Air-sea fluxes of dimethyl sulfide and acetone measured by the gradient flux technique in the equatorial, subtropical and subarctic Pacific Ocean

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Introduction

Quantification of the flux of dimethyl sulfide (DMS) and volatile organic compounds (VOCs) from the ocean to the atmosphere remains an essential task for assessing global budgets and environmental impacts of these species. The flux is commonly estimated by the air-sea concentration gradient (ΔC) and a gas transfer rate (k), **F = k ΔC.** The previous estimates of k are different between researchers and variable depending on the solubility of the gas. We applied the gradient flux (GF) technique using proton transfer reaction-mass spectrometry (PTR-MS) which allows online measurement of various VOCs with high sensitivity (pptv levels) and rapid response time. This technique has potential advantage of measuring the sea-to-air flux of multiple VOCs simultaneously.

The objective of this study is to investigate the flux of DMS and acetone from ocean to atmosphere in the equatorial, subtropical and subarctic Pacific Ocean using the GF technique combined with PTR-MS.

Study Sites

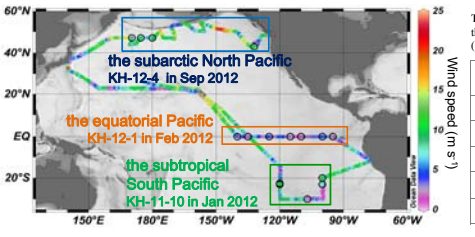


Figure 1. Study sites of the GF observation (black circles). The observations were made aboard the R/V *Hakuhou Maru* in three areas. Track chart is shown by the degree of wind speed.

Table 1. Temperature, wind speed and DMS concentration in the surface seawater at three areas. Each data is the average (1 SD).

	Equatorial	Subtropical	Subarctic
Date	2/8-14	1/14-21	9/3-27
Air temp (°C)	24.6	22.9	14.0
Sea temp (°C)	24.4	23.8	14.1
Wind speed at 14 m (m/s)	2.1	3.5	7.3
DMS sea (nM)	1.9 (0.3)	3.7 (0.9)	3.2 (1.0)

Gradient Flux technique

$$F_c = -\frac{\kappa u_*}{\phi_c}\frac{\partial c}{\partial \ln z}$$

Eddy diffusivity — Slope of VOC concentration

Figure 2. a) The profiling buoy
Air samples were obtained at 7 heights; from 1 to 210 cm at the buoy and about 1400 cm at the upper deck of the ship.

b) VOCs concentration measurement
DMS and acetone concentrations of sample air were continuously measured by PTR-MS. Sampling height was shifted by 1 min interval (1 profile = 7 min). Total observation time was 3-12 hours at each site.

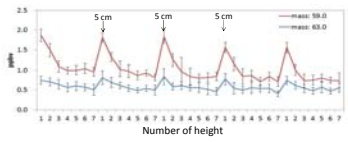
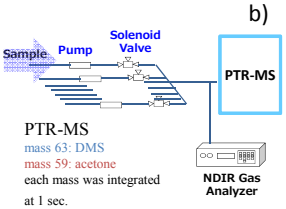
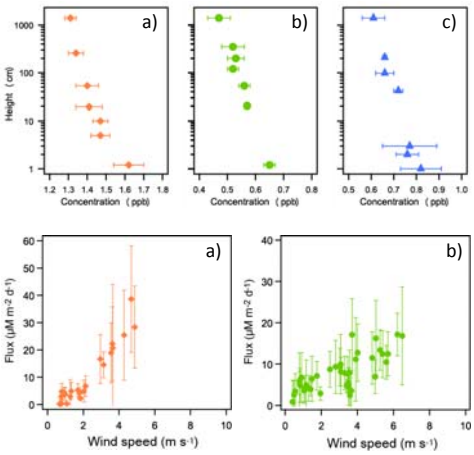


Figure 3. DMS and acetone concentrations during the GF observation. Error bars were 1 SD.



DMS profiles and flux



←**Figure 4.** Profiles of DMS in a) the equatorial, b) the subtropical and c) the subarctic oceans. The concentrations are averaged for 28 min (4 profiles) and error bars are 1 SD.

↓**Figure 5.** DMS flux as a function of wind speed in a) the equatorial, b) the subtropical and c) the subarctic oceans. The fluxes are averaged for 28 min and error bars represent the 95% confidence interval of the slope of the profiles.

Gas transfer rate of DMS

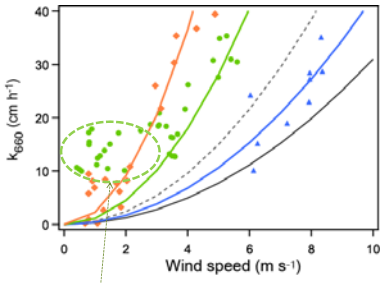


Figure 6. Gas transfer rate (k_{660}) of DMS flux.

$$k_{660} = \frac{Flux}{\Delta C \times (Sc_{DMS}/660)^{-1/2}}$$

Equatorial	k_{660} = 2.3 U^2 (R^2 = 0.83)
Subtropical *	k_{660} = 1.1 U^2 (R^2 = 0.90)
Subarctic	k_{660} = 0.43 U^2 (R^2 = 0.63)
Wanninkhof (1992) [1]	k_{660} = 0.31 U^2
Zemmelink et al. (2004) [2]	k_{660} = 0.60 U^2

*In the subtropical ocean, the relationship between k_{660} and U_2 is described using the data at wind speeds over 3.5 m s^{-1}.

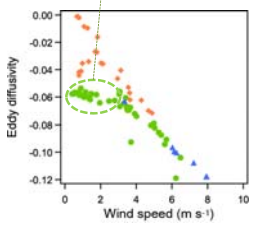


Figure 7. Eddy diffusivity as a function of wind speed.

- In the subtropical ocean, the transfer rate (k) was not driven by wind speed but by surface turbulent diffusion at weak wind speeds (< 3.5 m s^{-1}).

Acetone profiles and flux

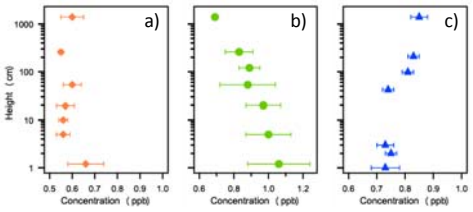


Figure 8. Same as Figure 4 but for acetone.

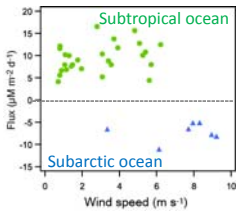


Figure 9. Acetone flux in the subtropical and subarctic oceans.

- The profiles and the calculated flux showed that the subtropical ocean was source region and the subarctic ocean was sink region for acetone.
- There was no clear relationship between acetone flux and wind speed.

Conclusion

- The GF technique combined with PTR-MS was able to determine the flux of DMS and acetone in the equatorial, subtropical and subarctic Pacific Ocean.
- The gas transfer rate depended on wind speed, and their relationships (k_{660} vs U_2) varied with the region. In the subtropical ocean, the transfer rate was dominated by the eddy diffusion at wind speeds up to 3.5 m s^{-1}.
- The acetone profiles demonstrated that the subtropical / subarctic Pacific Ocean was acetone source / sink region. No relationship between flux and wind speed implies the possibility that the flux of high soluble gas such as acetone is controlled by some factors other than wind speed.

Acknowledgment: This study is funded by the Global Environment Research Fund (RFa-1102) of the Ministry of the Environment, Japan. We thank the captain, officers, crew, and scientists for their help on board during the cruises of R/V *Hakuho Maru*.

Reference

1. Wanninkhof (1992) J. Geophys. Res., 97, 7373-7382. 2. Zemmelink et al. (2004)) J. Geophys. Res., 109, C08S10.