The solubility of very low concentratiions of carbon monoxide in aqueous solution

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ABSTRACT

The solubility of carbon monoxide in natural waters has been determined when the partial pressure of carbon monoxide in the gas phase approaches atmospheric concentrations. For both pure water and seawater the solubilities were found to be more than eight times the values which have previously been observed with an atmosphere of pure carbon monoxide present. Carbon monoxide therefore does not obey Henry's law over the pressure range from approximately 10^{-5} atmospheres to greater than one atmosphere. The exchange constant for the exchange of carbon monoxide across the boundary layer of aqueous solutions has also been determined. Values for seawater range from 1.5×10^{-7} m s^{-1} under calm conditions to 1×10^{-6} m s^{-1} under the most turbulent conditions studied. The data obtained has been used to re-evaluate the existence and size of the proposed oceanic source of carbon monoxide. A value of 10^{11} g of carbon monoxide has been calculated for the amount of carbon monoxide produced annually by the world's oceans, and this represents only 0.05 % of the estimated carbon monoxide produced by man, and less than 0.002 % of the largest natural source of carbon monoxide, which is the atmospheric oxidation of methane.

Introduction

In recent years, the difficulty in explaining the relatively short lifetime of CO in the atmosphere has been partially overcome by a proposed oceanic source of CO. Robinson & Robbins (1968*a*) observed frequent diurnal variations in atmospheric CO concentrations during a trans-Pacific cruise from San Francisco to New Zealand, and these variations could be explained if the surface ocean waters were acting as a source of CO. Swinnerton et al. (1969) simultaneously measured the CO concentrations of the atmosphere and of the surface waters at several locations during an Atlantic cruise. It was found that the actual measured CO concentration of the surface waters (w) at all sampling points ranged from 7 to 90 times (averaging 28 times) the theoretical CO concentrations of the surface waters (T), calculated using CO solubility data obtained by Douglas (1967). These findings have since been confirmed (Seiler et al., 1970; Swinnerton et al., 1970; Lamontagne et al., 1971) and indicate that the ocean, at least in the areas studied, is not a sink for atmospheric CO, but serves as an additional natural source.

Investigations have also been carried out by Swinnerton et al. (1971) which show up to a 200-fold supersaturation of CO in rainwater, relative to the partial pressure of CO in the atmosphere. This supersaturation was calculated using CO solubility data for pure water obtained by Winkler (1906), and again indicates the existence of an additional natural source of CO.

The degree of supersaturation of CO in natural waters which has been recorded depends critically on the value of the solubility coefficient used. For seawater the value obtained by Douglas (1967) for an atmosphere of pure CO was 0.020 at 298 K (solubility expressed as the volume of gas at STP absorbed by unit volume of seawater when the pressure of the gas equals one atmosphere). For pure distilled water the value obtained by Winkler (1906) for pure CO was 0.023 at 293 K. To substantiate the proposal of an oceanic source of CO, it is necessary to check the applicability of Henry's Law (relating solubility and pressure) for the case of CO, by determining the solubility of CO in

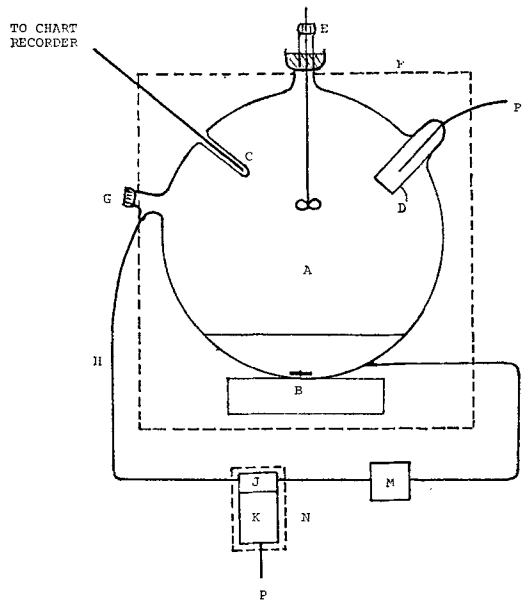

Fig. 1. Apparatus used to measure rate of exchange of CO across the gas/liquid interface. *A*, 5 l flask; *B*, magnetic stirrer motor; *C*, thermistor; *D*, thin end-window geiger counter; *E*, mercury-sealed stirrer; *F*, plastic canopy; *G*, septum for injection of ^{14}CO; *H*, 1 mm bore PVC tubing; *J*, glass flow cell; *K*, photomultiplier tube; *M*, peristaltic pump; *N*, counting head; *P*, signal leads to counting electronics.

natural waters when the partial pressure approaches that frequently observed in the ambient atmosphere. Results published by Douglas (1967) and Winkler (1906) were obtained for pure CO at pressures greater than or equal to one atmosphere. However, atmospheric CO partial pressures are normally in the region of 0.01–0.3 ppm. Results obtained in this region of CO partial pressure, which agree with the solubility coefficients obtained previously, will justify the extrapolations which have been made (Swinnerton et al., 1969, etc.). Also, data relating to the flux of CO across the air-water interface will be useful in determining characteristics of the oceanic source of CO. The object of this paper is therefore to report the results obtained, using a radiochemical technique, for the solubility of CO in natural waters at very low CO concentrations; and also to report data on kinetics of CO exchange across the air-water and air–seawater interfaces.

Experimental

In order to determine the solubility coefficient of CO in water and seawater, a number of 25 ml serum-cap bottles were partially filled with 10 ml of the aqueous solution under study.

A small amount of ^{14}CO was injected into the gas phase by means of a hypodermic syringe and the bottles were placed inverted into a water bath at 298 K and shaken mechanically for about 3 hours. The bottles were then removed and the pressure inside the bottles equilibrated with atmospheric pressure by passing a syringe needle through the serum cap. The bottles were then replaced in the water bath for a further 60 min after which time they were removed and immediately analysed for ^{14}CO in the two phases.

To determine the kinetics of the gaseous exchange across the phase boundary the apparatus shown in Fig. 1 was used. 250 ml of solution was exposed to ^{14}CO in a multiple-necked 51 flask. Positions were available for a mercury sealed Quickfit stirrer to stir the gas phase, and for a thermistor to give a continuous record of temperature when connected to a chart recorder. The activity of ^{14}CO in the gas phase was monitored by means of a Phillips 18505 Thin End-Window Geiger tube connected to a Baird Atomic Spectrometer (Model 530) and chart recorder. A further neck in the flask was present to enable injection of the ^{14}CO. 1 mm internal diameter P.V.C. tubing was connected to the remaining two openings in the flask. A peristaltic pump was used to pump the solution through this tubing into a calcium fluoride europium-activated glass flow-cell (Model NE 808, Nuclear Enterprises Ltd, England) which was positioned on top of a photomultiplier tube inside a counting head (NE5504 Basic Head Unit). The scintillations arising from the β-emission of ^{14}CO in solution were detected by the photomultiplier tube and registered on a Baird Atomic Spectrometer (Model 530) and continuously plotted on a chart-recorder. The complete solution pumping circuit had a volume of about 10 ml, and the solution in the flask was stirred with a magnetic stirrer. The flask itself was enclosed in a large plastic canopy which served to minimise temperature fluctuations. The temperature was kept slightly above room temperature by means of a heating tape coupled to a mercury-toluene switch. This gave

a temperature variation in most cases of less than ± 0.5 K.

The desorption of ^{14}CO from solution could also be studied by rapidly removing the ^{14}CO in the gas phase through a tube connected to a water pump and inserted into the opened injection port.

The concentration of CO in the gas phase was determined using a gas-phase counter constructed in this laboratory. A known volume of ^{14}CO gas was injected through a serum-cap into an all-glass enclosure above a Phillips 18505 thin end-window geiger tube. The observed countrate was compared with that obtained for a standard $^{14}CO_2$ sample which was standardized by absorbing 10 μl onto a small piece of filter paper soaked with ethanolamine which was inside a liquid scintillation vial fitted with a serum-cap. (A 99–100% absorption of $^{14}CO_2$ onto ethanolamine has previously been reported by Krzywanska & Mendecki (1966).) Counting was carried out on a Packard Tri-Carb Scintillation Spectrometer Model 3003, using the channels ratio method to determine the specific activity. A simple calculation then allowed the CO concentration of the sample to be determined. This method of analysis proved to be especially successful for low activity CO samples because of the negligible absorption characteristics of this gas (i.e. onto the walls of the counting chamber).

The determination of the solution CO concentration required a knowledge of the efficiency of the calcium fluoride glass flow-cell. This was obtained by passing a $H_2{}^{14}CO$ solution of known specific activity through the flow cell in the same manner as for ^{14}CO exchange experiments. The observed countrate could be expressed in terms of the flow-cell efficiency, and the CO concentration in solution at any particular time during an experiment could be determined from a simple equation involving the observed countrate and the calculated flow-cell efficiency.

It should be noted that before the injection of ^{14}CO into the reaction vessel in any experiment, the labelled gas was first extracted with ethanolamine solution to remove any $^{14}CO_2$ present. The absorption of CO_2 into the ethanolamine was shown to be 100% efficient by performing the extraction with only $^{14}CO_2$ in the gas phase. No activity was observed in the gas phase after extraction with ethanolamine solution, indicating complete removal of $^{14}CO_2$.

Table 1. *CO solubilities*

Solution	No. of results	α^a	σ^b	$(CO)_g \times 10^3$ (μg cm^{-3})
Doubly distilled water	12	0.18	0.06	3.84–22.4
Synthetic (Subow) seawater	9	0.14	0.05	6.57–11.6
Natural seawater	10	0.17	0.03	5.11–8.20

[a] Absorption coefficient, equal to the volume of gas at STP absorbed by unit volume of solution when the pressure of the gas itself is one atmosphere.
[b] Standard deviation.
Number of samples indicated in parentheses

Results and discussion

The CO solubility data obtained for doubly distilled water and seawater at 298 ± 1 K is summarised in Table 1. The solubility is expressed in terms of α, the solubility coefficient, which is the volume of gas at STP absorbed by Unit volume of water when the pressure of the gas itself, without the aqueous tension, equals one atmosphere. The value for doubly distilled water of 0.18 ± 0.06 can be compared with the value obtained by Winkler (1906) for an atmosphere of pure CO of 0.02142 at 298 K. Thus at CO partial pressures of $3.84 \times 10^{-3} - 22.4 \times 10^{-3}$ μg cm^{-3} (3.0 – 17.8 ppm) the solubility in pure water is about 8.6 times as great as when an atmosphere of pure CO is present. The range of gaseous CO concentrations able to be studied was limited by the specific activity of the ^{14}CO, but it is not unreasonable to assume that the solubility coefficient of CO at atmospheric concentration levels (about 10^{-1} ppm) will be close to 0.18 (and not 0.02142) since the extrapolation from 10 ppm to 10^{-1} ppm is much less than the extrapolation from one atmosphere (10^6 ppm) to 10^{-1} ppm. This also follows from the expected ideal behaviour of a gas at low concentrations rather than at high concentrations. Henry's Law should therefore be obeyed when CO concentrations are in the atmospheric concentration range, with deviations occurring at higher concentrations. The deviation at higher concentrations would be expected to occur in the direction which is in fact observed, since the presence of relatively large CO concentrations in solution will inhibit further dissolution of the gas. The resulting

Table 2. *CO supersaturation in rainwater*[a]

Location	R[b] Average	Range
Washington D.C. (17)	0.85	0.22–3.7
Pacific Ocean		
Day (4)	8.5	6.5–13
Night (1)	2.0	—
Hawaii (Saddle Road)		
Day (9)	14	6.4–24
Night (13)	6.1	1.9–12
Hawaii (C.P.O.)		
Day (13)	4.8	2.0–10
Night (14)	3.0	2.4–4.0

[a] Table published in original form in reference Swinnerton et al. (1971).

[b] Ratio of measured concentration of CO in rainwater to calculated concentration based on the partial pressure of CO in the atmosphere and a solubility of 0.18 at 298 K. ($R = 1$ at equilibrium.)

absorption coefficient at high concentrations will therefore be less than at low concentrations.

A value of 0.18 for the solubility coefficient of CO at atmospheric concentration levels (at 298 K) will greatly effect the degree of supersaturation of CO in rainwater reported by Swinnerton et al. (1971). The CO data obtained by these researchers has been re-evaluated and is shown in Table 2. The supersaturation in every instance is 8.6 times smaller than calculated previously and it can be seen that in certain samples the rainwater is unsaturated with respect to CO. In these cases the net transport will be from the atmosphere into the raindrop. This additional natural source of CO will therefore be much smaller than originally proposed (Swinnerton et al., 1971), and may be more adequately explained in terms of the photochemical oxidation of organic matter in rainclouds and/or the dissociation of CO_2 induced by electrical discharges. The revised supersaturation values in Table 2 also appear to be much more realistic than the very high values derived in the original report.

The solubility coefficient for CO in seawater is 0.15 ± 0.04 (at 298 K), and can be compared with the value of 0.018 obtained by Douglas (1967) for an atmosphere of pure CO at 298 K and a seawater salinity of 36 parts per thousand. Hence at CO partial pressures of $5.11 \times 10^{-3} - 11.6 \times 10^{-3}$ μg cm^{-3} (4.1 – 9.2 ppm) the solubility in seawater is approximately 8.3 times greater than the solubility when an atmosphere of pure CO is present. Assuming that 0.15 is a good approximation of the solubility coefficient of CO at atmospheric concentration levels, the existence and size of the proposed oceanic source must be reconsidered. The supersaturation of the surface waters of the Atlantic ocean reported by Swinnerton et al. (1969) will be smaller by a factor of 8.3. This means that at certain sampling points the surface waters will in fact be unsaturated with respect to CO, and the net transport of the gas will be from the atmosphere to the ocean, i.e. at these points the ocean will act as a sink for CO. The possibility that the ocean may act as both a source and a sink for CO is not unlikely, since the same phenomenon is known to occur in the case of CO_2 for example.

This phenomenon of CO supersaturation has also been reported by Seiler & Junge (1970) and Lamontagne et al. (1971) and their results must be similarly adjusted to take into account the increased solubility of CO at low partial pressures.

It is possible that microbiological conversion of ^{14}CO to $^{14}CO_2$ affected the solubility data reported in Table 1. This possibility is, however, considered to be very slight for the following reasons:

(*a*) Preliminary experiments on deionised water gave very high and irregular CO solubilities. When doubly-distilled water was used lower, and consistent, solubilities were obtained.

(*b*) The regime of micro-organisms present in natural seawater and synthetic seawater prepared from doubly-distilled water must be distinctly different. The CO solubilities found for both of these solutions are not experimentally distinguishable.

The exchange of CO across the gas-liquid phase boundary may be described in terms of the kinetic equation:

$$v = k_1 A(\mathrm{CO})_g - k_{-1} A(\mathrm{CO})_s \qquad (1)$$

where v = velocity of uptake of CO into solution,
k_1 = exchange constant for the transfer of CO from gas to liquid phase,
k_{-1} = exchange constant for the transfer of CO from liquid to gas phase,
$(\mathrm{CO})_g$ = gaseous CO concentration at any time.
$(\mathrm{CO})_s$ = corresponding solution CO concentration.

A = area of interface between the two phases. v, which has dimensions of quantity time^{-1} may be equated to the concentration gradient in solution multiplied by the volume of the aqueous phase, i.e.

$$v = V_s \frac{d(\mathrm{CO})_s}{dt} \tag{2}$$

where V_s = volume of the liquid phase.

Eqs. (1) and (2) give rise to the kinetic equation

$$\frac{d(\mathrm{CO})_s}{dt} = \frac{k_1 A}{V_s}(\mathrm{CO})_g - \frac{k^{-1} A}{V_s}(\mathrm{CO})_s \tag{3}$$

which can be solved with the appropriate boundary conditions. These are

(i) $(\mathrm{CO})_g$ = constant. (This is a consequence of the total gas volume (about 5 l) being much greater than the liquid volume (0.25 l) and also of the solubility being small.)

(ii) $k_1/k_{-1} = K$, the equilibrium constant, which may be obtained from the solubility coefficient since

$$k_T = \alpha_T \times T/273 \tag{4}$$

where T is the temperature in degrees Kelvin. The solution of eq. (3) under these boundary conditions is

$$(\mathrm{CO})_{s,t} = (\mathrm{CO})_{s,e}\left[1 - \exp\left(-\frac{k^{-1} A}{V_s} t\right)\right] \tag{5}$$

Table 3. *CO exchange constants for distilled water at 298 K (±1 K)*

Solution stirring speed (r.p.m.)	No. of results	$(\mathrm{CO})_g$ (av.) $\times 10^3$ (μg cm^{-3})	$k_1 \times 10^7$ (ms^{-1})	$k_{-1} \times 10^6$ (ms^{-1})
225	2	1.8	21	10.6
190	2	1.3	3.9	2.0
160	4	5.5	19	9.8
100	6	3.5	13	6.6
90	5	1.6	7.2	3.7
75	2	0.6	5.1	2.6
55	2	3.8	11	5.7
0	1	1.8	2.5	1.3

Table 4. *CO exchange constants for seawater at 298 K (±1 K)*

Solution stirring speed (r.p.m.)	No. of results	$(\mathrm{CO})_g$ (av.) $\times 10^3$ (μg cm^{-3})	$k_1 \times 10^7$ (ms^{-1})	$k_{-1} \times 10^6$ (ms^{-1})
230	4	3.7	10	6.1
150	2	3.6	5.2	3.2
110	4	2.0	4.1	2.5
75	2	1.8	7.5	4.6
0	2	1.8	1.5	0.9

where $(\mathrm{CO})_{s,t}$ is the solution CO concentration at any time and $(\mathrm{CO})_{s,e}$ is the equilibrium solution CO concentration. Rearrangement of (5) leads to a direct relationship between

$$\ln((\mathrm{CO})_{s,e} - (\mathrm{CO})_{s,t})$$

and t and from this k_{-1} (and consequently k_1 from the equilibrium constant K) may be determined.

A similar physical model can be developed to describe the desorption of CO from solution, the resulting kinetic equation being

$$(\mathrm{CO})_{s,t} = (\mathrm{CO})_{s,0}\exp\left(-\frac{k^{-1} A}{V_s} t\right) \tag{6}$$

where $(\mathrm{CO})_{s,0}$ is the initial CO concentration in solution. This therefore provides a second method of determining k_1 and k_{-1}. Results obtained for doubly distilled water at a number of different solution stirring speeds are given in Table 3. A similar set of results for seawater is given in Table 4. The error in the values of the exchange constants quoted is estimated to be about 30%.

The model chosen to describe the physical significance of the exchange constants k_1 and k_{-1} is normally the laminar layer model due to Lewis & Whitman (1924). In this model a liquid film at the surface is assumed to be relatively unstirred whereas the main body of the liquid is in turbulent flow with complete mixing. A similar situation is assumed to exist in the gas phase. Molecular diffusion is thought to regulate gaseous exchange across the two interfacial layers, with the rate controlling phenomenon usually being the slower diffusion in the liquid phase. In the laminar layer model the exchange

Table 5. *Liquid laminar layer thicknesses at the air–water interface*

CO exchange

Solution stirring speed (r.p.m.)	$k_{-1} \times 10^6$ (ms^{-1})	Liquid laminar layer thickness (mm)
0	1.3	1.7
55	5.7	0.4
75	2.6	0.9
90	3.7	0.6
100	6.6	0.3
160	9.8	0.2
225	10.6	0.2

Table 6. *Liquid laminar layer thicknesses at the air–seawater interface*

Solution stirring speed (r.p.m.)	$k_{-1} \times 10^6$ (ms^{-1})	Liquid laminar layer thickness (mm)
0	0.9	2.4
75	4.6	0.5
110	2.5	0.9
150	3.2	0.7
230	6.1	0.4

constant k_{-1} may be resolved into the ratio of the diffusion coefficient D in the liquid boundary layer over the thickness δ of this layer.

$$k_{-1} = D/\delta \qquad (7)$$

The diffusion coefficient of CO in water has been measured by Wise & Houghton (1968) to be 2.2×10^{-9} m^2 s^{-1} at 298 K. Using this value of D, the liquid boundary layer thickness corresponding to the exchange constant k_{-1} at various stirring speeds has been calculated from eq. (7), and the results for distilled water and seawater are shown in Tables 5 and 6 respectively.

Diffusion of gas through the liquid laminar layer proceeds at a rate determined not only by the thickness of the film but also by the partial pressure difference across it, and the solubility and diffusion coefficient of the gas being considered. This can be written as

Rate of exchange = (solubility × diffusion coefficient × partial pressure difference)/liquid l. l. thickness (8)

Data presented by Swinnerton et al. (1970) will enable the partial pressure difference between the atmosphere and the surface waters at two stations in the Atlantic ocean to be determined. Using eq. (8) this data, along with solubility and laminar layer thickness results obtained

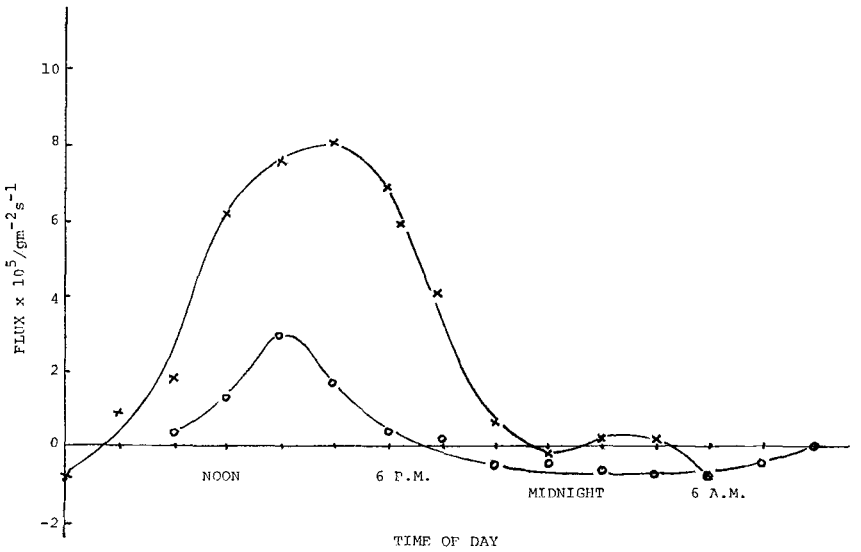

Fig. 2. Rate of exchange of CO across the air–sea interface. ×, 10°38′ N, 60°05′ W; 21–22 April 1969. ○, 13°13.9′ N, 59°07′ W; 18–19 April 1969.

here for seawater, it is also possible to calculate the overall rate of exchange of CO across the air–sea interface at these two stations. A value of 0.3 mm has been chosen to represent the average thickness of the oceanic layer, since it is felt that the most turbulent conditions of stirring in the experiments performed are the closest approximation to an average atmospheric turbulence.

The rate of exchange of CO across the air–sea interface over a 24-hour period for each of the two Atlantic sampling stations is shown graphically in Fig. 2. Negative values of exchange rate indicate transfer of CO from the atmosphere to the ocean. By measuring the areas beneath the curves it is possible to determine the net amount of CO transferred from the oceans to the atmosphere over a 24-hour period. For the station at 13°13.9′ N, 59°07′ W during the 24-hour period from the 18th to 19th April 1969, a net total of 0.21 μg m^{-2} was transferred from the oceans to the atmosphere, and for the station 10°38′ N, 60°05′ W during the 24-hour period from the 21st to 22nd April 1969, a net total of 2.5 μg m^{-2} was similarly transferred. The greater amount of CO transferred at the latter station was attributed by Swinnerton et al. (1969) to be due to a greater biological activity in this region.

On a worldwide basis the amount of CO transferred from the oceans to the atmosphere can be estimated. If the average rate of exchange of CO is approximately 1 μg m^{-2} per day, then in 1 year the oceans could contribute approximately 1×10^{11} g of CO to the atmosphere, based on a surface area of 3.6×10^{14} m^2 for the world oceans. Recent estimates by Jaffe (1968) and Robinson & Robbins (1968*b*) give a value of 2×10^{14} g yr^{-1} for the anthropogenic production of CO, which means that the oceans produce only about 0.05% of the estimated CO produced by man. This calculated oceanic source is also relatively insignificant when compared with other large natural sources. For example it has already been mentioned that CO is produced naturally at a rate of 5×10^{15} g per year, and that this large amount of CO production can be accounted for by methane oxidation (10). Hence the magnitude of the oceanic source is only about 0.002% the size of the largest known natural source of CO.

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О РАСТВОРИМОСТИ ОЧЕНЬ НИЗКИХ КОНЦЕНТРАЦИЙ CO В ВОДЯНЫХ РАСТВОРАХ

Определялась расторимость CO в естественной воде, когда парциальное давление CO в газовой фазе приближается к атмосферным концентрациям. Как для чистой воды, так и для морской воды было найдено, что растворимость превосходит в восемь раз значения, которые первоначально наблюдались при наличии атмосферы из чистого CO. Поэтому CO не подчиняется закону Генри в диапазоне давлений от 10^{-5} атмосферы до одной и более атмосферы. Константа обмена для диффузии CO через пограничный слой водяных растворов также была определена. Значения для морской воды колеблются от $1{,}5 \times 10^{-7}$ *мс*$^{-1}$ при спокойных условиях до 1×10^{-6} *мс*$^{-1}$ при наиболее турбулентных условиях. Полученные данные были использованы для новой оценки существования и величины возможного океанического источника CO. Количество CO, производимого ежегодно мировым океаном, было вычислено равным 10^{11} г., что составляет только 0,05 % CO производимого человеком и менее 0,002 % наибольшего естественного источника CO, каким является окисление метана в атмосфере.