Diurnal Variations of Carbon Monoxide Concentration in the Equatorial Pacific Upwelling Region

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Carbon monoxide (CO) concentrations in seawater were measured in the upwelling region of the equatorial Pacific (0°N, 159°W) during the Hakuho Maru KH-93-4 cruise. The surface water containing CO of 42–173 nl/l, which showed a marked diurnal variation with a maximum and minimum occurring early in the afternoon and morning, respectively, was supersaturated with respect to atmospheric CO mixing ratios. The estimated sea-to-air fluxes of CO fell within the range of 0.11–0.12 mg/m²/d. The CO concentrations in the water column decreased with depth to approach relatively constant and low levels of around 10 nl/l at depths beneath 70 m. A diurnal variation of CO concentrations was noticed down to depths of about 60 m where the light intensity reached 2.5% of the surface level, although it was most pronounced in the surface water layers. The diurnal variation should be caused by the photochemical CO production followed by \textit{in situ} biological CO oxidations. A rate constant of the biological oxidation of 0.13 ± 0.01 (h⁻¹) was estimated based on the CO decrease observed in the euphotic zone in the evening. The rapid biological CO oxidation would be due to a high bacterial activity depending on a high primary productivity and nutrient contents in the water.

1. Introduction

Concentrations of carbon monoxide (CO) dissolved in oceanic surface waters are much higher than expected by equilibration with atmospheric CO concentrations (Swinnerton \textit{et al.}, 1969, 1970; Seiler and Junge, 1970; Lamontagne \textit{et al.}, 1971; Linnenbom \textit{et al.}, 1973; Seiler and Schmidt, 1974; Wilkniss \textit{et al.}, 1979). It is therefore evident that the ocean acts as a source for atmospheric CO. A recent estimate based on computed CO concentrations in surface waters was given for the global oceanic CO flux to the atmosphere of 165 ± 80 Tg/y, which accounts for about 15% of the global CO flux from natural sources (Erickson, 1989). A more recent estimate based on measured CO concentrations in surface waters was given for the global oceanic CO flux to the atmosphere of 165 ± 80 Tg/y, which accounts for about 15% of the global CO flux from natural sources (Erickson, 1989). A recent estimate based on computed CO concentrations in surface waters was given for the global oceanic CO flux to the atmosphere of 165 ± 80 Tg/y, which accounts for about 15% of the global CO flux from natural sources (Erickson, 1989).

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A more recent estimate based on measured CO concentrations resulted in a much smaller flux of 13 Tg/y (Bates \textit{et al.}, 1995). A great difference between these estimates require more observations on the distribution and variability of the oceanic CO flux.

In the water column, CO concentration decreases with depth in the euphotic zone to approach relatively constant, low concentrations occurring in the deeper waters (Swinnerton \textit{et al.}, 1968; Swinnerton and Lamontagne, 1974). The CO concentration in the euphotic zone is much lower on cloudy days than on sunny days (Seiler and Schmidt, 1974). These variations in CO concentration reflect the relative contributions of the processes working toward the production and removal of CO. Photochemical oxidations of dissolved organic matter (DOM) are believed to be most responsible for the production of CO in the euphotic zone (Wilson \textit{et al.}, 1970; Bauer \textit{et al.}, 1980; Conrad and Seiler, 1980; Conrad \textit{et al.}, 1982), although some species of marine algae and bacteria can produce it (Loewus and Delwiche, 1962; Chapman and Tocher, 1966; Junge \textit{et al.}, 1971, 1972; Seiler and Schmidt, 1974).

As removal processes for CO in the euphotic zone, \textit{in situ} oxidations and an air-sea exchange are known to be important (Linnenbom \textit{et al.}, 1973; Conrad and Seiler, 1980, 1982). Conrad \textit{et al.} (1982) found that \textit{in situ} microbial oxidations, mainly by bacteria, function as the predominant process removing CO in the equatorial Atlantic Ocean, and that photochemical CO production and microbial CO oxidations result in a significant diurnal variation in CO concentration. By contrast, Jones (1991) found that microbial oxidations proceed very slowly in the Sargasso Sea due to extremely low trophic levels of the water. The air-sea exchange is thus almost the sole process removing CO from water, resulting in a long residence time of CO in water and no discernible diurnal variation in CO concentration in the euphotic zone.

These findings lead us to the presumption that a marked diurnal variation in CO content in the euphotic zone would...
occur only in nutrient-rich waters where biological activities, including bacterial CO oxidations, are at high levels. However, too little information is available at present to generalize this presumption to all areas of the world’s oceans because only a few field observations of diurnal CO variation in the euphotic zone have been carried out so far.

During the Hakuho Maru KH-93-4 cruise, we had a four-day stay at the upwelling site in the equatorial Pacific Ocean. Here we present the data on diurnal variations of CO concentrations in the euphotic zone and sea-to-air CO fluxes at the ocean site where both production and removal of CO are expected to be very active because of strong solar radiation and high biological activity due to high nutrient contents.

2. Materials and Methods

The standard CO gases (1.02 and 4.94 ppm) used in the present study were purchased from Taiyo-Toyo Sanso Corporation, Japan. Each standard gas was filled in a high-pressure 10-l steel cylinder with a brass valve. The procedures of standard-gas preparation were as follows. The inner surface of the cylinder was abraded, then blasted and dried with N₂. The cylinder was fitted with a brass valve and heated at 165°C under vacuum (10⁻⁴ torr) for 6 hours. For preconditioning of the cylinder, it was filled with N₂ containing CO at a concentration of about 1% and gently heated for 7 hours. After evacuating the gas mixture at 2 × 10⁻³ torr, the cylinder was filled with high-pure CO (>99.999%) diluted several times to the final concentration, 1 or 5 ppm, with ultrahigh pure N₂ (>99.9999%) by the manometric method. Change in CO concentration during the week after filling up the standard gas was tested by a non-dispersion IR analysis.

The observations and experiments were carried out on board the research vessel Hakuho Maru of the University of Tokyo during the second leg of the KH-93-4 cruise. This leg included a 4-day (Nov. 16–19, 1993) stay at station D2′ (0°N, 159°W) locating in the upwelling region of the equatorial Pacific (Koike, 1996).

Depth profiles of water temperature, salinity, oxygen, in situ fluorescence and irradiance in water were taken by the OCTOPUS (Octo Parameter Underwater Sensor) system (Ishimaru et al., 1984). The atmospheric solar radiation (0.3–2.8 µm) was measured on deck by a pyranometer (Ishikawa Trading Co.). The wind velocity was monitored at 20 m above sea level. Chlorophyll a and the nutrients were measured on board, and their concentrations are described elsewhere (Koike, 1996). Water samples from different depths were collected in 12-l Niskin bottles attached to the same OCTOPUS system. The surface water was sampled in a polyethylene bucket.

For on-board analysis of CO, each water sample was siphoned into a 100-ml glass flask with a greaseless glass stopcock. A 10-ml portion of the water sample in the flask was replaced by CO-free synthetic air to make a headspace. The flask was then shaken vigorously by hand for 1 min. and kept standing at 26–27°C for 5 min. in the dark in order to complete the equilibration between aqueous and gaseous phases. Preliminary experiments using a standard gas sample showed that equilibrium is established within 5 min.

A 1 or 2 ml gas sample was taken from the headspace in the flask by use of a gas syringe and injected into a gas chromatograph (Shimadzu GC-9A) fitted with a methanizer (Shimadzu MTN-1) and a flame ionization detector. A chromatographic column (2.6 mm in ID × 1 m) packed with molecular sieve 5A was used at 80°C to separate the CO from hydrogen and methane. The detection limit was 6 nl CO/l water, and the precision of the analysis was ±3%.

The CO concentrations thus determined were corrected at first based on the equilibrium constants of CO between the aqueous and gaseous phases in the flask for headspace preparation. The concentrations were further corrected for water vapor contained in the headspace gas at concentrations of 3.8–4.1% in volume at 26–27°C.

3. Results and Discussion

3.1 CO in the surface water

Carbon monoxide concentrations in the surface water on November 16 and 17 ranged from 42 to 173 nl/l (Fig. 1(A)). These concentrations fall within the range of 2–210 nl/l reported for CO in surface waters in the Atlantic and Pacific (Seiler and Schmidt, 1974). The CO concentration reached 246 nl/l at 14:30 on November 18. The intensity of solar radiation remained fairly constant throughout the three days (Fig. 1(B)), suggesting the CO production would not fluctuate much among these days. Therefore, the higher concentration observed on November 18 possibly resulted from fewer air-sea exchanges due to the relatively weak winds prevailing on that same day (Fig. 1(C)).

Throughout our observation period, CO concentrations revealed marked diurnal variations (Fig. 1(A)) whose patterns resemble those of solar radiation (Fig. 1(B)), supporting the conclusion that CO production is basically dependent on light intensity. However, it is worth noting that there is a time lag of 2–3 hours between the maximum CO concentration and the maximum solar radiation. This time lag may be explained by a probable reaction mechanism of CO production in which the reaction is initiated by light and releases CO through multi-step photosensitized reactions over a period of several hours (Conrad et al., 1982). Another explanation may be possible for this time lag (Ohta et al., 1996). That is, photochemical CO productions exceeded microbial CO oxidations in the late morning, resulting in an accumulation of residual CO fractions until around 14:30 when microbial oxidations overtook photochemical productions and predominated thereafter. However, there is no definitive data at present to conclude which mechanism was
Diurnal Variation of CO in the Eq. Pacific

Oceanic CO fluxes to the atmosphere were estimated, assuming (1) that the CO concentration sharply increased on the morning of November 16, and (2) that it sharply decreased after 17:00 on November 17 to reach, at 4:00 on November 18, a level as low as 45 nl/l observed at the same time on the day before. The model of Liss and Slater (1974), described below, was used for estimating the flux ($F$).

$$F = k_w (C_l - C_g / H)$$

where $k_w$ is the gas transfer velocity, $C$ is the concentration in the liquid or gas phase, and $H$ is the Henry’s law constant.

Atmospheric CO concentrations observed in the equatorial Pacific early in December, 1993, were about 60 ppb (Bates et al., 1995), giving $C_g / H$ of 1.1 nl/l at 27°C and a salinity of 35. This value is very small compared with measured $C_l$. Thus, $F \cong k_w C_l$.

The transfer velocity $k_w$ was calculated from the equations given by Liss and Merlivat (1986) and modified by Gabric et al. (1995).

$$k_w = \beta (2.85 U_{10} - 10.26) + 0.61 \alpha$$

for $3.6 < U_{10} \leq 13$, $\alpha = (600 / Sc)^{2/3}$ and $\beta = (600 / Sc)^{1/2}$

where $U_{10}$ is a wind velocity at 10 m above sea level and $Sc$ is a Schmidt number of CO. Since wind velocities were measured at 20 m above sea level in the present study, they were converted into $U_{10}$, assuming a logarithmic wind profile and a roughness length of $10^{-4}$ m (Blake, 1991). The measured wind velocities were thus reduced by $6\%$. The $Sc$ is a ratio of the kinematic viscosity of seawater to the gas diffusivity $D$, where kinematic viscosity is defined as the seawater viscosity $\eta$ divided by the density $\rho$ of the same seawater.

$$Sc = \eta / \rho / D.$$ 

Values of $D$, $\eta$ and $\rho$ in the present study were obtained according to Jähne et al. (1987), Millero (1974), and Millero and Poisson (1981), respectively.

In this way, the oceanic CO fluxes of 0.11–0.12 mg/m²/d were obtained (Table 1). They are similar to the flux of 0.12 mg/m²/d estimated by Bates et al. (1993) for the equatorial Pacific (15°N–10°S, 145–165°W) on the basis of measured CO concentrations and an estimation method similar to us. Erickson (1989) reported a CO flux of about 1.4 mg/m²/d for this region, which exceeds our fluxes by an order of magnitude. Such a high flux results primarily from high CO concentrations in the surface water, which were obtained not from observation but by a calculation using the experimental data of Conrad et al. (1982) on the relationship between solar radiation and CO concentrations in seawater. Our CO flux estimates as well as an observation-based global flux of 13 Tg CO/y by Bates et al. (1995) indicate that the global flux of 165 ± 80 Tg CO/y predicted by Erickson

<table>
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<th>Date</th>
<th>$C_l$ (nl/l)</th>
<th>$U_{10}$ (m/s)</th>
<th>$Sc$</th>
<th>$k_w$ (cm/h)</th>
<th>$F$ (mg/m²/d)</th>
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<td>4.9</td>
<td>417</td>
<td>5.2</td>
<td>0.11</td>
</tr>
<tr>
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<td>5.1</td>
<td>417</td>
<td>5.9</td>
<td>0.12</td>
</tr>
<tr>
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<td>4.5</td>
<td>417</td>
<td>3.9</td>
<td>0.11</td>
</tr>
</tbody>
</table>

Table 1. Carbon monoxide fluxes ($F$) from the equatorial Pacific (0°N, 159°W). Average CO concentrations in water ($C_l$), average wind velocities at the height of 10 m ($U_{10}$), Schmidt number ($Sc$) and gas transfer velocities ($k_w$) are also shown.
may be considerably reduced, at least in the equatorial Pacific.

### Vertical distribution of CO in water

Carbon monoxide in the water column gradually decreased with depth, the highest concentrations being found at the sea surface (Fig. 2). It showed relatively constant concentrations of around 10 nl/l beneath depths of 70 m. This profile resembles that of light intensity in water, although the light intensity dropped sharply with depth to approach a level of 1% of the surface light intensity at a depth of about 80 m and undetectable levels beneath 170 m (Fig. 3). No relationship was observed among the depth profiles of CO, water temperature and chlorophyll $a$ (Fig. 3), as was also pointed out by Conrad et al. (1982).

The vertical profile of CO concentrations revealed a marked diurnal variation with a sharp decrease in the late afternoon and a rapid increase in the morning to approach its maximum level early in the afternoon (Fig. 2). Although the diurnal variation was pronounced in the upper waters, it was discernible even at a depth of 60 m where the light intensity reached 2.5% of the surface level (Fig. 3). This indicates that photochemical reactions producing CO take place in almost the entire euphotic zone and also that the CO thus produced is removed effectively.

### Bacterial oxidation of CO in water

In situ bacterial oxidations are the predominant process removing CO in water except for the surface water layer where a sea-to-air transfer of CO occurs (Conrad and Seiler, 1980). Among bacteria, ammonium oxidizing bacteria are known as a CO oxidizer (Jones and Morita, 1983; Jones et al., 1984). Conrad et al. (1982) studied the biological CO oxidation process via incubation experiments with the surface water of the equatorial Atlantic. They reported that the CO concentration in the unfiltered water sample decreased from 135 to about 40 nl/l with a rate of 7 nl/h during a 13-hour incubation in darkness, while no decrease was observed for CO concentrations in the bacteria-free (0.2 µm-filtered) water sample. However, any rate constant of microbial oxidations, which could enable us to presume the lifetime of CO at different concentrations in water, was not reported by the same authors.

In the present study, an estimate of the reaction rate of biological CO oxidations was made using the data on CO decreases during the period of 3.7 hours between 19:30 and 23:10 on November 16 (Fig. 2), when the photochemical CO...
production was expected as being minimal because of no effective solar radiation (Fig. 1). The upwelling velocity of 1.23 m/d reported for an upwelling zone in the equatorial Pacific is too small to modify the vertical CO distribution during the period of 3.7 hours (Coale et al., 1996). Therefore, we assume that the decrease in CO concentration between 19:30 and 23:10 was mainly caused by the effect of biological oxidations in the water, except for the upper-most water layer releasing CO into the air.

An equation described below was used for calculating a reaction rate constant $k$, assuming that the biological CO oxidations keep being first-order.

$$-\ln \left( \frac{C_t}{C_0} \right) = kt$$

where $C_t$ and $C_0$ are the CO concentrations at 23:10 and 19:30, respectively, and $t$ is the reaction period of 3.7 hours. Giving the CO concentrations at depths of 5, 10, 20, 30 and 40 m to this equation, we obtained the reaction rate constant of $0.13 \pm 0.01$ (h$^{-1}$).

The rate constant thus obtained showed us that a half-life period of CO is about 5 hours and, further, 90% of CO can be biologically oxidized within 18 hours. This period of 18 hours is similar to that for CO (around 20 hours, if we deduce from the experimental data of Conrad et al. (1982)) in the equatorial Atlantic and a little longer than the turnover times (2–17 hours) measured for CO in estuarine waters by use of a $^{14}$C technique (Butler et al., 1987). However, it is much shorter than the turnover times of 30–1200 hours estimated by the $^{14}$C method for CO in the oligotrophic Sargasso Sea waters where no discernible diurnal variation of CO was observed (Jones, 1991). Our rate constant is to be used in our numerical simulation to predict CO production in the equatorial upwelling region in the manner described elsewhere (Ohta et al., 1996).

The high biological activity oxidizing photochemically-produced CO during short periods should be responsible, as a CO-decomposing process, for the diurnal CO variation observed in the euphotic zone in the equatorial Pacific upwelling region. Rapid biological CO oxidizations would be due to high bacterial activity which depends on high primary productivity and much nutrients in the water (Fig. 3).

Relatively constant and low CO concentrations found at depths beneath 70 m (Fig. 2) should be maintained by a mechanism different from that working in the euphotic zone. The biological production and consumption of CO may balance in the deeper waters (Junge et al., 1971, 1972; Seiler and Schmidt, 1974).

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References


