfate and methanesulfonic acid over the Pacific Ocean between 48°N and 55°S during summer

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### HIGHLIGHTS

- Atmospheric nss-SO<sub>4</sub><sup>2-</sup> and MSA were measured in the Pacific Ocean.
- High nss-SO<sub>4</sub><sup>2-</sup> concentrations were observed in the northern hemisphere.
- MSA concentrations showed higher values in the subpolar regions.
- Factors influencing the distribution of MSA/nss-SO<sub>4</sub><sup>2-</sup> ratio were discussed.
- Contributions of biogenic nss-SO<sub>4</sub><sup>2-</sup> to total nss-SO<sub>4</sub><sup>2-</sup> were estimated.

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### ABSTRACT

Atmospheric concentrations of non-sea-salt sulfate (nss-SO<sub>4</sub><sup>2-</sup>) and methanesulfonic acid (MSA) were measured over the Pacific Ocean between 48°N and 55°S during the KH-08-2 and MR08-06 cruises in summers of 2008 and 2009, in order to investigate spatial distributions of each species and MSA/nss-SO<sub>4</sub><sup>2-</sup> ratio. In the subarctic western North Pacific, mean concentrations of nss-SO<sub>4</sub><sup>2-</sup> and MSA in bulk (fine + coarse) aerosols were 1.1 μg m<sup>-3</sup> and 0.061 μg m<sup>-3</sup>, whereas those in the South Pacific were 0.25 μg m<sup>-3</sup> and 0.043 μg m<sup>-3</sup>, respectively. In the subtropical western North Pacific, it was observed that nss-SO<sub>4</sub><sup>2-</sup> concentration sharply increased from 0.45 μg m<sup>-3</sup> up to 4.2 μg m<sup>-3</sup> under the dominant influence of the Kilauea volcano, while that of MSA remained low. Mean MSA/nss-SO<sub>4</sub><sup>2-</sup> ratio observed in the South Pacific was approximately 3.7 times higher than that in the subarctic western North Pacific, although the mean MSA concentration in the subarctic western North Pacific was a factor of 1.4 higher than that in the South Pacific. The distributions of nss-SO<sub>4</sub><sup>2-</sup>, MSA, and MSA/nss-SO<sub>4</sub><sup>2-</sup> ratio suggested that aerosol nss-SO<sub>4</sub><sup>2-</sup> plays a key role in the latitudinal variation in MSA/nss-SO<sub>4</sub><sup>2-</sup> ratio over the North and South Pacific during summer periods, and that high MSA concentrations in the subarctic western North Pacific and the South Pacific were related to high biological productivity and low air temperature. During the cruises, an inverse relationship ( $r = -0.72$ ,  $p < 0.01$ ) was observed between satellite-derived chlorophyll a concentration and air temperature, showing that high biological productivity occurred at high latitudes, where air temperature were relatively low, in both hemispheres during the summer periods. Although both MSA concentration and MSA/nss-SO<sub>4</sub><sup>2-</sup> ratio showed inverse and positive relationships with air temperature and chlorophyll a concentration, respectively, the correlations between these variables were weak, suggesting that the distributions of MSA concentration and MSA/nss-SO<sub>4</sub><sup>2-</sup> ratio over the North and South Pacific during the summer periods were influenced by more complex factors. Estimates using the MSA/nss-SO<sub>4</sub><sup>2-</sup> ratios measured in different latitude regions in the Pacific Ocean indicated that the contributions from biogenic sources accounted for 9.6–58% of the total nss-SO<sub>4</sub><sup>2-</sup> in aerosols collected in the subarctic western North Pacific, 15–85%

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in the subtropical western North Pacific, 10–70% in the central North Pacific, and 12–97% in the South Pacific, showing strong influence of anthropogenic  $\text{nss-SO}_4^{2-}$  in the subarctic western North Pacific despite the higher mean concentration of MSA in the subarctic western North Pacific than in the South Pacific.

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## 1. Introduction

The biogeochemical cycle of sulfur between the marine atmosphere and the ocean has received considerable attention in the last two decades due to its potential for climate regulation. Dimethylsulfide (DMS), the most dominant sulfur species throughout the ocean, is a metabolic byproduct of the production of dimethylsulfoniopropionate (DMSP), which is produced primarily by phytoplankton (Saltzman et al., 2006; Becagli et al., 2013). Although most DMS is consumed by bacteria (Kiene, 1996), sea surface layers are always supersaturated with it, which implies a net flux of DMS to the atmosphere (Huebert et al., 2004). As a result, about 1% of the DMSP produced in seawater is transported to the atmosphere in the form of DMS through sea-to-air flux (Bates et al., 1994). After emission to the atmosphere, DMS is oxidized by the hydroxyl (OH) and nitrate ( $\text{NO}_3$ ) radicals to form sulfur-containing aerosols, such as non-sea-salt sulfate ( $\text{nss-SO}_4^{2-}$ ) and methanesulfonic acid (MSA). According to the CLAW hypothesis (Charlson et al., 1987), atmospheric  $\text{nss-SO}_4^{2-}$  and MSA derived from DMS oxidation could affect the Earth's radiation balance through the formation of cloud condensation nuclei and, thereby, exert a cooling effect by increasing planetary albedo. However, Quinn and Bates (2011) have recently argued that a dimethylsulfide biological control over cloud condensation nuclei is much more complicated than the climate feedback role of the DMS proposed by Charlson et al. (1987), but it is still clear that DMS emissions do contribute significantly to sulfur-containing aerosol cycling over the oceans (Lin et al., 2012).

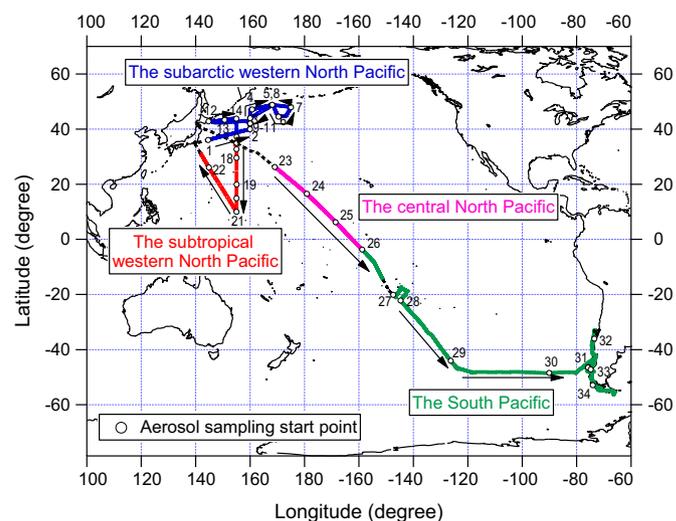
While  $\text{nss-SO}_4^{2-}$  can have multiple sources, including DMS oxidation, volcanic and industrial sulfur emissions, MSA is formed exclusively from DMS (Gondwe et al., 2003). Consequently, MSA/ $\text{nss-SO}_4^{2-}$  ratio has been used as an indication of the relative contributions of DMS and anthropogenic sources to total sulfate levels (e.g., Savoie and Prospero, 1989; Savoie et al., 2002; Gondwe et al., 2004). Although considerable effort has been devoted to estimating the contribution of biogenic source through the investigation of spatial and temporal characteristics of  $\text{nss-SO}_4^{2-}$  and MSA in aerosols collected over various regions and during different periods, relatively little data has been reported for the Pacific Ocean, compared to other oceans (e.g., the Atlantic Ocean) (Gondwe et al., 2004). Several researchers (e.g., Prospero et al., 1985; Saltzman et al., 1986; Savoie and Prospero, 1989; Savoie et al., 1994; Arimoto et al., 1996) have studied the temporal and spatial variability of  $\text{nss-SO}_4^{2-}$  and MSA in aerosols observed over the Pacific Ocean during long-term field campaigns (e.g., Sea-Air Exchange Program; SEAREX and Pacific Exploratory Mission-West; PEM-West). Nevertheless, these data are still not enough to present a comprehensive picture of the spatial distributions of atmospheric  $\text{nss-SO}_4^{2-}$  and MSA over the Pacific Ocean, since most studies have been carried out through a network of island based stations.

In this study, we report on the latitudinal distributions of two major sulfur containing aerosol species collected between 48°N and 55°S over the North and South Pacific in summers of 2008 and 2009. The objectives of this study are to (1) investigate spatial distributions of  $\text{nss-SO}_4^{2-}$ , MSA and MSA/ $\text{nss-SO}_4^{2-}$  ratio, (2) examine relationships between factors influencing the

distributions of MSA/ $\text{nss-SO}_4^{2-}$  ratio, (3) investigate differences of the ratio between different size modes under different ambient conditions, and (4) estimate contribution of biogenically-derived  $\text{nss-SO}_4^{2-}$  to total  $\text{nss-SO}_4^{2-}$ . The results for atmospheric  $\text{nss-SO}_4^{2-}$  and MSA from this study should be valuable for filling the data gap, especially for the subarctic western North Pacific and the South Pacific, and be useful for validation of modeling of sulfur-containing aerosols on a global ocean scale.

## 2. Methods

Aerosol sampling was carried out over the North and South Pacific during two cruises (Fig. 1). The first cruise, KH-08-2, was conducted over the subarctic (Leg 1, 29 July–19 August 2008) and subtropical (Leg 2, 23 August–17 September 2008) western North Pacific Ocean aboard R/V *Hakuho Maru*. The second cruise, MR08-06, was a diagonal transect across the Pacific leaving Mutsu, Japan on 15 January 2009 and arriving in Valparaiso, Chile on 8 April 2009 aboard R/V *Mirai* (Jung et al., 2011). During the MR08-06 cruise, aerosol sampling could not be carried out on board heading to the southeast between 15 and 21 January 2009 when the relative wind directions were outside the ranges of a wind-sector controller (see text below) because of the influence of strong westerly winds. Meteorological variables (e.g., wind speed, wind direction, air temperature) were continuously monitored by weather monitoring systems equipped on the research vessels during the cruises. Methods for aerosol sampling and chemical analysis used in this



**Fig. 1.** Cruise tracks of the KH-08-2 and the MR08-06. White circles and numbers indicate aerosol sampling locations and aerosol sample numbers, respectively. Each aerosol sampling start point represents the end of the previous sampling period. Dotted line indicates that no aerosol sampling was conducted. The two cruises were classified into four oceanic regions with different colors (the subarctic western North Pacific, blue; the subtropical western North Pacific, red; the central North Pacific, pink; the South Pacific, green). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

study have been described previously (Nakamura et al., 2005; Jung et al., 2011, 2013) and are briefly summarized here.

### 2.1. Aerosol collection

A high-volume ( $13 \text{ m}^3 \text{ h}^{-1}$ ) virtual impactor air sampler (AS–9, Kimoto Electric Co., Ltd.) was used to collect marine aerosols on a Teflon filter (PF040, 90 mm in diameter, Advantec). The sampler used an inertial force to separate aerosols according to their aerodynamic diameters, which were segregated into fine ( $D < 2.5 \mu\text{m}$ ) and coarse ( $D > 2.5 \mu\text{m}$ ) modes on the same filter. The aerosol sampler was put on the front of the upper deck (17 m above sea level for R/V *Hakuho Maru* and 20 m for R/V *Mirai*) of the ship. A wind-sector controller was used to avoid contamination from ship's exhaust during the cruises. The wind-sector controller was set to collect marine aerosol samples only when the relative wind directions were within plus or minus  $100^\circ$  relative to the ship's bow and the relative wind speeds were over  $1 \text{ m s}^{-1}$  during the cruises. The total aerosol sampling intervals for the KH-08-2 and MR08-06 cruises varied between 1 and 3 days and 3–5 days, representing total sampling air volume of  $310\text{--}930 \text{ m}^3$  and  $930\text{--}1500 \text{ m}^3$ , respectively. After sampling, the filter was stored frozen at  $-24^\circ \text{C}$  prior to chemical analysis. A total of 34 samples were collected during the cruises. Procedural blanks ( $n = 10$ ) were obtained by placing Teflon filters in the aerosol sampler for 5 min on idle systems (i.e., no airflow through the filters) and processed as other aerosol samples.

### 2.2. Chemical analysis

Aerosol samples were ultrasonically extracted using 50 ml of Milli-Q water. The extraction solution was then filtered through a

13-mm diameter,  $0.45\text{-}\mu\text{m}$  pore-size membrane filter (PTFE syringe filter, Millipore Co.). The filtrates were analyzed by ion chromatography (IC; Dionex-320, Thermo Scientific Dionex) for anions including  $\text{SO}_4^{2-}$  and MSA and for cations including  $\text{Na}^+$ . From replicate injections, the analytical precision was estimated to be  $<5\%$ . The IC method detection limits were  $<0.01 \text{ mg L}^{-1}$  for major ionic species. The concentrations of nss- $\text{SO}_4^{2-}$  were calculated as total  $\text{SO}_4^{2-}$  minus the  $\text{Na}^+$  concentration times 0.2516, the  $\text{SO}_4^{2-}/\text{Na}^+$  mass ratio in bulk seawater (Millero and Sohn, 1992).

## 3. Results and discussion

### 3.1. Distributions of nss- $\text{SO}_4^{2-}$ and MSA in aerosols over the North and South Pacific

Total concentrations of nss- $\text{SO}_4^{2-}$  and MSA in bulk (fine + coarse) aerosols during the two cruises ranged from  $0.094$  to  $4.1 \mu\text{g m}^{-3}$  and  $0.0027\text{--}0.17 \mu\text{g m}^{-3}$ , with  $\sim 77\%$  and  $\sim 76\%$  (median values for all data) of each species being present on fine mode aerosols, respectively (Fig. 2). Mean concentrations of nss- $\text{SO}_4^{2-}$  and MSA over the North Pacific were  $1.0 \pm 0.90 \mu\text{g m}^{-3}$  and  $0.039 \pm 0.042 \mu\text{g m}^{-3}$ , whereas those over the South Pacific were  $0.25 \pm 0.17 \mu\text{g m}^{-3}$  and  $0.043 \pm 0.026 \mu\text{g m}^{-3}$ , respectively.

To aid with interpretation, the data from the two cruises were divided into four oceanic regions: the subarctic western North Pacific ( $n = 14$ ), the subtropical western North Pacific ( $n = 8$ ), the central North Pacific ( $n = 3$ ), and the South Pacific ( $n = 9$ ). Mean concentrations of nss- $\text{SO}_4^{2-}$  and MSA in aerosols collected in the four regions are given in Table 1. In this study, the results for the central North Pacific will not be discussed in detail, since the aerosol sample numbers collected in the central North Pacific are too small.

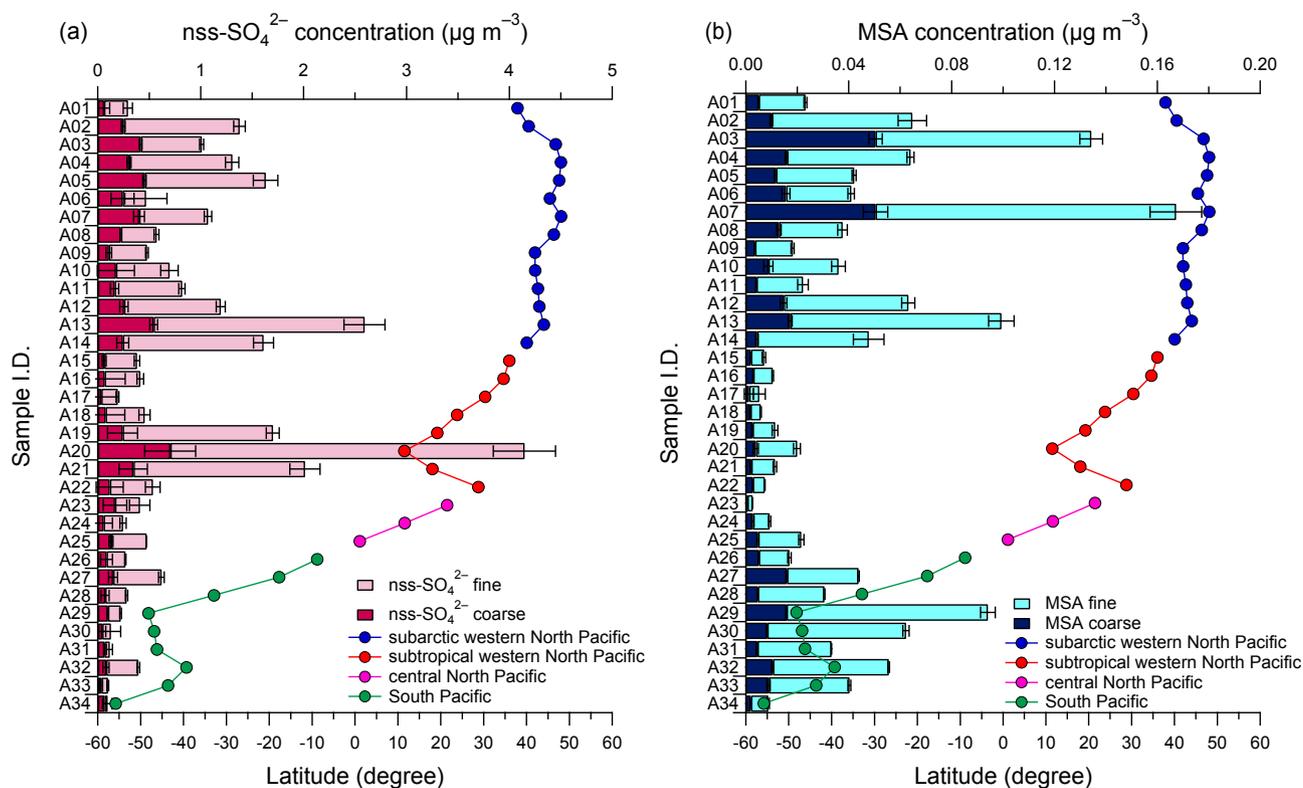


Fig. 2. Concentrations of nss- $\text{SO}_4^{2-}$  and MSA against sample I.D. in aerosols collected during the two cruises. The latitude of half-way point between each aerosol sampling start and end point (solid circle line) is shown with different colors (the subarctic western North Pacific, blue; the subtropical western North Pacific, red; the central North Pacific, pink; the South Pacific, green). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

**Table 1**

Mean concentrations of total nss-SO<sub>4</sub><sup>2-</sup> and MSA in aerosols, and the mean percentage of each component in fine ( $D < 2.5 \mu\text{m}$ ) aerosol particles collected in each of four oceanic regions during the KH-08-2 and MR08-06 cruises.

Region	Period	Nss-SO <sub>4</sub> <sup>2-</sup> ( $\mu\text{g m}^{-3}$ )				MSA ( $\mu\text{g m}^{-3}$ )			
		Mean <sup>a</sup>	Range	Fine %	n	Mean <sup>a</sup>	Range	Fine %	n
Subarctic western North Pacific	Jul–Aug 2008	1.1(0.61)	0.29–2.6	77	14	0.061(0.044)	0.018–0.17	76	14
Subtropical western North Pacific	Aug–Sep 2008	1.2(1.4) <sup>b</sup>	0.19–4.2 <sup>b</sup>	83 <sup>b</sup>	8 <sup>b</sup>	0.010(0.005)	0.005–0.020	74	8
		2.6(1.3) <sup>c</sup>	1.7–4.2 <sup>c</sup>	84 <sup>c</sup>	3 <sup>c</sup>				
		0.39(0.13) <sup>d</sup>	0.19–0.53 <sup>d</sup>	83 <sup>d</sup>	5 <sup>d</sup>				
Central North Pacific	Jan 2009	0.38(0.12)	0.25–0.47	75	3	0.011(0.010)	0.003–0.021	76	3
South Pacific	Jan–Mar 2009	0.25(0.17)	0.094–0.62	77	9	0.043(0.026)	0.009–0.094	79	9

<sup>a</sup> Mean with (standard deviation).

<sup>b</sup> The data for nss-SO<sub>4</sub><sup>2-</sup> collected during the sampling period.

<sup>c</sup> The data for nss-SO<sub>4</sub><sup>2-</sup> collected under the dominant influence of the Kilauea volcano.

<sup>d</sup> The data for nss-SO<sub>4</sub><sup>2-</sup> when the aerosol samples affected by the Kilauea volcano are excluded.

### 3.1.1. The subarctic western North Pacific

The high nss-SO<sub>4</sub><sup>2-</sup> and MSA concentrations were observed in aerosol samples collected over the subarctic western North Pacific. The nss-SO<sub>4</sub><sup>2-</sup> concentration varied from 0.29 to 2.6  $\mu\text{g m}^{-3}$ , with an average of 1.1  $\mu\text{g m}^{-3}$ . About 77% of the total nss-SO<sub>4</sub><sup>2-</sup> was enriched in the fine mode. The mean nss-SO<sub>4</sub><sup>2-</sup> concentration was in reasonable agreement with previously published results obtained in the northwestern North Pacific ( $0.91 \pm 0.44 \mu\text{g m}^{-3}$ ) from 15 to 29 July 1998 (Sasakawa and Uematsu, 2002) and at Shemya ( $52^{\circ}44'N$ ,  $174^{\circ}06'E$ ) (mean: 1.2  $\mu\text{g m}^{-3}$ , range: 0–8.3  $\mu\text{g m}^{-3}$ ) from January 1981–;March 1982 (Prospero et al., 1985). For MSA, its mean concentration was 0.061  $\mu\text{g m}^{-3}$ , with the highest concentration (range: 0.018–0.17  $\mu\text{g m}^{-3}$ ) occurring at  $48^{\circ}N$ . The enrichment of MSA in fine mode particles was 76%. Our mean MSA concentration was a factor of 1.6 lower than that (mean: 0.097  $\mu\text{g m}^{-3}$ , range: 0–0.23  $\mu\text{g m}^{-3}$ ) observed at Shemya from 1981 to 1982, but within the range of variation of MSA concentration during the summer periods (Savoie and Prospero, 1989).

Intense biological activity levels during summer are common at high latitudes, resulting from the utilization of nutrients accumulated during winter (Saltzman et al., 1986). During the sampling period, SeaWiFS satellite images exhibited high chlorophyll a levels in the subarctic western North Pacific (<http://oceancolor.gsfc.nasa.gov>) (Jung et al., 2013). Moreover, Lana et al. (2011) reported that the high-latitude regions in the North Pacific showed a common pattern of high average DMS concentrations (>5 nM) during the summer, suggesting high ocean-to-atmosphere DMS fluxes. During the sampling period in the subarctic western North Pacific, air masses originated from the Asian continent and the Kamchatka Peninsula and then circulated around the subarctic western North Pacific (Jung et al., 2011), indicating that these air masses were likely affected by both continental and marine sources, which could contribute to the high nss-SO<sub>4</sub><sup>2-</sup> and MSA concentrations observed in this region. In addition to high biological productivity, a faster oxidation of DMS in the polluted air masses due to the higher concentration of oxidants could be one of the reasons for high MSA concentration in the subarctic western North Pacific (Huebert et al., 1996). The high nss-SO<sub>4</sub><sup>2-</sup> and MSA concentrations in the subarctic western North Pacific are therefore likely due to strong influences of both anthropogenic (e.g., fossil fuel combustion) and marine sources (e.g., phytoplankton bloom).

### 3.1.2. The subtropical western North Pacific

In contrast to the subarctic western North Pacific, the nss-SO<sub>4</sub><sup>2-</sup> and MSA concentrations over the subtropical western North Pacific drastically decreased when stable easterly trade winds were reaching the sampling sites from the central Pacific (Jung et al., 2011), permitting input of relatively clean marine air. However, unlike MSA concentration, that of nss-SO<sub>4</sub><sup>2-</sup> sharply increased up to

4.2  $\mu\text{g m}^{-3}$  under the dominant influence of the Kilauea volcano. The Halemaumau Crater of the Kilauea volcano on the Big Island of Hawaii ( $19^{\circ}34'N$ ,  $155^{\circ}30'W$ ) became active on 19 March 2008 and continued to release large amounts of sulfur dioxide (SO<sub>2</sub>) gas until the end of 2008 (Swanson et al., 2009; Yuan et al., 2011; Eguchi et al., 2011). The SO<sub>2</sub> gas was carried downwind and formed a large plume of sulfate aerosols reaching as far as 6000 km downwind (Yuan et al., 2011). During the eruption, the total emission amount of SO<sub>2</sub> was estimated to be  $1.8 \pm 1.2 \text{ Tg}$  (Eguchi et al., 2011), which represents approximately 7% of the total SO<sub>2</sub> emission from China during 2008 (Lu et al., 2010). The mean concentration of nss-SO<sub>4</sub><sup>2-</sup> in aerosols affected by the Kilauea volcano (i.e., samples A19–A21) was  $2.6 \pm 1.3 \mu\text{g m}^{-3}$ , which was about 2.4 times higher than that observed in the subarctic western North Pacific where aerosol samples were affected more by anthropogenic and marine sources.

The nss-SO<sub>4</sub><sup>2-</sup> and MSA concentrations over the subtropical western North Pacific varied from 0.19 to 4.2  $\mu\text{g m}^{-3}$  and 0.005–0.020  $\mu\text{g m}^{-3}$ , with average values of 1.2  $\mu\text{g m}^{-3}$  and 0.010  $\mu\text{g m}^{-3}$ , respectively. The mean percentages of total aerosol concentration in the fine mode for nss-SO<sub>4</sub><sup>2-</sup> and MSA were 83% and 74%, respectively. The mean MSA concentration from this study was comparable to the results by Matsumoto et al. (1998) who reported that the mean concentration of MSA observed at Hahajima ( $26^{\circ}38'N$ ,  $140^{\circ}10'E$ ) from December 1994–;January 1997 was 0.0156  $\mu\text{g m}^{-3}$  (range: 0–0.08  $\mu\text{g m}^{-3}$ ); however, our mean nss-SO<sub>4</sub><sup>2-</sup> concentration was a factor of 1.5 lower than their result (mean: 1.75  $\mu\text{g m}^{-3}$ , range: 0–13  $\mu\text{g m}^{-3}$ ), reflecting a stronger contribution of east Asian continental sources to aerosol nss-SO<sub>4</sub><sup>2-</sup> at Hahajima. If the aerosol samples affected by the Kilauea volcano are excluded, the mean nss-SO<sub>4</sub><sup>2-</sup> concentration in the subtropical western North Pacific is 0.39  $\mu\text{g m}^{-3}$ , which is consistent with the observed value (mean: 0.37  $\mu\text{g m}^{-3}$ , range: 0–1.7  $\mu\text{g m}^{-3}$ ) at Oahu ( $21^{\circ}20'N$ ,  $157^{\circ}42'W$ ) (Prospero et al., 1985). This result suggests that the SO<sub>2</sub> gas derived from sporadic volcanic event could become a significant source of aerosol nss-SO<sub>4</sub><sup>2-</sup> in the remote ocean, even though the actual eruption site is thousands of kilometers away.

### 3.1.3. The South Pacific

The nss-SO<sub>4</sub><sup>2-</sup> concentration over the South Pacific remained low, with varying from 0.094 to 0.62  $\mu\text{g m}^{-3}$ . The mean concentration of nss-SO<sub>4</sub><sup>2-</sup> was 0.25  $\mu\text{g m}^{-3}$ , with ~77% of total nss-SO<sub>4</sub><sup>2-</sup> being present on fine mode aerosols. The mean value was in good agreement with the result by Ooki et al. (2007) who reported that mean nss-SO<sub>4</sub><sup>2-</sup> concentration in marine aerosols collected along  $160^{\circ}W$  line from  $3^{\circ}S$  to  $47^{\circ}S$  over the South Pacific was 0.29  $\mu\text{g m}^{-3}$  (range: 0.24–0.47  $\mu\text{g m}^{-3}$ ). In comparison, our mean nss-SO<sub>4</sub><sup>2-</sup> concentration was about 1.6 times lower than that ( $0.41 \pm 0.17 \mu\text{g m}^{-3}$ ) observed at American Samoa ( $14.25^{\circ}S$ ,

170.58°W) during the austral summer months of December through February from 1990 to 1992 (Savoie et al., 1994), but comparable to the value ( $0.24 \pm 0.16 \mu\text{g m}^{-3}$ ) obtained at Palmer Station (64.77°S, 64.05°W) from December 1990 through March 1991 (Savoie et al., 1993).

During the collection of aerosol samples in the South Pacific, SeaWiFS satellite images (<http://oceancolor.gsfc.nasa.gov>) revealed persistently high chlorophyll a levels in the Southern Ocean near Antarctica, and air masses originated from the South Pacific or the Southern Ocean near coastal Antarctica and then spent at least 7 days over the ocean before reaching at sampling sites (Jung et al., 2011), indicating input of marine origin aerosols with relatively little terrestrial and anthropogenic influences. According to Savoie et al. (1994 and references therein), the mean concentration of lead-210 ( $^{210}\text{Pb}$ ) ( $0.056 \text{ mBq m}^{-3}$ ), which is a tracer for air masses that have recently been in convective contact with continental land masses, at American Samoa was among the lowest reported for temperate and tropical ocean regions. They also reported that the mean  $^{210}\text{Pb}$  concentration at American Samoa was comparable to those over Antarctica. As already mentioned above, our mean  $\text{nss-SO}_4^{2-}$  concentration in the South Pacific was lower than that at American Samoa, but comparable to that at Palmer Station, suggesting that the  $\text{nss-SO}_4^{2-}$  concentration in the South Pacific from this study was affected less by anthropogenic sources compared to that at American Samoa. Moreover, high DMS concentrations in seawater have been observed or modeled in the Southern Ocean, especially in Antarctic coastal regions, during the austral summer (e.g., Bates et al., 1992; Kettle et al., 1999; Kettle and Andreae, 2000; Gondwe et al., 2003; Lana et al., 2011). Considering the results of satellite observations and air mass backward trajectory analyses, the  $\text{nss-SO}_4^{2-}$  concentration in the South Pacific from this study is most likely affected much more by biogenic than anthropogenic sources.

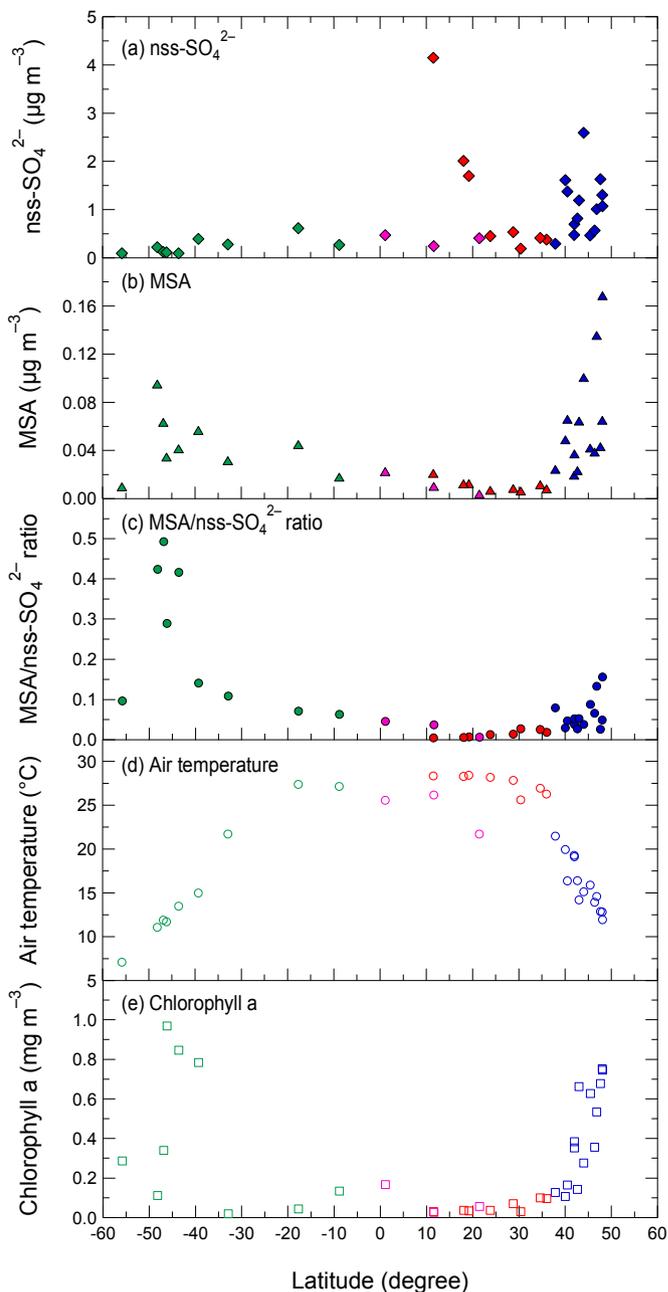
In contrast to  $\text{nss-SO}_4^{2-}$ , the MSA concentration increased and reached its highest value at 48°S. The MSA concentration varied from  $0.009$  to  $0.094 \mu\text{g m}^{-3}$ , with an average of  $0.043 \mu\text{g m}^{-3}$ . The MSA existed in fine mode aerosols contributed 79% of the total MSA. The mean MSA value from this study was about 1.9 times higher than that ( $0.0229 \pm 0.008 \mu\text{g m}^{-3}$ ) observed at American Samoa (Savoie et al., 1994), but about 2.8 times lower than that ( $0.122 \pm 0.127 \mu\text{g m}^{-3}$ ) at Palmer Station (Savoie et al., 1993). Previous studies have revealed that high MSA concentration in marine aerosols was observed near the Antarctic continent (60–70°S) during the austral summer. For example, Chen et al. (2012) reported that MSA concentrations in marine aerosols collected at  $\sim 63^\circ\text{S}$ ,  $23^\circ\text{W}$  and  $\sim 68^\circ\text{S}$ ,  $18^\circ\text{W}$  during austral summer Antarctic expedition cruises were  $0.24 \mu\text{g m}^{-3}$  and  $0.26 \mu\text{g m}^{-3}$ , respectively. These differences in the mean aerosol MSA concentrations among sampling locations presumably reflect regional differences in factors controlling MSA abundance in the marine atmosphere, such as spatial variations of phytoplankton bloom, emission flux of DMS, atmospheric oxidative capacity, atmospheric transport and removal (Arimoto et al., 1996; Gondwe et al., 2004; Chen et al., 2012).

### 3.2. $\text{MSA}/\text{nss-SO}_4^{2-}$ ratio over the Pacific Ocean during summer

#### 3.2.1. Distribution of $\text{MSA}/\text{nss-SO}_4^{2-}$ ratio

The spatial and seasonal (summer maxima and winter minima) variability of  $\text{MSA}/\text{nss-SO}_4^{2-}$  ratio over the Pacific Ocean has been observed by previous studies, with higher ratios occurring with increasing latitude (e.g., Saltzman et al., 1983, 1986; Savoie and Prospero, 1989; Bates et al., 1992; Savoie et al., 1994; Arimoto et al., 1996; Chen et al., 2012). The  $\text{MSA}/\text{nss-SO}_4^{2-}$  ratio in bulk aerosols from this study varied from 0.0048 to 0.49, with lower

ratios in marine aerosols collected over the tropical and subtropical regions and higher values over the subpolar regions (Fig. 3c). The  $\text{MSA}/\text{nss-SO}_4^{2-}$  ratio gradually decreased from the subarctic to the subtropical western North Pacific. The ratio slowly increased



**Fig. 3.** Latitudinal distributions of (a) total  $\text{nss-SO}_4^{2-}$  concentration (solid diamonds), (b) total MSA concentration (solid triangles), (c)  $\text{MSA}/\text{nss-SO}_4^{2-}$  ratio (solid circles) in bulk aerosols, (d) air temperature (open circles), and (e) satellite-derived chlorophyll a concentration (open squares). Each air temperature represents its mean value for each aerosol sampling time. The Moderate-Resolution Imaging Spectroradiometer (MODIS) Aqua (Reprocessing R2012.0)-derived chlorophyll a concentration at each half-way point between aerosol sampling start and end point was obtained from the Goddard Space Flight Center of NASA (<http://oceandata.sci.gsfc.nasa.gov/>). The spatial and temporal resolution of the data was approximately 4 by 4 km per pixel and 8-day composite, respectively (Park et al., 2010). The four oceanic regions show with different colors (the subarctic western North Pacific, blue; the subtropical western North Pacific, red; the central North Pacific, pink; the South Pacific, green). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

between 9°S and 40°S and sharply increased up to 0.49 at 47°S. Mean MSA/nss-SO<sub>4</sub><sup>2-</sup> ratios for four oceanic regions were as follows: the subarctic western North Pacific 0.063 ± 0.039, the subtropical western North Pacific 0.014 ± 0.0087, the central North Pacific 0.030 ± 0.020, and the South Pacific 0.23 ± 0.17. The MSA/nss-SO<sub>4</sub><sup>2-</sup> ratios observed in the subarctic and subtropical western North Pacific during this study were about a factor of 1.5 higher and a factor of 2.3 lower than those obtained at Shemya (52°44'N, 174°06'E) (0.043) and Oahu (21°20'N, 157°42'W) (0.032), respectively (Arimoto et al., 1996). In comparison, the mean MSA/nss-SO<sub>4</sub><sup>2-</sup> ratio in the South Pacific was approximately 4.2 times higher than that (0.055) at American Samoa (14.25°S, 170.58°W) (Savoie et al., 1994), but 2.5 times lower than that (0.58) at Palmer Station (64.77°S, 64.05°W) (Savoie et al., 1993), showing that the higher ratios occur in the South Pacific. Potential reasons for the higher ratios in the South Pacific are discussed in section 3.2.2.

### 3.2.2. Factors influencing the distribution of MSA/nss-SO<sub>4</sub><sup>2-</sup> ratio

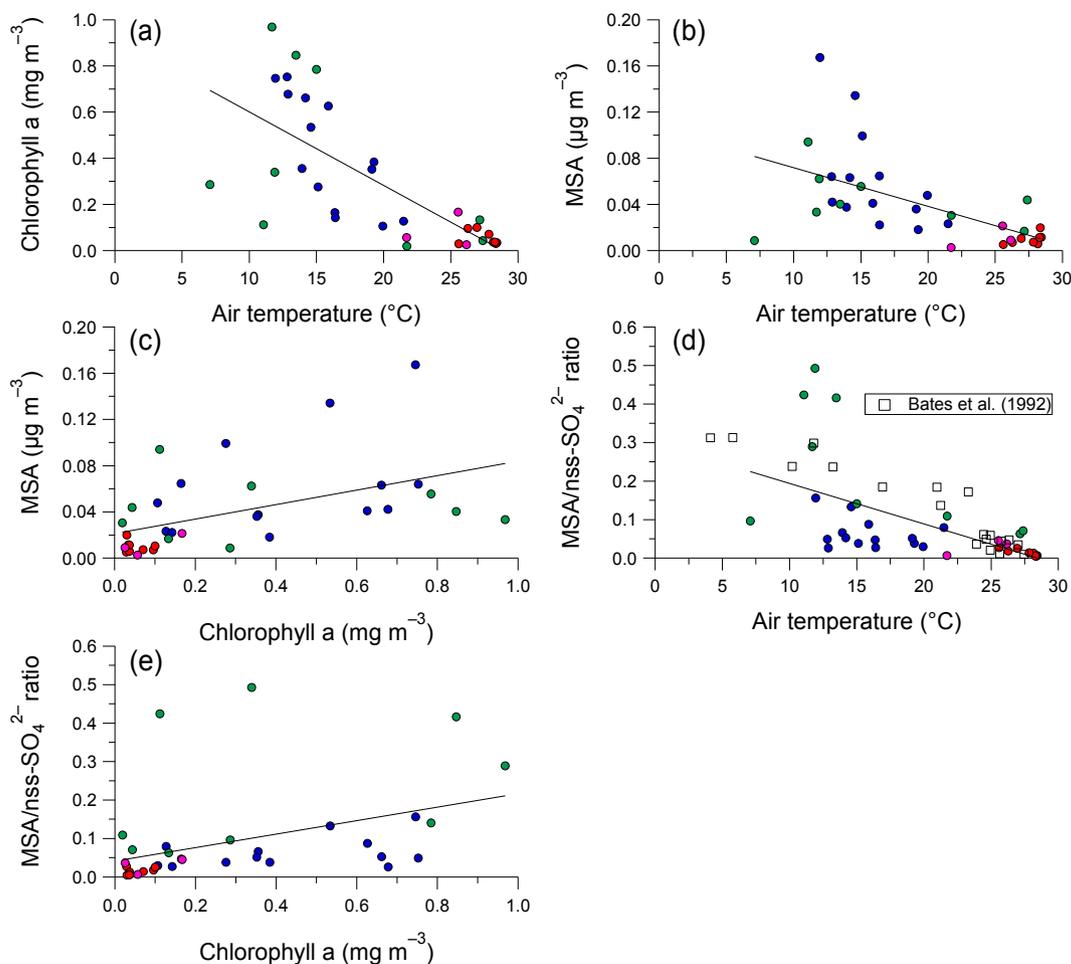
The distribution of MSA/nss-SO<sub>4</sub><sup>2-</sup> ratio over the ocean can be influenced by various factors. Primary factors include the long-range transport of MSA and nss-SO<sub>4</sub><sup>2-</sup> from source regions, the seasonal variations in seawater DMS concentration that reflect changes in marine biological productivity, meteorological condition and atmospheric deposition. Another important factor is the oxidation pathways of atmospheric DMS. During daytime, the oxidation of DMS proceeds mainly by the reaction with OH by either hydrogen abstraction or addition pathway (Hynes et al., 1986). The addition pathways lead to products such as dimethylsulfoxide (DMSO) and MSA, and the abstraction leads mainly to SO<sub>2</sub> and ultimately sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) (Barnes et al., 2006). Both reactions (i.e., abstraction and addition) have a significant dependence on temperature: the addition pathway is favored at cold temperatures (above -42 °C) and dominates over the abstraction pathway for temperatures lower than approximately 17 °C (Hynes et al., 1986; Albu et al., 2006; Castebrunet et al., 2009). In the case of the polluted marine boundary layer, DMS is also oxidized by NO<sub>3</sub> that is generally present in large concentration only at night because of its efficient photolysis (e.g., Wayne et al., 1991). The oxidation by NO<sub>3</sub> follows the abstraction pathway and predominantly produces SO<sub>2</sub>. In addition to OH and NO<sub>3</sub> radicals, halogen atoms (e.g., Cl, Br and I) and their oxides may be important oxidants for DMS in the marine troposphere. These halogen species in the atmosphere are expected to be at their highest concentration in the marine boundary layer (Singh and Kasting, 1988), since they originate from reactions involving sea-salt aerosol (Rossi, 2003). In this section, we discuss the factors influencing the distribution of MSA/nss-SO<sub>4</sub><sup>2-</sup> ratio over the Pacific Ocean during the summer periods.

The mean MSA/nss-SO<sub>4</sub><sup>2-</sup> ratio observed in the South Pacific was about 3.7 times higher than that in the subarctic western North Pacific, although the mean MSA concentration in the subarctic western North Pacific was a factor of 1.4 higher than that in the South Pacific (Fig. 3b), suggesting that atmospheric nss-SO<sub>4</sub><sup>2-</sup> observed in the subarctic western North Pacific was affected more by anthropogenic sources, and that aerosol nss-SO<sub>4</sub><sup>2-</sup> plays a key role in the latitudinal variation in MSA/nss-SO<sub>4</sub><sup>2-</sup> ratio over the North and South Pacific during the summer periods (Fig. 3a).

In general, the higher MSA/nss-SO<sub>4</sub><sup>2-</sup> ratios at high latitudes have been attributed to temperature dependent oxidation pathways of atmospheric DMS (i.e., higher yield of MSA at low temperatures) (e.g., Hynes et al., 1986; Ayers et al., 1991) and high biological productivity (e.g., Legrand and Pasteur, 1998; Minikin et al., 1998). During the sampling period of this study, the variation trend of air temperature in the northern hemisphere was quite similar to that in the southern hemisphere, with decreasing with increasing latitude (Fig. 3d), whereas chlorophyll a concentration

showed the opposite variation trend to that of air temperature (Fig. 3e). An inverse relationship was observed between chlorophyll a concentration and air temperature (chlorophyll a concentration (mg m<sup>-3</sup>) = -0.0318 air temperature (°C) + 0.9188,  $r = -0.72$ ,  $p < 0.01$ ) (Fig. 4a), showing that high marine biological productivity occurred at high latitudes, where air temperatures were relatively low, in both hemispheres during the summer periods. In addition, both MSA concentration and MSA/nss-SO<sub>4</sub><sup>2-</sup> ratio showed inverse and positive relationships with air temperature ( $r = -0.58$ ,  $p < 0.01$  and  $r = -0.55$ ,  $p < 0.01$ ) and chlorophyll a concentration ( $r = 0.48$ ,  $p < 0.01$  and  $r = 0.41$ ,  $p < 0.05$ ), respectively (Fig. 4b–e); however, the correlations between these variables were weak, and the highest MSA/nss-SO<sub>4</sub><sup>2-</sup> ratio and MSA concentration were not always associated with the lowest air temperature and the highest chlorophyll a concentration. Although high marine biological productivity and low air temperature, especially in the subarctic western North Pacific and the South Pacific, make a favorable condition for MSA formation, the poor correlations between MSA concentration, chlorophyll a concentration and air temperature can be resulted from long-range transport of MSA from source regions (e.g., Antarctic coastal region) where biological productivity and air temperature were different from those at the sampling sites and atmospheric deposition of MSA during long-range transport as well as air-sea exchange rate of DMS (O'Dowd et al., 1997) and the availability of oxidants (Gondwe et al., 2004). Furthermore, since nss-SO<sub>4</sub><sup>2-</sup>, which was used to investigate the influences of biological productivity and air temperature on the MSA/nss-SO<sub>4</sub><sup>2-</sup> ratios, contains both anthropogenic and biologically-derived nss-SO<sub>4</sub><sup>2-</sup>, the relationships between these variables may show the poor correlations. In addition to these factors, sea fog, causing a reduction of incident solar radiation, can be an important factor for DMS oxidation in the oceanic regions where sea fog occurs frequently (Bürgermeister et al., 1990). Moreover, sea fog can accelerate particle removal from the marine atmosphere by forming liquid droplets by condensation of water vapor on pre-existed particles acting as condensation nuclei (Sasakawa et al., 2003). The subarctic western North Pacific (>40°N) has a high sea fog frequency, with a maximum of ~50% during the summer time period from June to August (Wang, 1985). During the sampling period in the subarctic western North Pacific, over a dozen sea fog events occurred and aerosol samples were affected by these fog appearance (Jung et al., 2013). As shown in Fig. 4c, two distinctly different relationships between MSA and chlorophyll a concentrations were observed in the subarctic western North Pacific. The MSA concentrations in aerosol samples collected during non sea fog events were higher than those affected by sea fog events, although MSA concentrations in both aerosol samples showed positive correlations with chlorophyll a concentrations. Consequently, two different relationships between MSA and chlorophyll a concentrations in the subarctic western North Pacific are likely attributable to the reduced oxidation of DMS by atmospheric oxidants and the acceleration of particle removal during sea fog event. Although the correlations between MSA concentration, MSA/nss-SO<sub>4</sub><sup>2-</sup>, air temperature and chlorophyll a concentration were weak, our results suggest that biological productivity and air temperature did affect the distributions of MSA concentrations and MSA/nss-SO<sub>4</sub><sup>2-</sup> ratios over the Pacific Ocean during the summer periods, and that the MSA concentrations and MSA/nss-SO<sub>4</sub><sup>2-</sup> ratios increased with increasing latitude because of high marine biological productivity and low air temperature at high latitudes.

A detailed study of MSA/nss-SO<sub>4</sub><sup>2-</sup> ratios in the South Pacific (0°N–60°S) during the austral summer (February–March) as a function of latitude showed a strong inverse relationship between air temperature and MSA/nss-SO<sub>4</sub><sup>2-</sup> ratios (i.e., MSA/nss-SO<sub>4</sub><sup>2-</sup> = -0.015 air temperature (°C) + 0.422,  $r^2 = 0.87$ ) (Bates et al.,



**Fig. 4.** Relationship between (a) satellite-derived chlorophyll a concentration and air temperature, and their influences on the variations of (b, c) MSA concentration and (d, e) MSA/nss-SO<sub>4</sub><sup>2-</sup> ratio in the Pacific Ocean during the summer time periods. The four oceanic regions show with different colors (the subarctic western North Pacific, blue; the subtropical western North Pacific, red; the central North Pacific, pink; the South Pacific, green). Data from Bates et al. (1992) are also presented (open black squares). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

1992) as shown in Fig. 4d. This inverse relationship has been considered as a result of temperature dependencies in the DMS oxidation kinetics (Hynes et al., 1986). In addition, this finding opened the possibility to use air temperature in order to trace back the MSA/nss-SO<sub>4</sub><sup>2-</sup> ratio in a sampling region and to estimate the contribution of biogenically-derived nss-SO<sub>4</sub><sup>2-</sup> to total nss-SO<sub>4</sub><sup>2-</sup> (e.g., Nakamura et al., 2005; Mihalopoulos et al., 2007; Yang et al., 2009). During this study, the ratios observed in the subarctic western North Pacific were lower than those by Bates et al. (1992). Moreover, the results for MSA/nss-SO<sub>4</sub><sup>2-</sup> ratio in several aerosol samples collected over the South Pacific did not support the relationship by Bates et al. (1992). These results suggest that the variation in MSA/nss-SO<sub>4</sub><sup>2-</sup> ratio over the North and South Pacific during the summer periods cannot be explained solely by the MSA-temperature dependent theory as previous studies already mentioned. Consequently, considering the inverse relationship between chlorophyll a concentration and air temperature, and the strong influence of anthropogenic nss-SO<sub>4</sub><sup>2-</sup> in the subarctic western North Pacific, the relationship between MSA/nss-SO<sub>4</sub><sup>2-</sup> ratio and air temperature observed in this study most likely resulted from complex linkage between these factors rather than the sole effect of temperature dependencies in the DMS oxidation kinetics. Therefore, simple application of the relationship between air temperature and MSA/nss-SO<sub>4</sub><sup>2-</sup> ratio for the evaluation of biogenic nss-

SO<sub>4</sub><sup>2-</sup> would lead to inaccurate estimate of the contribution of biogenically-derived nss-SO<sub>4</sub><sup>2-</sup> to total nss-SO<sub>4</sub><sup>2-</sup>. Although air temperature and marine biological productivity exerted large influences on the MSA/nss-SO<sub>4</sub><sup>2-</sup> ratios and MSA concentrations in the subarctic western North Pacific and the South Pacific, the values in the subtropical western North Pacific appeared to be almost unaffected by the two factors. Similar results were reported by Saltzman et al. (1986) and Savoie et al. (1994) who observed fairly constant MSA/nss-SO<sub>4</sub><sup>2-</sup> ratios at Fanning and American Samoa throughout the year, presumably due to less pronounced seasonal cycle of DMS concentration (Lana et al., 2011) and more stable air temperature in the tropic region (Gondwe et al., 2003).

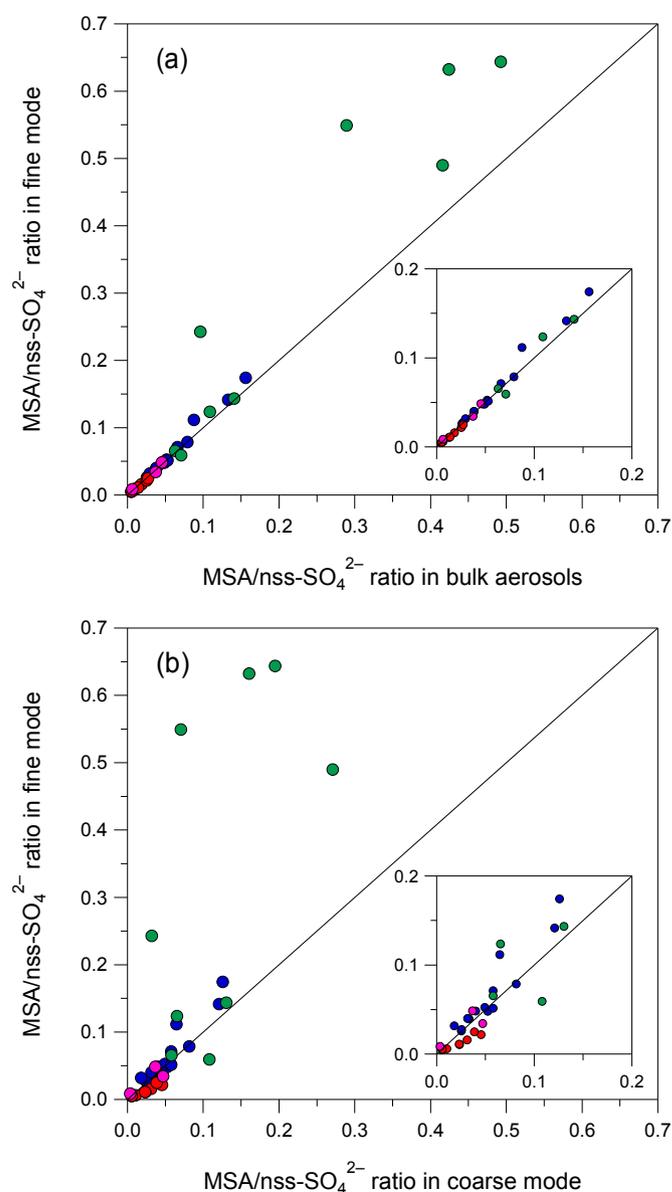
In this study, satellite-derived chlorophyll a concentration was used as an indirect indication of the source strength for DMS. It is worth noting that chlorophyll a concentration does not always represent the DMS source strength. However, Simó and Dachs (2002) found an empirical relationship that allows predicting DMS concentration (nM) in the productive waters of high latitudes (subpolar and Antarctic coastal regions) and equatorial upwellings from satellite chlorophyll a concentration (mg m<sup>-3</sup>) and climatological mixed layer depth (m) (DMS = 55.8(chlorophyll a concentration/mixed layer depth) + 0.6,  $r^2 = 0.84$ ), although the relationship could not resolve satisfactorily the variability of DMS in oligotrophic regions where DMS concentrations varied between

0.8 and 4 nM. For oligotrophic regions, they found a negative correlation between DMS and mixed layer depth ( $\text{DMS} = -\ln(\text{mixed layer depth}) + 5.7$ ,  $r^2 = 0.68$ ). Vallina et al. (2006) also used satellite-derived chlorophyll a concentration as a proxy for oceanic DMS emissions. They reported that correlations between chlorophyll a and aqueous DMS concentrations showed strong positive ( $r > 0.5$ ), especially in the subarctic western North Pacific and Southern Ocean (i.e., high latitude regions). In addition, Kameyama et al. (2013), who attended the cruise conducted over the subarctic western North Pacific (i.e., Leg 1 of the KH-08-2 cruise), observed a significant correlation between seawater DMS and chlorophyll a concentrations ( $r = 0.66$ ,  $p < 0.05$ ,  $n = 333$ ) at low DMS levels ( $< 5 \text{ nmol L}^{-1}$ ), although seawater DMS and chlorophyll a concentrations were uncorrelated at high DMS levels ( $6\text{--}10 \text{ nmol L}^{-1}$ ). Minikin et al. (1998) also found a strong correlation between the chlorophyll a concentration in the surface of the South Polar Ocean and the levels of nss sulfur species present in the atmosphere of coastal Antarctic regions, supporting a domination of DMS-producing algae species in coastal Antarctic ecosystem. Moreover, Park et al. (2013) revealed a strong and positive correlation ( $r = 0.89$ ) between atmospheric DMS mixing ratios and satellite-derived chlorophyll a concentrations observed in the Atlantic sector of the Arctic Ocean (Svalbard, Norway;  $78.5^\circ\text{N}$ ,  $11.8^\circ\text{E}$ ) from early April–mid-June. These previous reports mentioned above suggest that it is not unreasonable to assume that chlorophyll a concentration represents the source strength for DMS. However, to improve understanding biogeochemical cycle of sulfur species between the atmosphere and the ocean, simultaneous measurements of factors influencing the distribution of  $\text{MSA/nss-SO}_4^{2-}$  ratio, such as seawater DMS and atmospheric oxidants as well as gaseous (e.g., atmospheric DMS and  $\text{SO}_2$ ) and particulate (e.g., MSA and  $\text{SO}_4^{2-}$ ) sulfur species, are required.

### 3.2.3. Comparisons of $\text{MSA/nss-SO}_4^{2-}$ ratios between bulk, fine and coarse modes

The  $\text{MSA/nss-SO}_4^{2-}$  ratio has been used in evaluating the contribution of biogenic sources to total  $\text{nss-SO}_4^{2-}$  over various geographical locations, and in exploring the relative significance of different DMS oxidation pathways (Kerminen et al., 1997). However, most studies have used the  $\text{MSA/nss-SO}_4^{2-}$  ratio in bulk aerosols, despite the fact that the size range of the sampled particles can have a large effect on the measured  $\text{MSA/nss-SO}_4^{2-}$  ratio (Bates et al., 1992). For example, Ayers et al. (1991) found that the  $\text{nss-SO}_4^{2-}/\text{MSA}$  ratios in bulk aerosols collected at Cape Grim (Ayers et al., 1986) were about a factor of 2 lower than those in the sub-micron fraction ( $D < 1 \mu\text{m}$ ). Bates et al. (1992) reported that the  $\text{MSA/nss-SO}_4^{2-}$  ratio over the total particle size range was 2.7–22% larger than that of the size range less than  $0.6 \mu\text{m}$  in the Pacific Ocean. In addition, Kerminen et al. (1997) found the high  $\text{MSA/nss-SO}_4^{2-}$  ratios in the Aitken mode ( $D < 0.1 \mu\text{m}$ ) compared to larger-size particles collected at Sevetijärvi station ( $69^\circ 30'\text{N}$ ,  $28^\circ 50'\text{E}$ ) in the northernmost Finland. Turekian et al. (2001) observed in Bermuda ( $32^\circ 22'\text{N}$ ,  $64^\circ 40'\text{W}$ ) that biogenic  $\text{nss-SO}_4^{2-}/\text{MSA}$  ratios increased with increasing particle size. These results suggest that the size cut of aerosol sampling method controls the magnitude of  $\text{MSA/nss-SO}_4^{2-}$  ratio (Bates et al., 1992).

In this study, the  $\text{MSA/nss-SO}_4^{2-}$  ratios in fine ( $D < 2.5 \mu\text{m}$ ) mode was compared to those in bulk (fine + coarse) aerosols. Although previous studies described the effect of particle size on  $\text{MSA/nss-SO}_4^{2-}$  ratio, we found no significant difference of the ratios between fine mode and bulk aerosols, except for those in five aerosol samples collected in the South Pacific (Fig. 5a). In five aerosol samples collected in the South Pacific, the  $\text{MSA/nss-SO}_4^{2-}$  ratios in fine mode were a factor of 1.1–2.5 (mean: 1.6) higher than those in bulk aerosols. If the ratios in aerosols collected over the South Pacific are



**Fig. 5.** Comparisons between  $\text{MSA/nss-SO}_4^{2-}$  ratios in fine mode ( $D < 2.5 \mu\text{m}$ ) and (a)  $\text{MSA/nss-SO}_4^{2-}$  ratios in bulk (fine + coarse) aerosols and (b)  $\text{MSA/nss-SO}_4^{2-}$  ratios in coarse mode ( $D > 2.5 \mu\text{m}$ ). The four oceanic regions show with different colors (the subarctic western North Pacific, blue; the subtropical western North Pacific, red; the central North Pacific, pink; the South Pacific, green). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

removed from Fig. 5a, the  $\text{MSA/nss-SO}_4^{2-}$  ratios in fine mode shows a significant correlation (slope = 1.12, intercept =  $-0.003$ ,  $r = 0.99$ ,  $p < 0.01$ ) with those in bulk aerosols, suggesting that the  $\text{MSA/nss-SO}_4^{2-}$  ratios in fine mode could be representative of those in bulk aerosols collected over the subarctic and the subtropical western North Pacific during summer periods when aerosol particles are separated into fine ( $D < 2.5 \mu\text{m}$ ) and coarse ( $D > 2.5 \mu\text{m}$ ) modes.

Further comparison of  $\text{MSA/nss-SO}_4^{2-}$  ratios in fine mode to those in coarse mode showed the slightly higher ratios in coarse mode, especially in aerosol samples collected in the oceanic region where air temperature was relatively high (e.g., the subtropical western North Pacific) (Fig. 5b). Pszenny (1992) and Huebert et al. (1993), who observed the size distribution of aerosol sulfur species in the tropical Pacific Ocean, reported that MSA was condensed



on larger particles ( $D > 0.5 \mu\text{m}$ ) as a function of aerosol surface area, while  $\text{nss-SO}_4^{2-}$  was associated primarily with submicron particles, in contrast to the observations by Pszenny et al. (1989) in the Antarctic, Kerminen et al. (1997) in the Finnish Arctic and Xu et al. (2013) in the Southern Ocean ( $40^\circ\text{S}$ – $65^\circ\text{S}$ ,  $76^\circ\text{E}$ – $115^\circ\text{E}$ ), who observed that both  $\text{nss-SO}_4^{2-}$  and MSA were largely associated with fine particles ( $D < 1 \mu\text{m}$ ). The previous reports by Pszenny (1992) and Huebert et al. (1993) support our result for the higher MSA/ $\text{nss-SO}_4^{2-}$  ratios in coarse mode observed in the tropical Pacific regions. The possible explanation for our result is the saturation of MSA over submicron particles. According to Kerminen et al. (1997) and references therein, the MSA solubility decreases rapidly with increasing acidity of the solution. Therefore, MSA saturates more easily over submicron particles than over alkaline sea-salt particles, since submicron particles become more acidic by sulfate particles. When submicron particles become saturated, MSA cannot be absorbed into submicron particles any more, but can into supermicron particles. Kerminen et al. (1997) also concluded that the saturation effect drives more MSA into supermicron particles, especially for acidic aerosol systems at high temperatures, since MSA solubility is smaller for more acidic particles and for higher ambient temperatures. Indeed, previous studies mentioned above showed that most MSA in high-latitudes sites was found in submicron particles, whereas over tropical oceans a significant fraction of MSA was associated with supermicron particles. In this study, we observed the strong influence of the Kilauea volcano on  $\text{nss-SO}_4^{2-}$  concentration during aerosol collection in the subtropical western North Pacific. Furthermore, sulfate particles are usually not sufficiently neutralized due to the lack of ammonia gas in the remote marine atmosphere. Quinn et al. (1990) reported that the mean molar ratio of  $\text{NH}_4^+/\text{nss-SO}_4^{2-}$  in fine particles over the subtropical Pacific Ocean ( $15^\circ\text{N}$ – $29^\circ\text{N}$ ) was 0.38, suggesting that  $\text{nss-SO}_4^{2-}$  was not fully neutralized by  $\text{NH}_4^+$ , and that fine aerosols collected in the subtropical western North Pacific during this study are provably acidic. Consequently, the higher MSA/ $\text{nss-SO}_4^{2-}$  ratios in coarse mode observed in the subtropical western North Pacific likely resulted from the saturation effect.

In contrast to the subtropical western North Pacific, the higher MSA/ $\text{nss-SO}_4^{2-}$  ratios in fine mode compared to coarse mode were observed in the subarctic western North Pacific and the South Pacific (Fig. 5b). The higher ratios in fine mode in the subarctic western North Pacific could result from the shift in aerosol surface area toward smaller particle near continents by the greater number of small particles in the continental region (Huebert et al., 1993). Another possible explanation is that larger aerosols near continents can become more acidified by the incorporation of nitric ( $\text{HNO}_3$ ) acid and/or  $\text{H}_2\text{SO}_4$  (Andreae and Crutzen, 1997), thus decreasing the MSA solubility relative to that over the large aerosols in more remote regions. For the higher ratios in fine mode in the South Pacific, it could be caused by enhancement of sea-salt particles in fine mode and/or a more rapid removal of  $\text{nss-SO}_4^{2-}$  and MSA in coarse mode during long-range transport. The Southern Ocean between  $40^\circ$  and  $60^\circ$  is high wind speed region (Kloster et al., 2006; Lana et al., 2011). In this region, Jung et al. (2011) observed that mean percentage (46%) of sea-salt particles in fine mode aerosols (mean:  $0.66 \mu\text{g m}^{-3}$ ) was a factor of 1.6–2.3 higher than those (21–29%) in the subarctic (mean:  $0.22 \mu\text{g m}^{-3}$ ) and subtropical (mean:  $0.21 \mu\text{g m}^{-3}$ ) western North Pacific. In addition, the incorporation of  $\text{SO}_2$  and MSA by larger sea-salt particles in the marine boundary layer shifts the size distributions of aerosol  $\text{nss-SO}_4^{2-}$  and MSA towards larger sizes and accelerates their removal from the marine atmosphere, since atmospheric removal processes include gravitational settling, impaction and diffusion of particles, all of which vary in complex functions of particle size and meteorological conditions (e.g., wind speed and rainfall) (Duce et al., 1991). These

results for comparison of MSA/ $\text{nss-SO}_4^{2-}$  ratios between fine and coarse mode aerosols suggest that MSA/ $\text{nss-SO}_4^{2-}$  ratios can vary with not only aerosol size range but also meteorological conditions of sampling regions.

### 3.2.4. Contribution of biogenically-derived $\text{nss-SO}_4^{2-}$ to total $\text{nss-SO}_4^{2-}$

Considerable effort has been devoted to investigating the contribution of biogenically-derived atmospheric sulfur species (e.g., Savoie and Prospero, 1989; Bates et al., 1992; Arimoto et al., 1996, 2001; Savoie et al., 2002; Gondwe et al., 2004; Lin et al., 2012). For example, Savoie and Prospero (1989) reported that the biogenic source accounts for ~80% of the annual average  $\text{nss-SO}_4^{2-}$  over the mid-latitude North Pacific using the mean MSA/ $\text{nss-SO}_4^{2-}$  ratio of 0.065 observed at relatively pristine sites on Fanning ( $3^\circ 51'\text{N}$ ,  $159^\circ 21'\text{W}$ ) and American Samoa ( $14.25^\circ\text{S}$ ,  $170.58^\circ\text{W}$ ). However, when the MSA/ $\text{nss-SO}_4^{2-}$  ratio by Savoie and Prospero (1989) was used in this study, the contributions of biogenically-derived  $\text{nss-SO}_4^{2-}$  for samples collected over the subarctic western North Pacific and the South Pacific were highly overestimated. Clearly, there was a problem in applying the ratio by Savoie and Prospero (1989) to our full data set, suggesting that careful application of the observed MSA/ $\text{nss-SO}_4^{2-}$  ratio is required in estimating the contribution of biogenic sources to total  $\text{nss-SO}_4^{2-}$  in different environments.

It is worth noting that this study was conducted over the Pacific Ocean in both hemispheres during the summer periods. Therefore, to estimate the contribution of biogenically-derived  $\text{nss-SO}_4^{2-}$  to total  $\text{nss-SO}_4^{2-}$ , the MSA/ $\text{nss-SO}_4^{2-}$  ratios, which are measured in different latitude regions in the Pacific Ocean during summer time periods, should be used. In this study, we applied the following the MSA/ $\text{nss-SO}_4^{2-}$  ratios, which can be representative of four oceanic regions: the subarctic western North Pacific 0.27 (Arimoto et al., 1996), the subtropical western North Pacific 0.065 (Savoie and Prospero, 1989), the central North Pacific 0.065 (Savoie and Prospero, 1989), and the South Pacific 0.508 (Savoie et al., 1993). For the subarctic western North Pacific and the South Pacific, the mean MSA/ $\text{nss-SO}_4^{2-}$  ratios of 0.27 and 0.508 measured at Shemya ( $52^\circ 44'\text{N}$ ,  $174^\circ 06'\text{E}$ ) (Arimoto et al., 1996) and Palmer Station ( $64.77^\circ\text{S}$ ,  $64.05^\circ\text{W}$ ) (Savoie et al., 1993) during summer months were used, respectively. For the subtropical western North Pacific and the central North Pacific, the MSA/ $\text{nss-SO}_4^{2-}$  ratio of 0.065 observed at Fanning ( $3^\circ 51'\text{N}$ ,  $159^\circ 21'\text{W}$ ) and American Samoa ( $14.25^\circ\text{S}$ ,  $170.58^\circ\text{W}$ ) was used because of fairly constant MSA/ $\text{nss-SO}_4^{2-}$  ratio at Fanning and American Samoa throughout the year (Savoie and Prospero, 1989). Based on these ratios, the mean contributions of biogenically-derived  $\text{nss-SO}_4^{2-}$  accounted for about 23% (range: 9.6–58%) of the total  $\text{nss-SO}_4^{2-}$  in aerosols collected in the subarctic western North Pacific, 45% (range: 15–85%) in the subtropical western North Pacific, 46% (range: 10–70%) in the central North Pacific, and 46% (range: 12–97%) in the South Pacific, suggesting that the contribution of biogenic  $\text{nss-SO}_4^{2-}$  is greatest in the relatively pristine South Pacific, and that the influence of anthropogenic  $\text{nss-SO}_4^{2-}$  in the subarctic western North Pacific is strong despite the higher mean concentration of MSA in this region than in the South Pacific.

As mentioned earlier, several aerosol samples (i.e., samples A19–A21) collected over the subtropical western North Pacific were affected by the Kilauea volcano (see section 3.1.2). If these aerosol samples are excluded, the mean contribution of biogenically-derived  $\text{nss-SO}_4^{2-}$  in this region increases from 45% to 61% (range: 40–85%). In comparison, the mean contribution of biogenically-derived  $\text{nss-SO}_4^{2-}$  in these aerosol samples was estimated to be 18% (mean:  $0.44 \mu\text{g m}^{-3}$ ), indicating that about 82% (mean:  $2.16 \mu\text{g m}^{-3}$ ) of  $\text{nss-SO}_4^{2-}$  was derived from anthropogenic

and volcanic sources. To distinguish between anthropogenic and volcanic sources, aerosol nitrate ( $\text{NO}_3^-$ ) was used as an indicator of anthropogenic contributions (Savoie et al., 2002), and  $\text{nss-SO}_4^{2-}/\text{NO}_3^-$  ratio (1.06) measured at Oahu ( $21^\circ 20' \text{N}$ ,  $157^\circ 42' \text{W}$ ) and  $\text{NO}_3^-$  concentrations in aerosols collected over the subtropical western North Pacific were obtained from Prospero et al. (1985) and Jung et al. (2011), respectively. As a result, it was estimated that about 6% (mean:  $0.16 \mu\text{g m}^{-3}$ ) and 76% ( $2.0 \mu\text{g m}^{-3}$ ) of  $\text{nss-SO}_4^{2-}$  were derived from anthropogenic and volcanic sources, respectively.

In this study, the contributions of biogenically-derived  $\text{nss-SO}_4^{2-}$  to total  $\text{nss-SO}_4^{2-}$  were estimated using only results observed during limited sampling period, but these results contributed to the distribution of biogenic  $\text{nss-SO}_4^{2-}$  over the Pacific Ocean.

#### 4. Conclusions

Latitudinal distributions of  $\text{nss-SO}_4^{2-}$ , MSA and  $\text{MSA/nss-SO}_4^{2-}$  ratio were investigated over the North and South Pacific during summer periods. While  $\text{nss-SO}_4^{2-}$  concentrations varied from 0.29 to  $2.6 \mu\text{g m}^{-3}$  and  $0.19\text{--}4.2 \mu\text{g m}^{-3}$  in the subarctic and subtropical western North Pacific due to significant influences of anthropogenic and volcanic sources, respectively, the mean MSA concentrations in the subarctic western North Pacific and the South Pacific, where air temperatures were relatively low and marine biological productivity was high, were  $0.061 \mu\text{g m}^{-3}$  (range:  $0.018\text{--}0.17 \mu\text{g m}^{-3}$ ) and  $0.043 \mu\text{g m}^{-3}$  (range:  $0.009\text{--}0.094 \mu\text{g m}^{-3}$ ), respectively. Although the mean concentration of MSA in the subarctic western North Pacific was a factor of 1.4 higher than that in the South Pacific, the mean  $\text{MSA/nss-SO}_4^{2-}$  ratio in the South Pacific was 3.7 times higher than that in the subarctic western North Pacific, indicating that aerosol  $\text{nss-SO}_4^{2-}$  plays an important role in the variation in  $\text{MSA/nss-SO}_4^{2-}$  ratio over the North and South Pacific during the summer periods. Furthermore, quite similar variation trends of air temperature between northern and southern hemispheres and a significant inverse relationship between air temperature and satellite-derived chlorophyll a concentration suggested that the latitudinal variations in  $\text{MSA/nss-SO}_4^{2-}$  ratio resulted from complex linkage between the distributions of  $\text{nss-SO}_4^{2-}$ , air temperature and biological productivity over the Pacific Ocean during the summer periods, and that the distributions of  $\text{nss-SO}_4^{2-}$ , MSA and  $\text{MSA/nss-SO}_4^{2-}$  ratio over the Pacific Ocean varied with latitude. Based on our results, we propose that the  $\text{MSA/nss-SO}_4^{2-}$  ratios observed through long-term monitoring in each oceanic region divided by latitude according to biological productivity and meteorological conditions, should be used to estimate the contribution of biogenically-derived  $\text{nss-SO}_4^{2-}$  to total  $\text{nss-SO}_4^{2-}$ . In addition, there is a strong need to continue aerosol sampling in both the subarctic western North Pacific and the South Pacific ( $>30^\circ \text{S}$ ) in order to compare seasonal variations of atmospheric sulfur species between these oceanic regions and to evaluate the continental influence on the variation, since the variation trends of air temperature and biological productivity were quite similar in these two regions.

It is worth noting that most previous studies used data on  $\text{nss-SO}_4^{2-}$  and MSA in marine aerosols observed through long-term monitoring to investigate temporal and spatial variations of these species, whereas we used only results observed during two cruises conducted over the North and South Pacific during the summer periods. However, the results for latitudinal variations of  $\text{nss-SO}_4^{2-}$ , MSA and  $\text{MSA/nss-SO}_4^{2-}$  ratio from this study will fill the data gap, especially for the subarctic western North Pacific and the South Pacific, and offer another perspective on distributions of these species over the Pacific Ocean since most previous studies were carried out at terrestrial sampling sites. Nevertheless, to improve

understanding of sulfur biogeochemical cycles more clearly, future fieldwork should focus on simultaneous and long-term monitoring of atmospheric oxidants as well as sulfur species in the marine atmosphere and the ocean.

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