Carbon monoxide in the South Pacific Ocean[1]

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ABSTRACT

During a recent oceanographic cruise (November 1972) of the U.S. Coast Guard icebreaker GLACIER, both surface sea water and atmospheric samples were collected for CO analysis. The ship followed a cruise track from Long Beach, California to McMurdo Sound in the Antarctic. Atmospheric carbon monoxide concentrations in the south Pacific were found to be much lower than those measured in the north Pacific, 0.04 ppm to 0.13 ppm, respectively. CO concentrations in sea water of the south Pacific range between 1 and 30×10^{-5} ml/l and compare favorably to levels measured in the oceans of the northern hemisphere. In all sea water samples, the carbon monoxide was supersaturated relative to the surrounding atmosphere. Sea water carbon monoxide concentrations were highest in regions of upwelling or water convergence zones. These areas were also associated with high biological activity.

Ten vertical profiles of carbon monoxide in sea water were obtained between Long Beach and McMurdo Sound. In general, the carbon monoxide concentration was highest in the upper 30 m with a steady decrease to near 0 concentration at 100 me. Carbon monoxide was also measured in sea ice collected in the Antarctic. The highest concentrations of carbon monoxide was found to be on the bottom of the sea ice. The bottom ice had heavy concentrations of brown algae which penetrated half a meter into the ice. The surface snow exhibited concentrations of carbon monoxide which were comparable to those found in the surface sea water for the same area.

Introduction

In 1967 the Naval Research Laboratory embarked on a program to measure carbon monoxide in the marine atmosphere and in the oceans. The primary purpose was to determine the role that the oceans play in the geochemical cycle of carbon monoxide. Since then, sea water samples have been collected for CO analysis in the Arctic, the north Atlantic, the tropical north Atlantic, the Caribbean and the north tropical Pacific Ocean; Linnenbom et al. (1973). Other investigators (Seiler & Junge, 1973) have also measured CO in the north and south Atlantic. In this paper, we report additional data on carbon monoxide in the south Pacific Ocean, the ice-covered Ross Sea and the atmosphere above.

Cruise track and sampling procedures

We participated in a recent oceanographic cruise of the U.S. Coast Guard icebreaker, GLACIER. The ship departed Long Beach, California on 15 November and arrived in McMurdo, Antarctica on 25 December 1972. During the transit, surface water and atmospheric samples were collected between 30° N and 77° S in the Antarctic.

Samples were taken at three-hour intervals while the ship was underway, and were analyzed for carbon monoxide and methane. Fig. 1 shows the cruise track of the GLACIER. In addition to surface water samples, we also obtained 10 vertical profiles down to 100 m. The vertical profiles sere taken at three-day intervals at 1 400 hours, local time. Fig. 1 also shows the location of these stations.

CO in the atmosphere

Fig. 2 shows the atmospheric results for carbon monoxide. Dates are shown on the lower abscissa of Fig. 2; the corresponding latitudes and longitudes are given on the upper abscissa. The concentration units for carbon monoxide are shown on the ordinate, and are expressed

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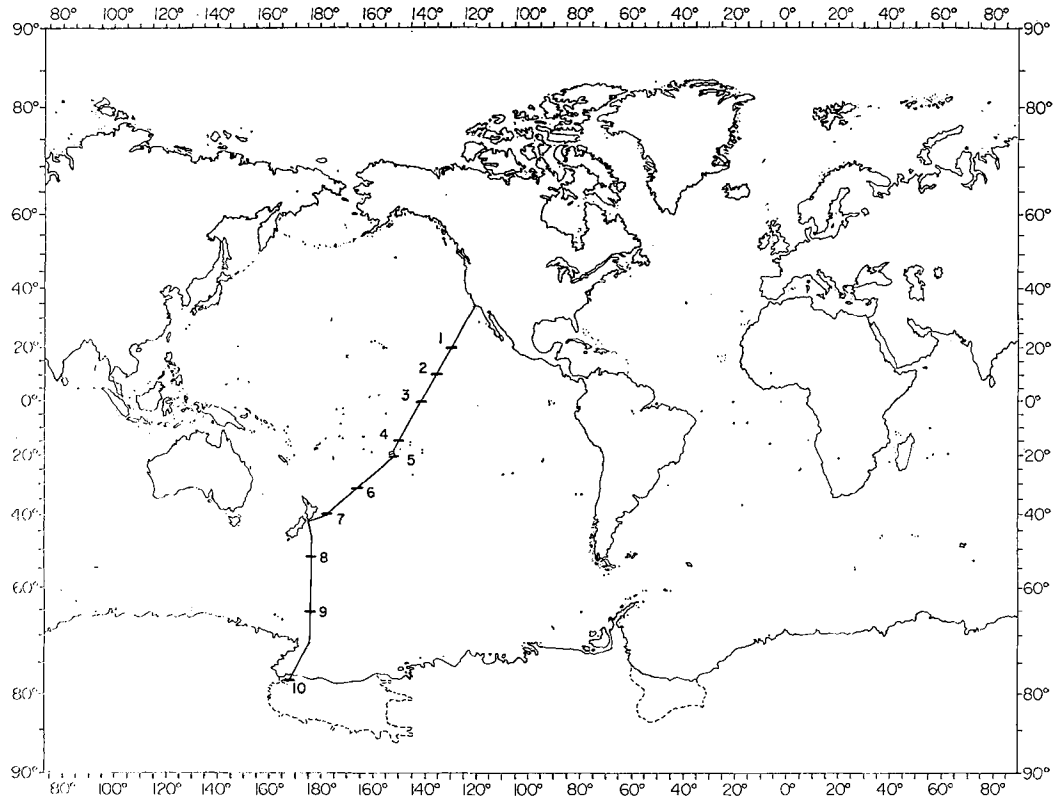

Fig. 1. 1972 cruise track between California and Antarctic.

in parts-permillion (ppm) by volume. The triangles represent duplicate samples.

Our Pacific atmospheric CO data closely parallel the CO results of Seiler & Junge (1971) for the south Atlantic. They observed a decrease in the CO concentration at the intertropical convergence zone (ITC). The ITC zone was located at 3° N. We observed a similar decrease in carbon monoxide concentration when passing through the ITC zone in the Pacific. The ITC was well defined at 7° N a little higher in latitude than in the Atlantic. The atmospheric CO concentrations north of the ITC were 0.13 ± 0.06 ppm. This value agrees favorably with our earlier measurements of CO in the atmosphere of the north Pacific where we obtained an average concentration of 0.126 ± 0.020 ppm (Lamontagne et al. 1971).

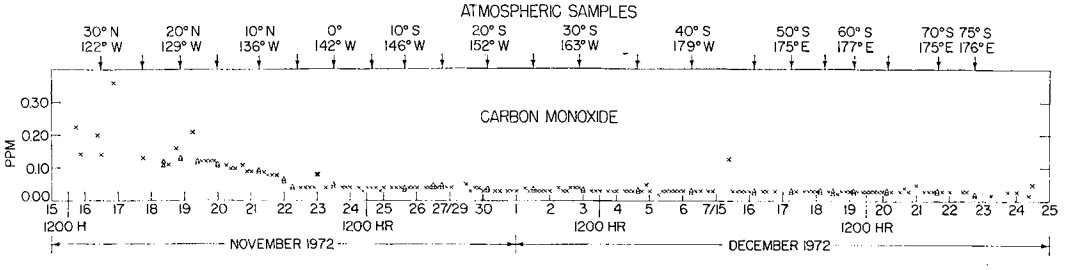

Fig. 2. Plot of atmospheric CO as a function of time and position. Samples were taken over the Pacific Ocean between 30° N and 77° S; concentration of gases expressed in ppm.

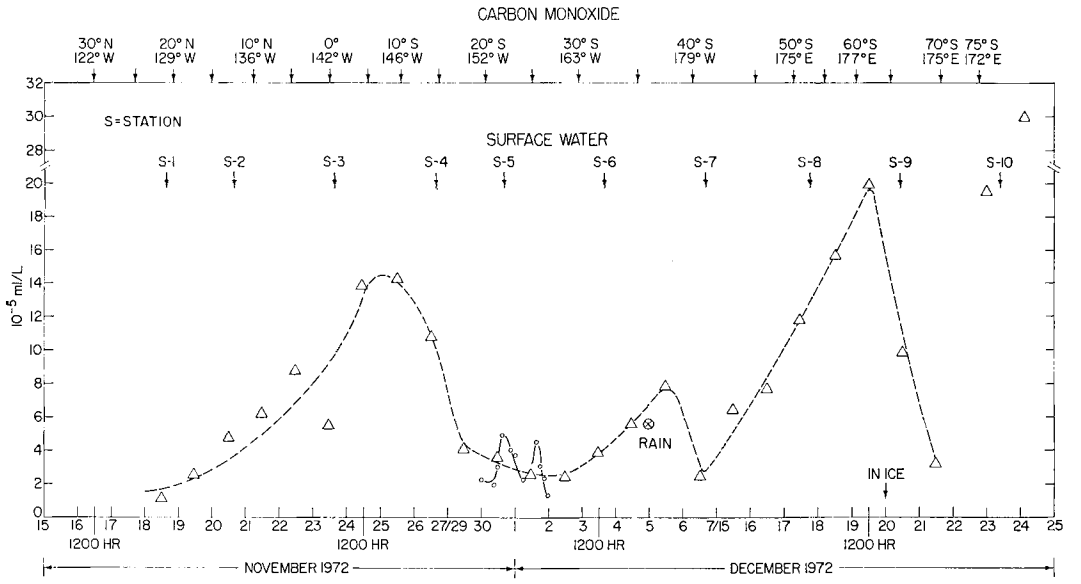

Fig. 3. Plot of dissolved CO in surface sea water of the Pacfic Ocean as a function of time and position. Samples collected between 30° N and 77° S. Concentration units for dissolved CO expressed in 10^{-5} ml/l.

South of the ITC to ~20° S the CO concentration was 0.039 ±0.008 ppm and between 20° S and the Antarctic (77° S) the CO concentration decreased to 0.031 ±0.005 ppm, which is in good agreement with the earlier and only other data available (Robinson & Robbins, 1970).

Our results on atmospheric CO are summarized in Table 1. Only one carbon monoxide data point (0.13 ppm) deviates from the southern hemisphere average. It was an air sample taken in the harbor of Wellington, New Zealand, and is probably not representative of the main atmosphere.

Table 1. *Carbon monoxide partial pressure in the marine atmosphere*

Location	No. of samples	Range of values	Mean value (ppm)
1. N. Atlantic April 1969	30	0.05–0.17	0.114 (±.020)
2. N. Atlantic May 1970	33	0.06–0.18	0.126 (±.032)
3. N. Pacific June 1970	50	0.06–0.17	0.123 (±.020)
4. N. Atlantic May 1971	26	0.08–0.15	0.118 (±.015)
5. Arctic August 1971	94	0.08–0.18	0.111 (±.018)
6. N. Pacific November 1972[a]	37	0.06–0.40	0.128 (±.06)
7. N–S Pacific November 1972[b]	47	0.03–0.08	0.040 (±.008)
8. S. Pacific Antarctic December 1972[c]	103	0.02–0.04	0.031 (±.005)

[a] 30° N–10°N. [b] 10° N–20° S. [c] 20° S–77° S.

Carbon monoxide in seawater

Shown in Fig. 3 are the carbon monoxide results for the surface Pacific Ocean and the Ross Sea between 30° N and 77° S. Surface samples were collected from the ship's auxiliary sea chest. This sea chest was continually flushed with fresh sea water. Samples from the sea chest were compared with samples taken on a vertical cast when the ship was stopped; no difference was observed. The lower abscissa (Fig. 3) shows the transit dates of the USCGC GLACIER and the upper abscissa, the corresponding geographic positions. Concentration units are 10^{-5} ml/l for dissolved carbon monoxide. These are given on the ordinate. A break occurs in the ordinate scale at 20×10^{-5} ml/l.

The "S" numbers with arrows indicate the location of vertical Niskin bottle casts. The

triangles of Fig. 3 represent the mean concentration of dissolved carbon monoxide over a 24-hour period. Each triangle data point is based on the mean of three to seven individual samples. For convenience, the triangles are plotted at 1 200 hours, and are connected by the dashed line. Superimposed on the dashed line is a diurnal plot. The circles represent individual measurements obtained at three-hour intervals. The circle data show the diurnal variations, which were observed in the southern hemisphere surface water. These variations are similar to those measured in the north Pacific (Lamontangne et al., 1971). The figure becomes too confusing when all the three-hour interval data points are included, therefore, only one set of diurnal data is shown.

Refering to the dashed line of Fig. 3, there are three distinct concentration peaks of carbon monoxide in the surface water. They appear at 10° S, 38° S and 62° S. It is evident then, that a broad CO concentration peak exists in the water and extends from 5° N to approximately 15° S ($\approx$1 200 miles north to south). The south equatorial current of the Pacific Ocean passes directly through this region. The water is flowing in a well-developed westward pattern, between 3° N and 10° S. In addition to the south equatorial current there exists along the west coast of South America, and in particular along the coast of Peru, a well-defined area of upwelling. This upwelling area is approximately 3 000 miles to the east of the ship's transit. Fleming and Laevastu (1956) have shown that a tongue of seawater, high in biological productivity, extends from the Galapagos Islands to well west of the north-south track of the GLACIER. The north–south latitudinal distance of this tongue at 145° W is approximately the same as the width of the south equatorial current. The biological productivity at 146° W is high in the center of the tongue (100 to 200 g carbon $m^{-2} yr^{-1}$) and low outside (25 g carbon $m^{-2} yr^{-1}$) or a ratio of 6 to 1, if we assume an average of 150 g carbon $m^{-2} yr^{-1}$ for center sample. The ratio of the carbon monoxide concentration in water at the center of the tongue to that at its outer edges (at 146° W) is $13 \times 10^{-5}/2.4 \times 10^{-5}$ ml/l, which is equal to a ratio of 5.4 to 1.

Another, but smaller, CO concentration peak was observed at 40° S (Fig. 3). The Subtropical Convergence is located at this latitude. In this area, the colder water from the south sinks beneath the warmer water of the north. A slight increase in biological productivity has been reported by Fleming & Laevastu (1956) for this region of 30° S to 40° S. The convergence, together with the presence of increased biological activity, may account for the observed increase in carbon monoxide production, which we observed at 40° S.

South of New Zealand a steady and continuing increase in the average carbon monoxide concentration was recorded. The CO level reached a peak at 60° S, after which it began to decrease.

In the Pacific the Antarctic Convergence occurs at 60° S and primary productivity during the austral summer is highest at this latitude. These biologically-active regions extend from 50° S to 75° S, and are comparable in magnitude to the productivity along the Peruvian coast. Again, at 60° S, there is a combination of convergence and productivity which may account for the observed increase in CO concentration. A single sample taken on 23 December 1972 and two vertical profiles taken in the sea ice on 20 and 23 December gave very high hydrocarbon and CO concentrations. It has been shown through laboratory experiments by Wilson et al. (1970) and Junge et al. (1970) that the production of light hydrocarbons and carbon monoxide are related in part to biological activity and/or primary productivity. Unfortunately, no biological data, which could correlate CO production with biological activity, were taken on this expedition. At all three locations, 10° S, 40° S and 60° S, upwelling or convergence accompanied by high biological activity resulted in increased CO concentrations.

Our measurements have shown that carbon monoxide levels in the surface waters of the South Pacific Ocean are orders of magnitude higher than the calculated amount of CO based on Henry's Law. The solubility coefficient of CO varies between 30.0 ml/l at -1.0°C and 17.4 ml/l at 28°C. If the average atmospheric concentration in the southern hemisphere equals 0.035 ppm, a typical surface water concentration of carbon monoxide in equilibrium with the atmosphere would be 0.1×10^{-5} ml/l at -1.0°C to 0.05×10^{-5} ml/l at 30°C. The lowest measured carbon monoxide concentration in the surface waters was 1.0×10^{-5} ml/l,

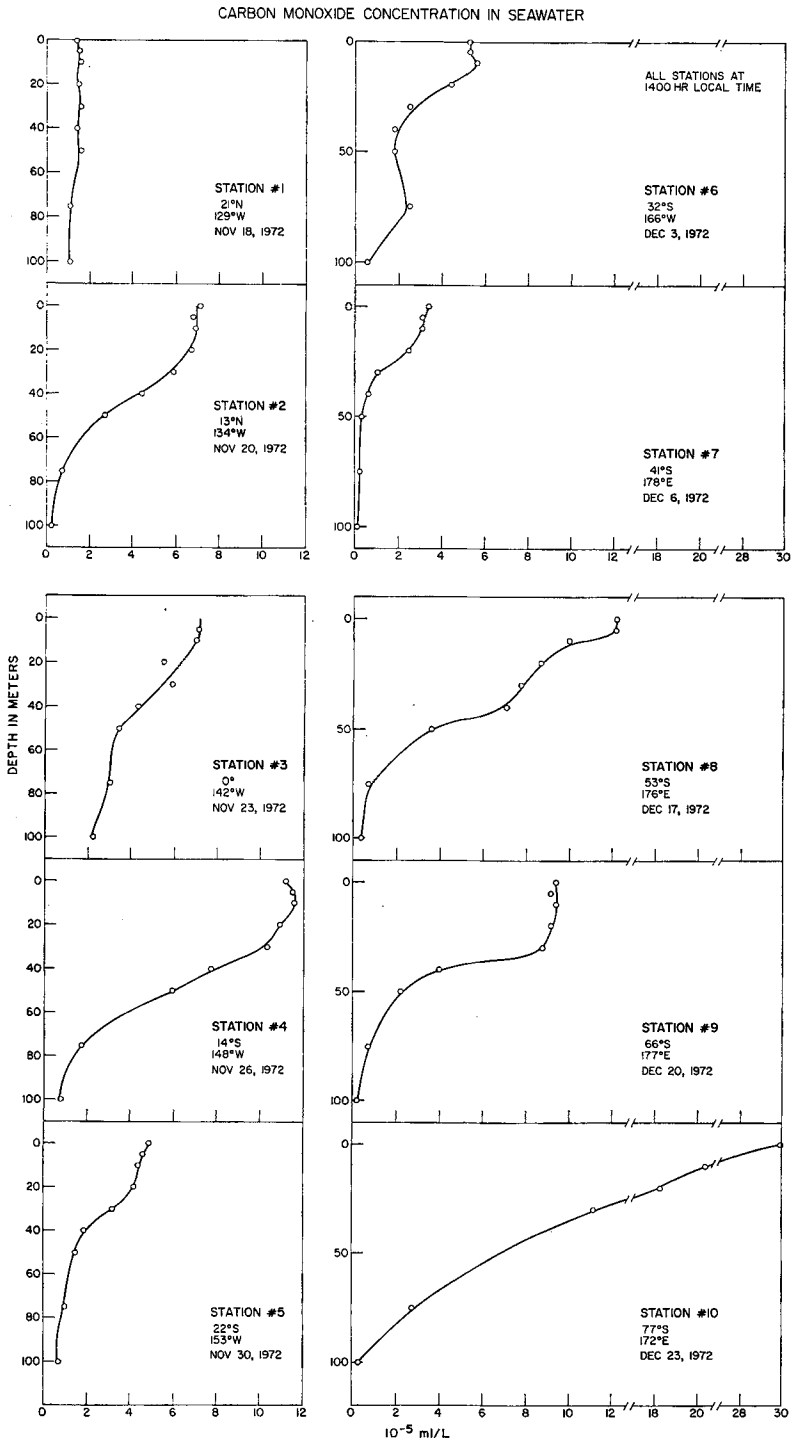

Fig. 4. Plot of vertical profiles of CO in sea water, depth in meters vs. concentration of CO in units of 10^{-5} ml/l.

while the highest was 30.0×10^{-5} ml/l. Therefore, all surface water CO concentrations in the southern hemisphere are supersaturated relative to the atmospheric CO concentration. The ratio (R) of measured to calculated CO varies from 10 to 400 (a value of 1 would be an equilibrium condition). Carbon monoxide data for the oceans have, in all cases, shown supersaturation relative to the overlying atmospheric levels. Average surface water concentrations of carbon monoxide for various areas investigated are: Arctic, 5.6×10^{-5} ml/l; north Atlantic, 7.0×10^{-5} ml/l; north Pacific, 6.0×10^{-5} ml/l; and south Pacific, from the Equator to the Antarctic, 8.0×10^{-5} ml/l.

Vertical profiles

In Fig. 4 the results of the ten vertical profiles taken with Niskin bottles to a depth of 100 m are given. Concentration units of 10^{-5} ml/l for carbon monoxide are on the abscissa. All the vertical profiles follow a similar pattern, i.e., they show a maximum in the surface and a rapid decrease with depth. Station 1 is the only exception to this general picture. The vertical profiles for Station 10, which was in a very thick ice had the highest concentrations of CO for a given depth. In this case, the hydrocarbon concentrations were also the highest measured.

CO in rain, snow and ice

During the cruise, one rain sample was collected at 35° S. The carbon monoxide concentration in the rain water was 6×10^{-5} ml/l. This concentration is slightly lower than the level measured in rain collected in the North Pacific (Swinnerton et al., 1970). This South Pacific rain sample was found to be supersaturated in carbon monoxide with a ratio of 85 to 1.

Sea ice was collected in McMurdo Sound for the purpose of measuring carbon monoxide and hydrocarbons. The hydrocarbon results are reported elsewhere (Lamontagne, et al., 1973). Sampling of sea-ice was divided into three distinct zones: (1) Surface snow, (2) "blue ice", (3) "brown ice". Blue ice is the older and more compact ice. The brown ice was in direct contact with the water. The brown color is the result of high concentrations of algae which penetrate several feet into the bottom of the ice (Bunt & Lee, 1970). The carbon monoxide concentration in the surface snow was 10×10^{-5} ml/l, which compared favorably with the surface water samples where the concentration averaged 6×10^{-5} ml/l. The blue ice has a carbon monoxide concentration about twice that of the snow, 18×10^{-5} ml/l and the brown ice has a concentration of about four times that of the snow (37×10^{-5} ml/l).

Summary

It is apparent from the results of this study that atmospheric carbon monoxide concentrations are lower in the southern hemisphere than those measured in the northern hemisphere. CO concentrations decrease abruptly when crossing the ITC zone from the north to the south.

Surface samples of sea water collected in the south Pacific are shown to be supersaturated in carbon monoxide relative to the overlying atmosphere. The concentration levels of carbon monoxide in sea water are comparable to those obtained in the northern hemisphere. The production of high concentrations of carbon monoxide in the sea water appear to be related to upwelling or convergence zones which are also associated with increased biological activity. It appears that the south Pacific Ocean could be a source of carbon monoxide rather than a sink.

Several vertical profiles were taken during the cruise, which show that carbon monoxide concentrations in sea water decrease with depth. Generally, the CO concentration was highest near the surface between 0 and 30 m. Samples of Antarctic sea ice were found to contain carbon monoxide concentration levels that are two to four times higher than those measured in the open sea water.

Acknowledgement

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ОКИСЬ УГЛЕРОДА В ЮЖНОЙ ЧАСТИ ТИХОГО ОКЕАНА

Во время последней океанографической экспедиции на борту ледокола США «Гласиер» отбирались пробы как из атмосферы, так и с поверхности воды для анализа содержания CO. Корабль проследовал от Лонг Бич в Калифорнии до пролива Мак Мердо в Антарктисе. Концентрации CO в атмосфере в южной части Тихого океана были найдены много меньшими, чем в его северной части: $0{,}4 \cdot 10^{-7}$ и $1{,}3 \cdot 10^{-7}$, соответственно. Концентрации CO в воде в южной части Тихого океана находятся в пределах от 1 до $30 \cdot 10^{-5}$ *мл/л*, что вполне сравнимо с уровнями, измеряемыми в океанах северного полушария. Во всех водных пробах содержание окиси углерода было перенасыщено по отношению к окружающей атмосфере. Наибольшие концентрации CO в воде были в областях поднятия или конвергенции вод. Эти области также связаны с высокой биологической активностью. На пути между Лонг Бич и проливом Мак Мердо было получено десять вертикальных профилей CO в воде. В общем, концентрация CO была наибольшей в пределах верхних 30 метров с устойчивым падением ее до нуля на глубине 100 *м*. Наивысшие концентрации CO были найдены на дне морского льда. Нижняя часть льда содержит большое количество коричневых водорослей, которые проникают снизу на расстоянии до полуметра в лед. Снег на поверхности льда содержит CO_2 в количествах, сравнимых с теми, которые имеются в поверхностных водах в той же области.