Contrasting Marine Carbon Monoxide Cycles in the North Pacific and the Amundsen Sea

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Introduction

Carbon monoxide (CO) plays a primary role in regulating the oxidizing power of the atmosphere. In the upper ocean, CO exhibits a strong diurnal cycle being produced by photolytic decomposition of chromophoric dissolved organic matter (CDOM), consumed by microbes, and outgassed by the gas exchange processes (**Figure 1**). To investigate dominant processes that govern the budget of dissolved CO in the mixed layer, we measured air-sea flux, microbial consumption , and CDOM absorbance in the field expeditions. CO cycles in the mixed layer were simulated using a simple box model and we demonstrated that diurnal variations in both regions were mainly governed by biologically related processes and mixed layer thickness driven by radiative heating at the surface.

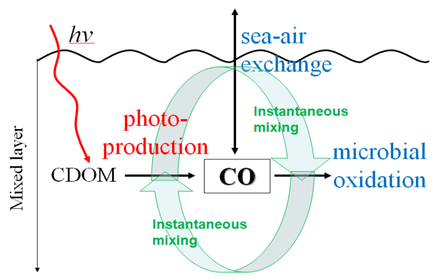

Fig. 1. CO dynamics in the surface mixed layer

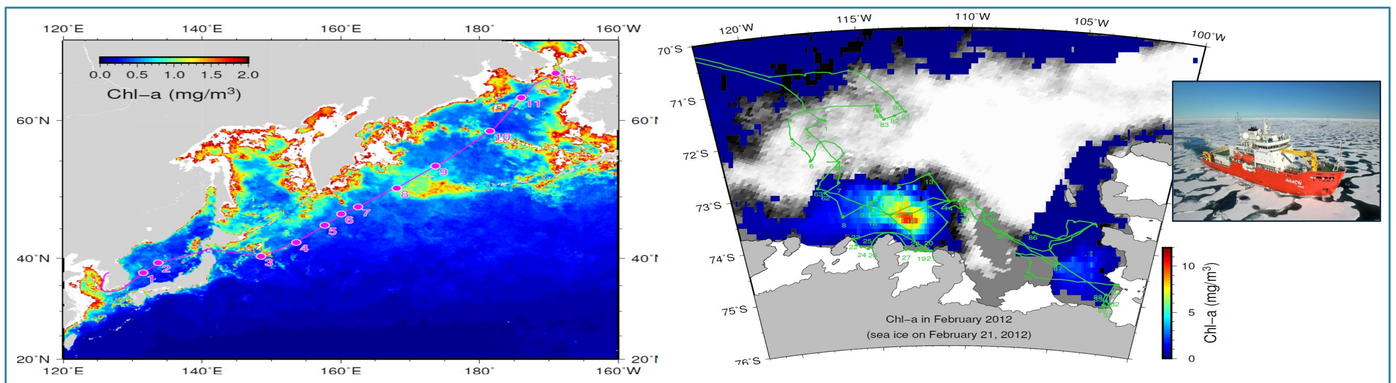

Fig. 2. Study area in the North Pacific (left) and the Amundsen Sea (right). Blue lines denote the cruise tracks and black dots the hydrographic stations where dark incubation experiments were conducted.

Study Areas and Methods

The underway measurements of CO in seawater and overlying air were conducted using a gas chromatographic system (RGA-3) along the cruise tracks of icebreaking R/V, *Araon*, during two expeditions in 2012 (**Figure 2**); one is an Amundsen expedition from Christchurch, New Zealand, to the Amundsen Sea of the western Antarctica between January 31 and March 20 and the other a SHIpborne Pole-to-Pole Observations (SHIPPO) expedition from Incheon, Korea, to Nome in Alaska, U.S.A. through western limb of the North Pacific between July 13 and 29. At hydrographic stations we conducted dark incubation experiments to determine microbial consumption rate. To calculate photoproduction rate, CDOM absorbance and irradiation were also measured during the expeditions.

Results

1) Gas Exchange

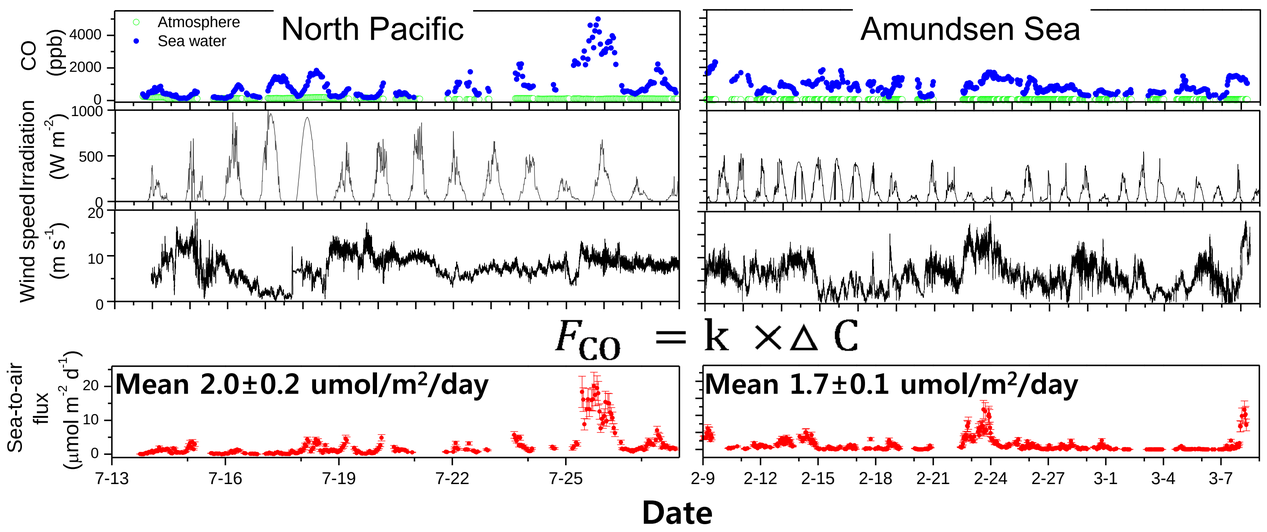

Fig. 3. CO concentrations, irradiation, and wind speeds obtained from the underway measurements. Irradiation was measured with an Eppley Precision Spectral Pyranometer (model PSP) integrating radiation over 285-2800 nm. Wind speed was measured at 29 m-height above sea level and converted at 10 m standard height. F_{CO}, flux of CO, was calculated as product of gas transfer velocity (k) and the difference of [CO] between water and air converted in unit using *Henry's Law* constant.

Dissolved CO concentrations in the two regions are at similar level (about 1 nM), but clear diurnal variation is shown in the North Pacific only (**Figure 3**). Because wind speed was higher in the North Pacific (mean 7.6 m/s in the North Pacific and 6.5 m/s in the Amundsen Sea), CO outgassing rate from the ocean to the air is larger than in the Amundsen Sea by about 1.24 times.

2) Microbial Consumption

The time series data obtained from dark experiments were fitted to exponential decay to determine the loss rates, k_{CO}:

$$\frac{d[CO]}{dt} = -k_{co} \times [CO]$$

Figure 4 shows k_{co} arranged by hydrographic stations. Accounting for the mean values, CO is consumed 15 times faster in the North Pacific.

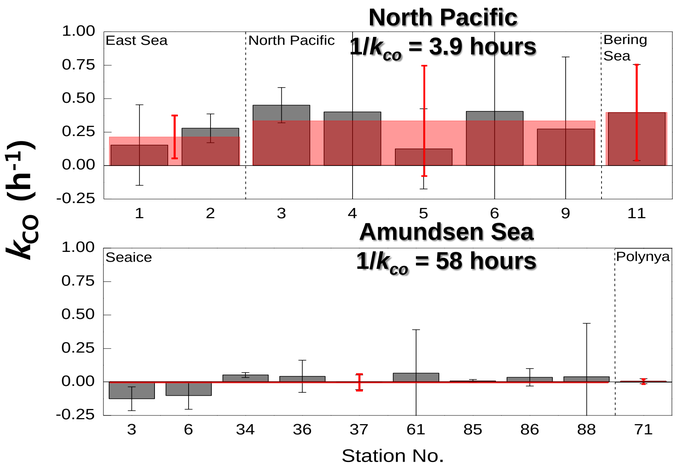

Fig. 4. Microbial consumption rates in (a) the North Pacific and (b) the Amundsen Sea. If k_{CO} is smaller than zero, CO could not be consumed during the experiments.

3) Photoproduction

Two approaches were chosen to determine the photoproduction rate; one from *Kettle* (2000) (P_K) providing an apparent quantum yield (AQY; Φ), the other from *Gnanadesikan* (1996) (P_G) using a constant, P_{con} (nmol CO W^{-1} h^{-1}) in the whole range of the wavelength:

$$P_K(t) = \int_{280}^{700} I_0(\lambda) \times (1 - e^{-K_d z}) \times \Phi(\lambda) \times f_{CDOM}(\lambda)$$

$$P_G(t) = Q_0 \times P_{con} \times \left(1 - e^{-\frac{z}{L}}\right)$$

Mean value of daily integrated photoproduction of CO was about 4 times larger in the North Pacific than in the Amundsen Sea (**Figure 5**).

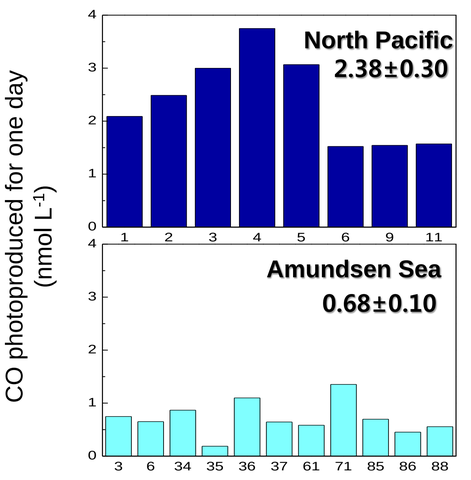

Fig. 5. Daily integr-ated photoproduc-tion in (a) the North Pacific and (b) the Amundsen Sea cal-culated by Gnanade-sikan (1996) (sky-blue) and Kettle (2000) (navy).

Important Length Scales and Mass Balance Model

We estimated three length scales for CO dynamics using wind speed, vertical profile of sigma-t, and optical properties of seawaters (Gnanadesikan 1996): 1. L_{mix} is the depth in which vertical mixing occurs over the microbial consumption time scale, which indicates mixed layer depth here. 2. L_p is *e*-folding depth for photochemically active solar radiation. 3. L_{out} is the depth in which outgassing can compete with microbial consumption as sink for CO. In the Amundsen Sea mean L_p is 3.2 times shallower while mean L_{mix} is 3.6 times deeper than in the North Pacific (**Figure 6**).

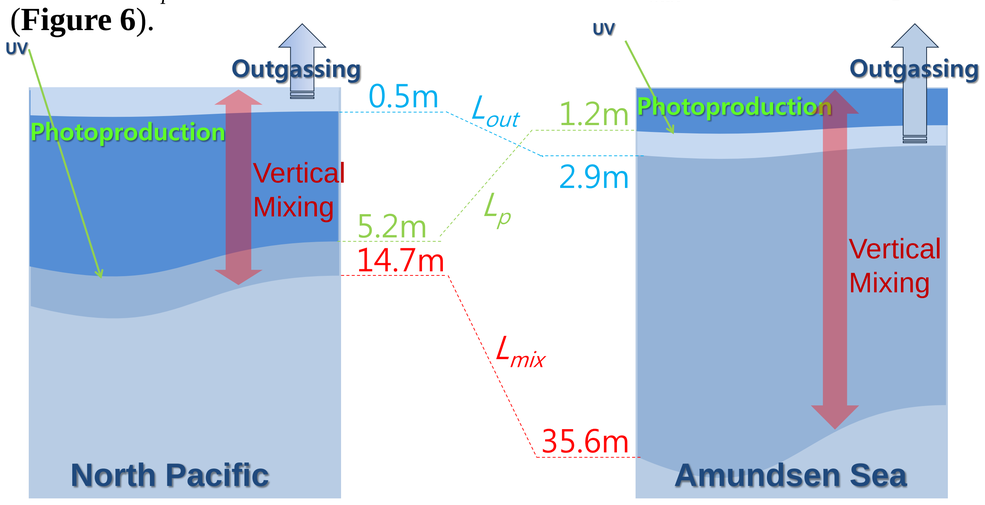

Fig. 6. Three length scales in average for CO including of the North Pacific and the Amundsen Sea.

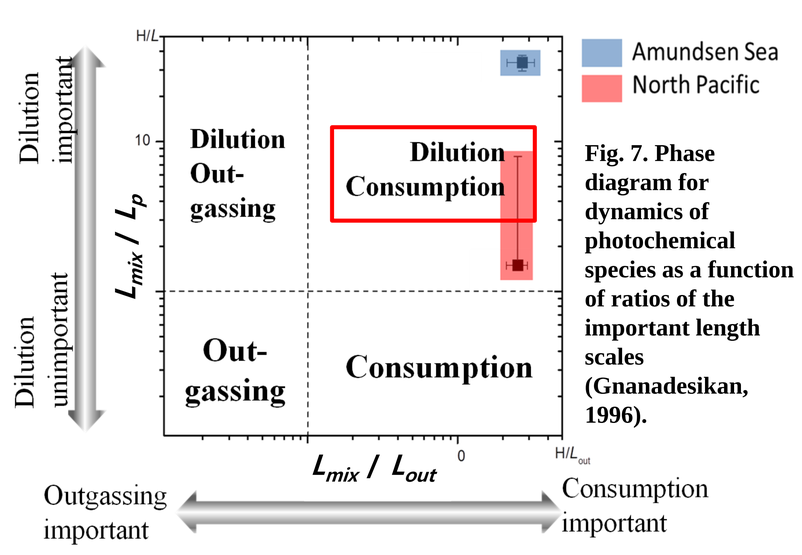

Fig. 7. Phase diagram for dynamics of photochemical species as a function of ratios of the important length scales (Gnanadesikan, 1996).

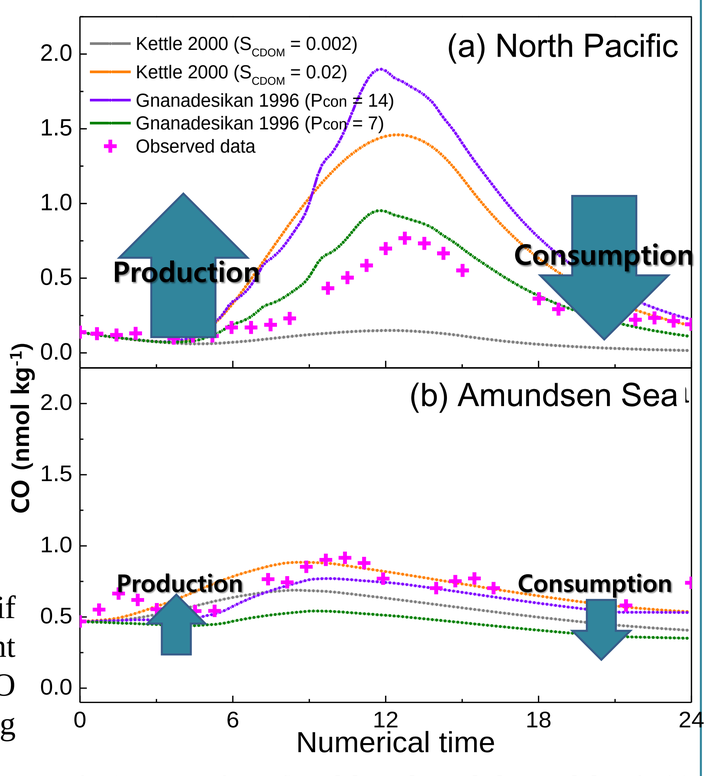

Fig. 8. Comparison of model results and observed data in (a) the North Pacific and (b) the Amundsen Sea. Photoproduction varies depending on production constant or slope of CDOM spectrum.

The ratio of L_{mix} to L_p can be used to estimate importance of dilution to the photoproduction, and the ratio of L_{mix} to L_{out} determines if microbial oxidation is more dominant than outgassing (**Figure 7**). Mean L_{mix} in the Amundsen Sea was 35.6 m, deep enough for efficient dilution of CO photoproduced within L_p which was only 1.2 m. On the other hand, in the North Pacific the dilution hardly affected CO because of shallow L_{mix} (14.7 m). In both regions microbial consumption turn out to be a major sink process overwhelming the outgassing since L_{out} was much shallower than L_{mix}.

To simulate the diurnal variations of CO in the mixed layer, a simple box model was applied based on the observed data from experiments above. Assuming there are only three processes including photoproduction, air-sea gas exchange, and microbial consumption, we can express the temporal variation of CO concentration by :

$$\frac{d[CO]}{dt} = \sum \text{Source} - \sum \text{Sink} = \text{Photoproduction} - \text{Consumption} - \text{Outgassing}$$

The model calculation for one station in each region gives clear diurnal cycles for the North Pacific but not for the Amundsen Sea (**Figure 8**). This reflects that both production and consumption rates were higher in the North Pacific.

Conclusion

Our experiments showed that that both production and destruction of CO in the surface mixed layer were larger in the North Pacific than in the Amundsen Sea (**Figure 9**). However, regardless of the production and consumption rate, the quantity of CO escaping to the atmosphere was very low (less than 10 % of total sink process in the both regions). That is, the photoprocution rate in the ocean cannot affect the atmospheric CO level because of intense microbial consumption and also the ocean is not a strong source for the atmospheric CO.

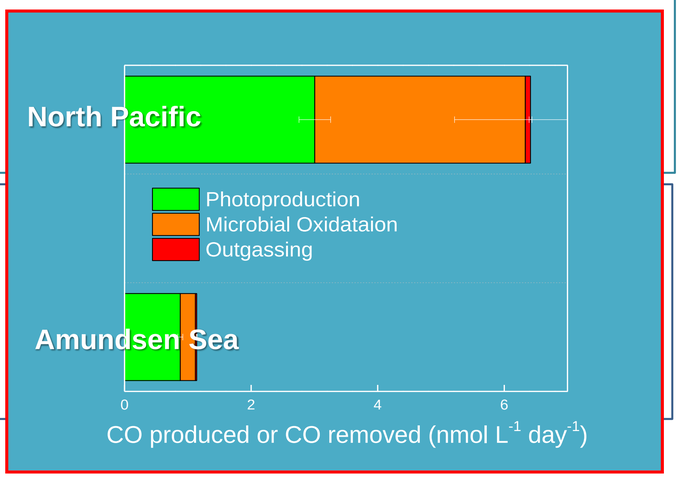

Fig. 9. Total budget of CO in the North Pacific and the Amundsen Sea estimated from this study.

References

1. Kettle, A. J. (2000) *Extrapolation of the oceanic flux of DMS, CO, COS, and CS_2*, Ph. D. thesis, York Univ., Toronto, Canada
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Acknowledgements

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