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Reconstruction of sea surface dimethylsulfide in the North Pacific during 1970s to 2000s

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Abstract

We proposed an empirical equation of sea surface dimethylsulfide (DMS, nM) using sea surface temperature (SST, K), sea surface nitrate (SSN, μM) and latitude (L , $^{\circ}\text{N}$) to reconstruct the sea surface flux of DMS over the North Pacific between 25°N and 55°N : $\ln DMS = 0.06346 \cdot SST - 0.1210 \cdot SSN - 14.11 \cdot \cos(L) - 6.278$ ($R^2 = 0.63$, $p < 0.0001$). Applying our algorithm to climatological hydrographic data in the North Pacific, we reconstructed the climatological distributions of DMS and its flux between 25°N and 55°N . DMS generally increased eastward and northward, and DMS in the northeastern region became to 2 - 5 times as large as that in the southwestern region. DMS in the later half of the year was 2 - 4 times as large as that in the first half of the year. Moreover, applying our algorithm to hydrographic time series datasets in the western North Pacific from 1971 to 2000, we found that DMS in the last three decades has shown linear increasing trends of $0.03 \pm 0.01 \text{ nM y}^{-1}$ in the subpolar region, and $0.01 \pm 0.001 \text{ nM yr}^{-1}$ in the subtropical region, indicating that the annual flux of DMS from sea to air has increased by $1.9 - 4.8 \mu\text{mol m}^{-2} \text{ yr}^{-1}$. The linear increase was consistent with the annual rate of increase of 1 % of the climatological averaged flux in the western North Pacific in the last three decades.

Keywords: Dimethylsulfide; Algorithm; Decadal change; North Pacific

1. Introduction

DMS is produced by marine phytoplankton activity, and its content in the surface mixed layer is supersaturated with respect to the atmosphere. Consequently, the net flux of DMS is driven from sea to air. In the atmosphere, DMS is rapidly oxidized to form sulfur aerosols, and the cloud condensation nuclei derived from DMS acts to counter global greenhouse warming. Thus it is important to understand the spatiotemporal distribution of DMS flux for predicting future global climate change (e.g., Andreae, 1990). To understand the global oceanic distribution of DMS, several attempts have been tried to parameterize the global spatiotemporal distribution of sea surface DMS using oceanic climatological parameters (chlorophyll-a (Chl), light intensity (I), nutrients (N), surface mixed layer depth (MLD)) or using ocean models (Anderson et al., 2001; Simó and Dachs, 2002; Aumont et al., 2002; Chu et al., 2003; Belviso et al., 2004a). However, Belviso et al. (2004b) demonstrated that there were large uncertainties and spatial differences of sea surface DMS between these studies. Especially, in the North Pacific, even the algorithm of Simó and Dachs (2002) showing the results of being the most similar to the observational sea surface DMS, gave the values under half of the observational data.

On the other hand, recent studies of global climate change have reported the possibility that recent oceanic conditions have changed due to the effect of anthropogenically induced greenhouse warming and/or natural climate change (e.g., Levitus et al., 2000; Hansen et al., 2002). In the North Pacific, some studies have already showed the changes of chemical components with the decrease of sea surface water density, suggesting the weakening of the surface-deep water mixing derived from artificial greenhouse warming effects and/or natural climate change (Ono et al., 2001; Watanabe et al., 2001; Watanabe et al., 2003; Emerson et al., 2004). Consequently, the abundances of phytoplankton and Chl in the surface mixed layer have been shown to decrease in the North Pacific subpolar and subtropical regions (e.g., Gregg and Conkright, 2002; Chiba et al., 2004; Watanabe et al., 2005). In addition, Karl et al. (2001) indicated the increase of nitrogen fixing smaller-size phytoplankton in the subtropical region, and Ishida et al. (2006) demonstrated a possible of a shift in the phytoplankton

from larger size of $>3 \mu\text{m}$ to smaller size of $<3 \mu\text{m}$, suggesting the possibility a domain shift of phytoplankton from large size species to small size species as a high-producer group of DMS (e.g., Malin and Kirst, 1997). According to these biogeophysical decadal changes in the North Pacific, it is important to clarify whether the flux of oceanic DMS has changed or not. In the North Pacific, therefore, we tried to construct a spatiotemporal algorithm of sea surface DMS based on the observational sea surface DMS with other hydrographic multiple parameters in the North Pacific, and to reconstruct the long-term change of sea surface DMS in the North Pacific subpolar and subtropical regions during the last several decades.

2. Data and Method

2.1. Concept for construction of DMS algorithm

As the concentration of sea surface DMS relates to the phytoplankton activity (e.g., Malin and Kirst, 1997), we here assumed the concentration of DMS as the biological parameters relating to a growth rate of phytoplankton. It can be generally expressed by the following exponential function:

$$DMS = a \cdot B_o \cdot \exp(f_{(SST, I, N)}) \quad (1)$$

where ‘ a ’, ‘ B_o ’, ‘ SST ’, ‘ I ’ and ‘ N ’ are the coefficient of transformation from B_o to DMS , the initial phytoplankton biomass, the sea surface temperature, the light intensity, and the concentration of nutrient, respectively. Until now, it was difficult to measure both B_o and I with DMS in the observational time simultaneously. In many hydrographic observations, Chlorophyll-a (Chl) has generally been measured as an index of biological activity. It is possible that an averaged meridional pattern of I is roughly similar to that of the cosine of latitude due to derivation of sun radiation. Most of phytoplankton activities are generally limited by nitrate or iron in the surface mixed layer (e.g., Imai et al., 2002). We therefore tried to use Chl, the cosine of latitude at the observational position ($\cos(L)$) and the sea surface nitrate (SSN), as proxies of B_o , I and N , respectively:

$$DMS = a \cdot b \cdot Chl \cdot \exp (f_{(SST, \cos(L), SSN)}) \quad (2)$$

where ‘*b*’ is the coefficient of transformation from B_0 to *Chl*.

It is actually difficult to know $f_{(SST, \cos(L), SSN)}$ directly. In such case, the multiple linear regression technique has been generally useful to clarify the relationship between several parameters in many hydrographic researches (e.g., Sabine et al., 2004). Assuming that $f_{(SST, \cos(L), SSN)}$ can be expressed by multiple linear regression, therefore, we can obtain the following equation:

$$DMS = a \cdot b \cdot Chl \cdot \exp (c \cdot SST + d \cdot \cos (L) + e \cdot SSN + f) \quad (3)$$

where ‘*c - f*’ are constants. ‘*f*’ is the intercept in the multiple linear regression. Expressing Eqn. (3) as natural logarithm form, we can obtain the following equation:

$$\begin{aligned} \ln DMS &= \ln a + \ln b + \ln Chl + c \cdot SST + d \cdot \cos (L) + e \cdot SSN + f \\ &= \ln Chl + c \cdot SST + d \cdot \cos (L) + e \cdot SSN + g \end{aligned} \quad (4)$$

where ‘*g*’ is the sum of $\ln a$, $\ln b$ and *f*. Substituting all the observational DMS data equipped with Chl, SST and SSN for Eqn. (4) over the North Pacific, we tried to carry out a statistical test in order to validate the usefulness of each parameter in the multiple linear regression.

2.2. Data

To construct an algorithm of sea surface DMS (nM) over the North Pacific based on Eqn. (4), we used all the observational DMS data set equipped with Chl ($\mu\text{g/l}$), SST (K) and SSN (μM) from the 1980s to the 2000s over the northern North Pacific (Watanabe et al., 1995a; Watanabe et al., 1995b; Aranami et al., 2002; Wong et al., 2005; Institute of Ocean Sciences, 2006; our new data) (the

component in each decade: 1980s (14 %), 1990s (67 %), 2000s (19 %)) (Fig. 1 and Table 1). All the data set we addressed were 504 data set collected in 0 m – 20 m depths in the region from 25 °N to 55 °N, including all seasons (the component in each period: January-March (18 %), April-June (43 %), July-September (36 %), October-December (3 %)). DMS was usually measured by the general pre-concentrated gas-chromatographic method (e.g., Watanabe et al., 1995a). We also used the datasets of Chl and SSN measured by the solvent extraction photofluorimetric method (Yentsch and Menzel, 1963), and the copper-cadmium sulfanilamide reduction method (Strickland and Parsons, 1968). The precisions of DMS, SSN and Chl were estimated to be approximately $\pm 6\%$, $\pm 2\%$ and $\pm 10\%$, respectively, which were obtained from duplicate determinations in the surface water.

3. Results and Discussion

3.1. Parameterization of sea surface DMS over the North Pacific

In general, the F-test is used to validate the usefulness of each parameter in the multiple linear regression. In this our study, the parameter with F value of more than 2.4 has a significant meaning (e.g., Wilks, 1995), indicating that it is useful to obtain an empirical equation in the multiple linear regression. By using a stepwise linear fitting regression for Eqn. (4) with F-test, the first term of right-hand side in Eqn. (4), $\ln Chl$ was only found to become negligible ($F = 1.9$) due to $F < 2.4$ and it can therefore be deleted. We obtained the algorithm for sea surface DMS as follows (Fig. 2a).

$$\ln(DMS) = 0.06346 \cdot SST - 0.1210 \cdot SSN - 14.11 \cdot \cos(L) - 6.278$$

$$(R^2 = 0.63, p < 0.0001, RMSE = 0.65, n = 504; F = 12 \text{ for } SST, F = 35 \text{ for } SSN, F = 630 \text{ for } \cos(L)) \quad (5)$$

where ' R^2 ', ' p ', ' $RMSE$ ' and ' n ' are the coefficient of determination, the probability at a 95 % confidence level, the root mean standard error of regression and the number of samples, respectively.

This algorithm can explain 63 % of the variance of sea surface DMS with RMSE of 1.9 nM over the North Pacific in the last three decades, without using Chl. The sensitivity of our algorithm to each parameter between 25 °N and 55 °N was 0.1 nM/°C, 0.2 nM/μM-SSN and 0.3 nM/degree-L, which was derived from the coefficient of each parameter in Eqn. (5). Our algorithm of DMS largely depends on $\cos(L)$ as a function of latitude. Kettle et al. (1999) showed that sea surface DMS had good correlation with latitudinal position from 25 °N to 70 °N although there are no similar correlations on a global scale. Some studies also reported no correlation between sea surface DMS and Chl (e.g., Watanabe et al., 1995a). Thus the selection of parameters in our algorithm could be adequate to reconstruct the sea surface DMS in the North Pacific.

We here tried to compare our DMS algorithm with the previous study's algorithm that showed the results of being the most similar to the observational DMS (Simó and Dachs, 2002). The algorithm of Simó and Dachs (2002) was based on the ratio of Chl and the surface mixed layer depth with a difference of $0.125 \sigma_\theta$ from the surface density (MLD, m). Thus we here used the same data set of Chl as used to construct our DMS algorithm (see Subsection 2.2). In these observational data positions, we calculated the monthly MLD based on climatological monthly data of temperature and salinity from World Ocean Atlas 2001 (WOA 2001) (Stephens et al., 2002; Boyer et al., 2002). Applying the above Chl and MLD into their algorithm, we compared the results of sea surface DMS between theirs and our algorithm. Their algorithm led to significant scatter ($R^2 = 0.19$, $RMSE = 0.96$, $n = 504$) (Fig. 2b), suggesting that our algorithm is more advantageous way than the previous other ones due to $R^2 = 0.63$ for our algorithm, in order to reconstruct the spatiotemporal distribution of sea surface DMS over the North Pacific.

Furthermore, evaluating the usefulness of our algorithm of sea surface DMS in the North Pacific, we tried to apply our algorithm to the independent observational data of sea surface DMS, the eastern Pacific (EP) line data along 140 °W from 25 °N to 55 °N (April-May in 1993, $n = 163$) (Bates and Quinn, 1997) which were not used to obtain Eqn. (5), because this region was covered by the construction of our algorithm (Fig. 1 and Table 1). We here used an empirical equation of SSN

derived from SST and Chl (Goes et al., 2000) in order to apply SSN to Eqn. (5) because the EP line had no data of SSN despite being of the dataset of SST and Chl. In both observed and predicted DMS, we found that an averaged concentration of sea surface DMS increased northward in EP line (Fig. 2a), which were consistent with the general previous work (Kettle et al., 1999). The predicted DMS agreed with these independent observational data of sea surface DMS within the uncertainty of our approach that discussed in the above section, suggesting that our algorithm of sea surface DMS is useful over the North Pacific at least in the region from 25 °N to 55 °N.

3.2. Reconstruction of climatological monthly sea surface DMS in the North Pacific using WOA 2001

To understand the climatological distributions of sea surface DMS and its flux is an essential step for clarifying the long-term changes of DMS in the North Pacific. Thus we estimated the monthly mean concentration of sea surface DMS in the North Pacific by using climatological monthly mean dataset of SST and SSN from WOA 2001 (Stephens et al., 2002; Conkright et al., 2002) with our DMS algorithm (Fig. 3). In the North Pacific, the concentration of sea surface DMS generally increased eastward and northward. DMS in the northeastern region become to 2 - 5 times as large as that in the southwestern region, which agreed with the previous observational works (e.g., Kettle et al., 1999). In addition, we found that the concentration of sea surface DMS in the later half of the year (July – December) was 2 - 4 times as large as that in the first half of the year (January – June). In this period, DMS in the northeastern region remarkably increases by more than 10 nM while DMS almost did not change in the southwestern region, which agreed with the previous observational results (Wong et al., 2005; Kettle et al., 1999). We estimated that the annual mean concentration of sea surface DMS was 2.2 nM between 25 °N and 55 °N in the North Pacific, which was equal to that in the previous observational work (Kettle et al., 1999). In general, larger size phytoplanktons such as *diatoms* are dominant to other species in the North Pacific. The concentration of silicate in the North Pacific surface mixed layer decreases eastward (Conkright et al., 2002), and consequently the

abundance of phytoplanktons with calcification such as *coccolithophorids* increases eastward (e.g., Honda, 2003). Compared to the western North Pacific, in the eastern North Pacific region where low *diatom* production and high calcification occurs (e.g., Wong et al., 2002), the increase of phytoplanktons with calcification such as *coccolithophorids*, seemed to bring the higher concentration of sea surface DMS. In the first half of the year, *diatoms* bloom and their biomass decreases with the depletion of silica and/or iron. In the second half of the year, smaller size phytoplanktons such as *coccolithophorids* become dominant instead of *diatoms* (e.g., Honda et al., 2002). The difference of phytoplankton species as a producer group of DMS (e.g., Malin and Kirst, 1997) between the eastern and western regions may mainly cause the spatiotemporal distribution of DMS in the North Pacific.

According to Fig. 3, multiplying the monthly DMS_p with the climatological monthly wind data at 10 m height calculated from the NCEP/NCAR reanalysis data (NCEP/NCAR Reanalysis Project, 2006), the gas transfer velocity according to Wanninkhof and McGillis (1999), and the Schmidt number calculated according to Saltzman et al. (1993), and integrating the above estimation between 25 °N and 55 °N in the North Pacific, we here calculated the annual total flux of DMS from sea to air (F_{DMS}) over this region. In this region, we estimated the climatological seasonal F_{DMS} to be 0.08 Tg-S yr⁻¹ ($T=10^{12}$) from January to March, 0.07 Tg-S yr⁻¹ from April to June, 0.15 Tg-S yr⁻¹ from July to September, and 0.17 Tg-S yr⁻¹ from October to December, indicating that F_{DMS} in the later half of the year (July – December) is about 70 % of total annual flux of DMS over this region (0.47 Tg- S yr⁻¹). In this region that corresponds to 8 % of global ocean's area, the climatological annual total flux of DMS from sea to air was found to be 1 – 3 % of global flux of DMS predicted in the previous works (e.g., Bates et al., 1992; Watts, 2000), which is smaller than the global mean flux of DMS per area. The main reason may be due to exiguousness of small size species as a high-producer group of DMS (e.g., Malin and Kirst, 1997) compared to the North Atlantic Ocean despite this region being one of the largest primary productivity derived from the *diatom* species (e.g., Honda et al., 2002).

3.3. Decadal changes of sea surface DMS

To understand the possibility of decadal change of DMS in the ocean is an important step for clarifying the impact of DMS flux from sea to air on global warming. However, it may be difficult for the present DMS algorithms to estimate the decadal change of DMS. In even our algorithm of DMS, there was a large error of 1.9 nM. If we here try to apply our algorithm to an arbitrary fixed ocean observational point, the third term of right-hand side ($\cos(L)$) in Eqn. (5) of our algorithm can be addressed as a constant for time although both SST and SSN have temporal changes. The relative error of $\cos(L)$ becomes zero. Consequently, if we focus on the relative temporal change of sea surface DMS in arbitrary fixed observational point, RMSE can decrease by 0.7 nM in our algorithm, which is about one third relative to original RMSE in our algorithm. Thus it may allow us to estimate the decadal change of sea surface DMS in the arbitrary fixed observational point by using our algorithm of DMS.

We here applied our algorithm to the time series data of hydrographic parameters including SST and SSN in the subpolar (SP) and subtropical (ST) regions in the western North Pacific from 1971 to 2000 that was conducted by Japan Meteorological Agency (2001) (Fig. 1 and Table 1), which is also available from the Japan Oceanographic Data Center [<http://www.jodc.go.jp/service.htm>]. In SP region, the R/V Kofu-Marui has conducted the hydrographic observations 4 - 5 times a year at one degree interval along 42 °N in the Oyashio region. In general, in the western North Pacific subpolar region, we can find the largest phytoplankton bloom from April to June and the strongest stratification of the surface mixed layer from July to September (e.g., Tsurushima et al., 2002). Thus we divided the time series data into four seasonal periods (January – March (J-M), April - June (A-J), July-September (J-S), October – December (O-D)). On the other hand, in ST region, the R/V Ryofu-Marui has observed the hydrographic data at one degree interval from 25 °N to 34 °N along 137 °E in the winter (January–February (J-M)) and the summer (August – September (J-S)). We addressed an averaged seasonal value of each parameter (SST and SSN) in the two regions, which was expressed as three-year running mean composites with standard errors (SE, $\pm 1\sigma$) for neglecting large anomaly of DMS derived from anomalies of observed SST and SSN.

We here demonstrated the temporal change of sea surface DMS (DMS_p) reconstructed in each season in the western North Pacific by using Eqn. (5) (Figs. 4a and 4b). To confirm the temporal usefulness of our algorithm, we also plot the independent observational data of sea surface DMS (DMS_o) (2004 in SP region; 1991 in ST region) in each season (Figs. 4a and 4b, Table 1), which were not used to obtain Eqn. (5). In SP region, an averaged difference between DMS_p and DMS_o was 0.3 ± 0.01 nM, and DMS_p in all seasons were consistent with DMS_o within RMSE of 0.7 nM. On the other hand, in ST region, we found that DMS_p agreed with DMS_o within the difference of 0.2 ± 0.1 nM, which was also consistent with DMS_o within RMSE of 0.7 nM although DMS_p in wintertime was slightly higher than DMS_o due to probably the insufficient of wintertime data for constructing our algorithm and due to the low SSN values close to detection limit. Considering the above results, it is possible that our algorithm could be useful for reconstructing the decadal change of sea surface DMS in the western North Pacific.

We tried to clarify the decadal changes of DMS in the western North Pacific. In both SP and ST regions, we found that the climatological averaged value of DMS_p from July to December was significantly higher (average: SP region = 2.8 ± 0.1 nM; ST region = 1.5 ± 0.02 nM) than that from January to June (average: SP region = 0.7 ± 0.1 nM; ST region = 0.9 ± 0.01 nM). In general, *diatoms* are dominant to other species in the North Pacific. In the first half of the year, they bloom and their biomass decreases with the depletion of silica and/or iron. In the second half of the year, smaller size phytoplanktons such as *coccolithophorids* become dominant instead of diatoms (e.g., Honda et al., 2002). In addition, from the first to the second halves of the year, Imai et al. (2002) found the remarkable decrease of larger size phytoplankton ($>10\mu\text{m}$ fraction) from 34 % to 8% in the western North Pacific. The differences of sea surface DMS between the first and second halves of the year, may be influenced by the seasonal change of different phytoplankton species.

Moreover, we here focused on the long-term trend of sea surface DMS. By using the simple linear regression, DMS_p has significantly shown an averaged linear increase of 0.03 ± 0.01 nM yr^{-1} in SP region ($p < 0.01$), and 0.01 ± 0.001 nM yr^{-1} in ST region ($p < 0.01$), indicating that the sea surface

DMS has increased by 0.9 nM in SP region, and by 0.3 nM in ST region during the past three decades. Even if considering RSME of 0.7 nM in our algorithm, DMS in SP region significantly had shown the linear increasing trend at least in the last three decades while that in ST region may increase although it was not significant. In the two regions, some studies reported that water temperature has increased by 0.2 - 1.5 °C yr⁻¹ and the concentration of nitrate has decreased by 0.3 – 1.5 μM yr⁻¹ in the past three decades (Watanabe et al., 2003; Chiba et al., 2004; Watanabe et al., 2005). Because the sensitivity of DMS in our algorithm between 25 °N and 55 °N has 0.1 nM/°C and 0.2 nM/μM-SSN respectively, these parameters' changes can explain 75 % of an averaged increase of DMS in the two regions in the past three decades in the case of maximum decadal changes of water temperature and nitrate. It suggested that our algorithm is almost useful to construct the spatiotemporal distribution of sea surface DMS at least in the western North Pacific.

In order to clarify the extent of decadal periodicity of DMS with the long-term linear trend, according to previous studies (Ono et al, 2001; Watanabe et al., 2003; Watanabe et al., 2005), we assumed that the long-term change of sea surface DMS can be expressed by the Fourier sine expansion as follows:

$$DMS = h \cdot y + i + j \cdot \sin \{2\pi(y - k) / l\} \quad (6)$$

where 'y' is the calendar year, 'h'-'l' are constants. Applying this equation to time series of DMS_p in Fig. 4, we found the averaged periodicity of 11.9 ± 0.5 years in the two regions ($R = 0.70 \pm 0.05$, $p < 0.05$), superimposed on the above linear increasing trend. Although the periodicity of DMS has slightly been shorter than those of O₂, PO₄ and Chl over the North Pacific (oscillation of about 18 year) (Ono et al., 2001; Watanabe et al., 2003; Watanabe et al., 2005), the increasing trend of DMS seemed to be opposite to the temporal decreasing trends in diatom and zooplankton biomass (Chiba et al., 2004). The decreases of diatom and zooplankton biomass may affect the increase of sea surface DMS due to the increase of smaller size phytoplankton as a high producer group of DMS and the

decline of grazing effect of zooplankton, although it is actually difficult to clearly explain the cause of decadal periodicity of DMS due to the complicated changes of hydrographic biogeophysical parameters.

Recent reports showed that Chl has declined in the past three decades in both the subpolar and subtropical regions in the western North Pacific due to the weakening of the surface-deep water mixing (Watanabe et al., 2001; Gregg and Conkright, 2002; Chiba et al., 2004; Watanabe et al., 2005), indicating the decrease of larger size phytoplankton as *diatoms* (Chiba et al., 2004). The weakening of the surface-deep water mixing was caused by both the increasing temperature and the decreasing salinity in the two regions (Ono et al., 2001; Andreev and Watanabe, 2002; Watanabe et al., 2003; Watanabe et al., 2005). Consequently, MLD has shoaled although the long-term trend of MLD has been not significant due to large variation, and the nutrients in the surface mixed layer have decreased (Watanabe et al., 2005). In addition, some studies have already reported that the blooms of phytoplankton producing DMS tend to be restricted in shallower mixed layer (e.g., Malin and Kirst, 1997). Karl et al. (2001) and Ishida et al. (2006) also showed the possibility of a domain shift of phytoplankton from larger size to smaller size in the North Pacific in the past several decades. In the high latitude of North Pacific, smaller size phytoplanktons such as *coccolithophorids* may tend to be dominant with the decline of grazing effect of zooplankton instead of diatoms (e.g., Chiba et al., 2004). Thus the linear increasing trend of sea surface DMS with the decadal periodicity may be caused by the above domain shift of phytoplankton derived from the weakening of the surface-deep water mixing in the North Pacific.

Moreover, we estimated the decadal change in flux of DMS from sea to air (F_{DMS}) in SP and ST regions, by multiplying DMS_p with the seasonal wind data at 10 m height from the NCEP/NCAR reanalysis data (NCEP/NCAR Reanalysis Project, 2006), the gas transfer velocity according to Wanninkhof and McGillis (1999), the Schmidt number calculated according to Saltzman et al. (1993) and Eqn. (5) (Figs. 4c and 4d). We found that the annual averaged F_{DMS} was $248 \pm 10 \mu\text{mol m}^{-2} \text{yr}^{-1}$ in ST region, and $336 \pm 53 \mu\text{mol m}^{-2} \text{yr}^{-1}$ in SP region. In the later half of the year, we found higher

averaged F_{DMS} over $250 \mu\text{mol m}^{-2} \text{yr}^{-1}$ in both regions (J-S in ST region = $280 \pm 10 \mu\text{mol m}^{-2} \text{yr}^{-1}$; J-S in SP region = $303 \pm 30 \mu\text{mol m}^{-2} \text{yr}^{-1}$; O-D in SP region = $872 \pm 81 \mu\text{mol m}^{-2} \text{yr}^{-1}$), which were derived from the high content of DMS, the low Schmidt number and/or the strong wind speed. In the second half of the year in the past thirty years, the linear trend of F_{DMS} has increased by $2.8 \mu\text{mole m}^{-2} \text{yr}^{-1}$ in ST region ($p < 0.01$), and by $18.8 \mu\text{mole m}^{-2} \text{yr}^{-1}$ in SP region ($p < 0.01$), which was equal to the seasonal rate of increase of 1 - 2 % of the climatological seasonal averaged F_{DMS} in the two region. Converting the above seasonal linear increasing trends of F_{DMS} into annual averages, we estimated a linear increase of $1.9 - 4.8 \mu\text{mole m}^{-2} \text{yr}^{-1}$, which was equal to the annual rate of increase of about 1 % of the climatological annual averaged F_{DMS} in the two regions in the last three decades in the western North Pacific.

4. Concluding remarks

We established an empirical equation of sea surface DMS (nM) using sea surface temperature (SST, K), sea surface nitrate (SSN, μM) and latitude (L, $^{\circ}\text{N}$) to reconstruct the sea surface flux of DMS over the North Pacific between 25°N and 55°N : $\ln \text{DMS} = 0.06346 \cdot \text{SST} - 0.1210 \cdot \text{SSN} - 14.11 \cdot \cos(L) - 6.278$ ($R^2 = 0.63$, $p < 0.0001$).

Applying our algorithm to climatological hydrographic datasets in the North Pacific, we reconstructed the climatological monthly distribution of DMS. We found that the concentration of sea surface DMS generally increased eastward and northward, and DMS in the northeastern region became to 2 - 5 times as large as that in the southwestern region. The concentration of DMS in the later half of the year (July – December) was 2 - 4 times as large as that in the first half of the year (January – June).

Furthermore, applying our algorithm to hydrographic time series datasets in the western North Pacific from 1971 to 2000, we demonstrated that sea surface DMS in the last three decades has shown the linear increasing trends of $0.03 \pm 0.01 \text{ nM yr}^{-1}$ in the subpolar region, and $0.01 \pm 0.001 \text{ nM yr}^{-1}$ in the subtropical region, indicating that the annual flux of DMS from sea to air has increased by 1.9 –

4.8 $\mu\text{mol m}^{-2} \text{yr}^{-1}$ in the western North Pacific. The increase was equal to the annual rate of increase of about 1 % of the climatological annual averaged F_{DMS} in the western North Pacific in the last three decades

Satellite measurements have recently reproduced detailed spatiotemporal distribution of SST, Chl and the wind speed. On the other hand, Goes et al. (2000) has already reported an algorithm of SSN derived from SST and Chl with high precision. Using satellite data with their SSN algorithm, our algorithm will allow us to estimate the detailed spatiotemporal distributions of sea surface DMS and its flux over the North Pacific, and to detect the detailed seasonal change and decadal trend of DMS in the future.

However, it may be difficult to apply our present algorithm to the future prediction of DMS due to insufficient observational time-series of DMS with other hydrographic parameters. It would be necessary to improve the algorithm of DMS based on the many observational data. To improve the algorithm, it is an essential step to collect DMS data equipped with multiple hydrographic parameters such as chlorophyll-a, water temperature and nutrients in the data centers having many hydrographic observational data (e.g., Global Surface Seawater Dimethylsulfide Database, 2006). Unfortunately, there were actually few datasets of multiple hydrographic parameters with DMS data in the data centers. In the future, it will be necessary to continue obtaining accurate and long time series data of DMS with other hydrographic parameters and collecting them over the North Pacific to predict the effect of DMS on global warming.

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Figure Captions

Figure 1

Map for the North Pacific indicating the positions of data set of DMS, Chl, SST and SSN used in this study. A bold dotted line, ‘EP’ indicates the positions of independent DMS dataset set along 140 °W from 25 °N to 55 °N (Bates and Quinn, 1997) which were not used to construct our DMS algorithm (see Subsection 3.1 and Table 1). Bold lines, ‘SP’ and ‘ST’ are the subpolar and subtropical time series datasets of hydrographic parameters from 1971 to 2000, respectively (Japan Meteorological Agency, 2001) (see Subsection 3.3 and Table 1).

Figure 2

Plots of the observed DMS (DMS_o , nM) versus the predicted DMS (DMS_p , nM) over the North Pacific. (a) The plot of DMS_o and DMS_p estimated from Eqn. (5) in our study ($R^2 = 0.63$, $RMSE = 0.65$ (or ± 1.9 nM), $n = 504$). Solid line represents the 1:1 line between DMS_o and DMS_p . Both DMS_o and DMS_p are shown as natural logarithm values. We also showed the comparison between DMS_o and DMS_p in the EP line. Gray triangle, square and circle were the averaged value of sea surface DMS south of 30 °N, that from 30 °N to 40 °N, and that north of 40 °N, respectively. We here applied an empirical equation of SSN derived from SST and Chl (Goes et al., 2000) to the EP line because the EP line had no data of SSN despite being of the dataset of SST and Chl. The error bars indicate the standard errors of averaged values (SE). (b) Same as Fig. 2a, but calculated from the algorithm of Simó and Dachs (2002) ($R^2 = 0.19$, $RMSE = 0.96$ (or ± 2.6 nM), $n = 504$). The algorithm was based on the ratio of Chl and the surface mixed layer depth with a difference of $0.125 \sigma_\theta$ from the surface density (MLD, m). Thus we here used the same data set of Chl as used to construct our DMS algorithm (see Subsection 3.1, Fig. 1 and Table 1). In these hydrographic data positions, we calculated the monthly MLD based on climatological temperature and salinity data from World Ocean

Atlas 2001 (Stephens et al., 2002; Boyer et al., 2002). Applying the above Chl and MLD into their algorithm, we obtained the relationship between DMS_o and DMS_p .

Figure 3

Climatological distributions of monthly sea surface DMS_p (nM) in the North Pacific between 25 °N and 55 °N. These results were reconstructed by using Eqn. (5) with climatological monthly SST and SSN of World Ocean Atlas 2001 (Stephens et al., 2002; Conkright et al., 2002).

Figure 4

Time series of DMS_p (nM) and F_{DMS} ($\mu\text{mol m}^{-2} \text{yr}^{-1}$) in SP and ST regions of the western North Pacific. DMS_p was estimated by substituting SST and SSN in the time series datasets for Eqn. (5) (see Subsection 3.3, Fig. 1 and Table 1). We also estimated F_{DMS} by multiplying DMS_p with the seasonal wind data at 10 m height from the NCEP/NCAR reanalysis data (NCEP/NCAR Reanalysis Project, 2006), the gas transfer velocity according to Wanninkhof and McGillis (1999), the Schmidt number calculated according to Saltzman et al. (1993). We showed an averaged value as three-year running mean composites with the standard error (SE) (J-M: black open circles; A-J: green open squares; J-S: red open triangles, O-D: blue open diamonds). Each solid symbol with SE is the averaged value of sea surface DMS observed in the same region in 2004 in SP region and in 1991 in ST region, which was not used to obtain our DMS algorithm. We also showed the linear regression line (solid line) and the non-linear fitting curve (bold dotted curve) which was estimated by the Fourier sine expansion with a 95 % confidence level. (a) DMS_p in SP region. (b) DMS_p in ST region. (c) F_{DMS} in SP region. (d) F_{DMS} in ST region. The linear increasing trends of DMS_p and F_{DMS} were significantly found as follows: DMS_p (J-M) in SP = 0.01 nM yr^{-1} ($p < 0.01$); DMS_p (J-S) in SP = 0.03 nM yr^{-1} ($p < 0.05$); DMS_p (O-D) in SP = 0.04 nM yr^{-1} ($p < 0.01$); DMS_p (J-M) in ST = 0.01 nM yr^{-1} ($p < 0.01$); DMS_p (J-S) in ST = 0.01 nM yr^{-1} ($p < 0.01$). F_{DMS} (J-M) in SP = 1.4 $\mu\text{mol m}^{-2} \text{yr}^{-1}$ ($p < 0.05$); F_{DMS} (A-J) in SP = -1.1 $\mu\text{mol m}^{-2} \text{yr}^{-1}$ ($p < 0.05$); F_{DMS} (O-D) in SP = 18.8 $\mu\text{mol m}^{-2} \text{yr}^{-1}$ ($p < 0.01$); F_{DMS} (J-M) in ST

= $0.9 \mu\text{mol m}^{-2} \text{yr}^{-1}$ ($p < 0.05$); F_{DMS} (J-S) in ST = $2.8 \mu\text{mol m}^{-2} \text{yr}^{-1}$ ($p < 0.01$).

Table 1. A list of cruise information for DMS data set used in this study.

Cruise name	Sampling date	Sampling area	Numbers of data	References
<DMS, Chl, SSN and SST data set to construct DMS algorithm>				
KH1988	Jun.-Aug. 1988	54°N-31°N, 140°E-126°W	71	Watanabe et al. (1995a, 1995b)
KH1997	Jun.-Sep. 1997	55°N-42°N, 148°E-140°W	20	Aranami et al. (2002)
IOS-1996-2001	May 1996 – Aug. 2001	50°N-48°N, 144°W-126°W	255	Wong et al. (2005), IOS (2006)*
OS1990	Jul. 1990-Jul.2002	54°N-37°N, 160°W-148°W	37	this study
KH1991	Jan.-Feb. 1991	27°N-30°N, 135°E-141°W	67	this study
KT1991	Jun. 1991	34°N-27°N, 133°E-142°E	40	this study
HNF2002-2003	Jun. 2002-Jun.2003	43°N-39°N, 145°E-147°E	14	this study
<DMS data set to evaluate the validity of DMS algorithm>				
(Eastern Pacific: EP)				
Surveyor 1993	Apr.-May 1993	25°N-55°N, 140°W	163	Bates and Quinn (1997)
(Subpolar region: SP)				
HNF2004-2005	Jan. 2004 - Jan. 2005	43°N-39°N, 145°E-147°E	39	this study
(Subtropical region: ST)				
KH1991	Jan.-Feb. 1991	27°N-30°N, 137°E-139°W	6	this study
KT1991	Jul. 1991	27°N-30°N, 135°E-141°W	7	this study
<Hydrographic data set to reconstruct the time series of DMS >				
(Subpolar region: SP)				
Kofu	Feb.1971 – Dec. 1998	42°N, 144°E-147°E	866	JMA(2001)**
(Subtropical region: ST)				
Ryofu	Jan.-Feb. Aug.-Sep. 1971 – 2000	34°N-25°N, 137°E	1100	JMA(2001)**

*: Institute of Ocean Sciences

**: Japan Meteorological Agency

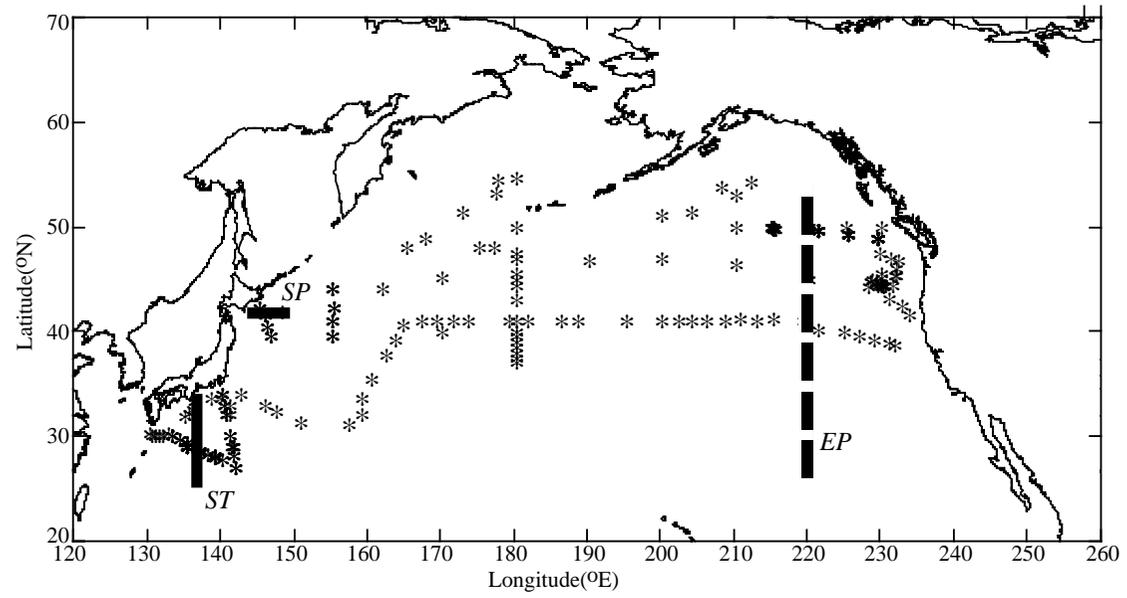


Fig. 1/Watanabe et al.

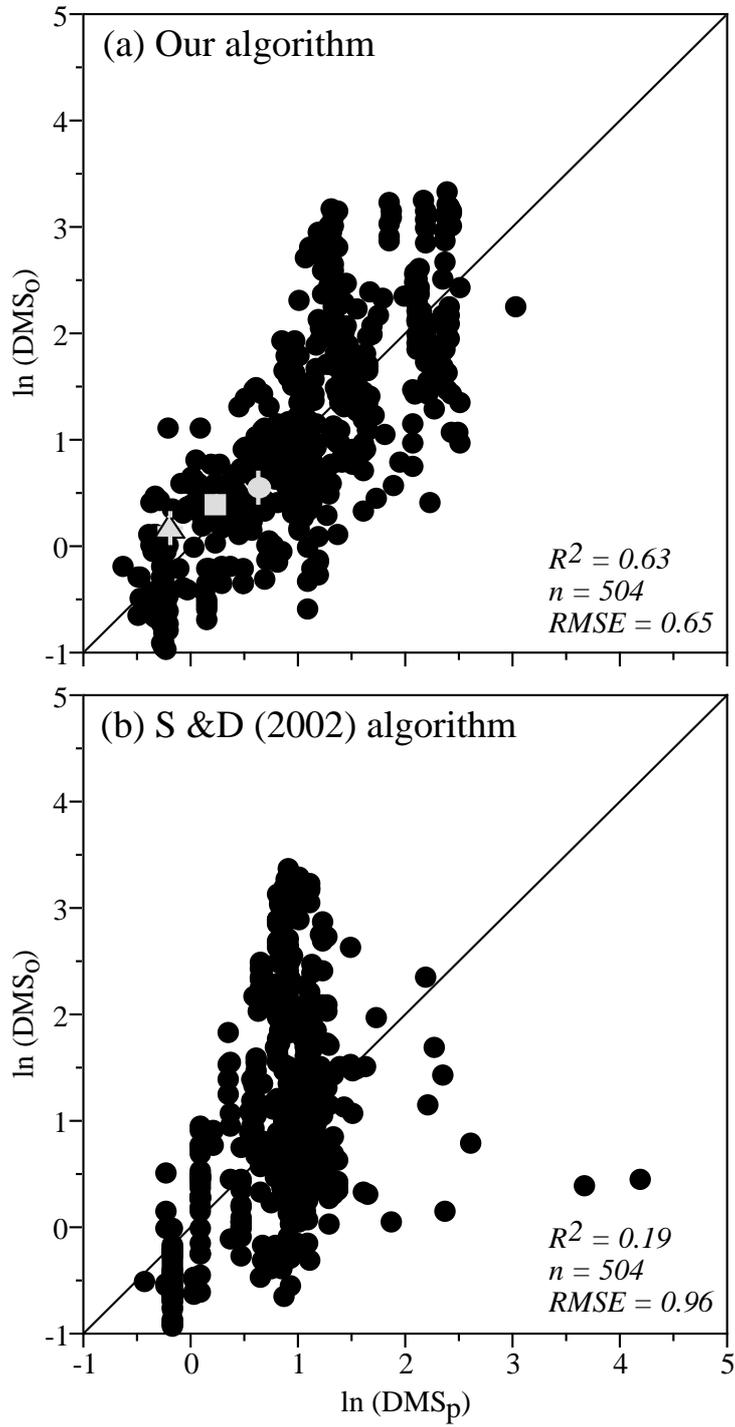


Fig. 2/Watanabe et al.

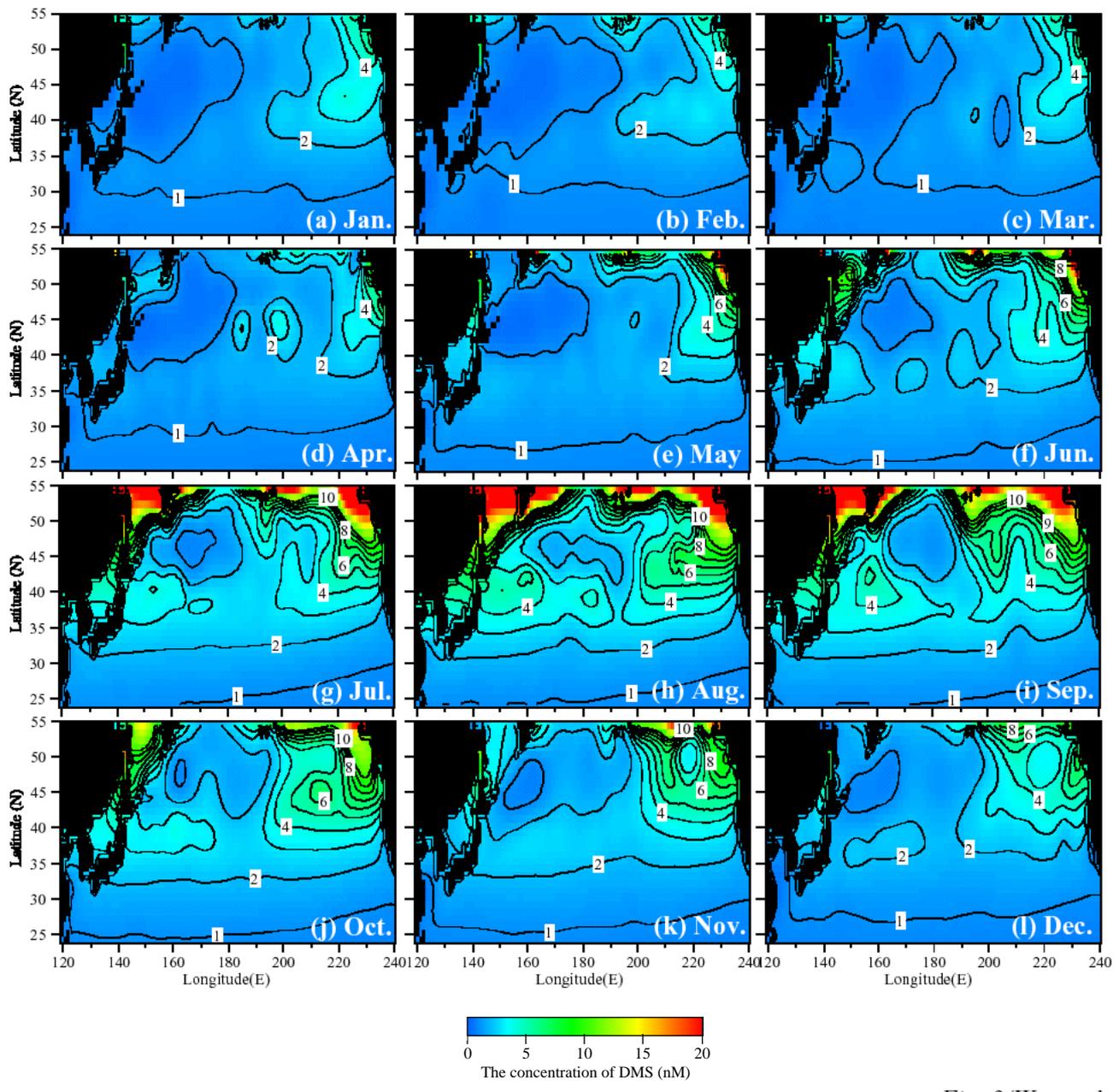


Fig. 3/Watanabe et al.

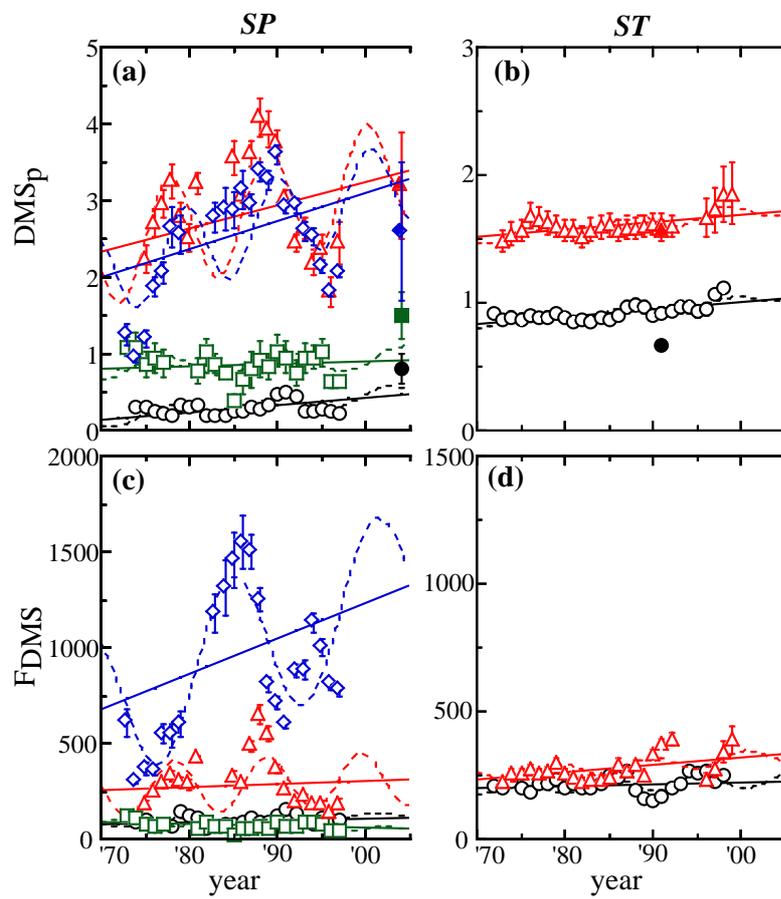


Fig.4/Watanabe et al.