Carbon Monoxide in Seawater (Atlantic Ocean)

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In 1978–1980, measurements of dissolved carbon monoxide in seawater were carried out during three ship expeditions in the northern and southern Atlantic Ocean, covering an area between 53°N and 35°S. Measurements in surface water were performed by a continuously working equilibration technique that allowed for the determination of small and rapid variations of the dissolved CO. Carbon monoxide concentrations in the water body increased toward the sea surface, there reaching saturation factors of up to 50 with respect to atmospheric CO. The daily average CO saturation increased with average chlorophyll a concentration and light intensity and decreased with wind speed. The dissolved CO showed strong diurnal variations, with maximum values in the afternoon. Diurnal variations were observed within the entire euphotic zone, indicating that CO is both produced and consumed in the seawater. Carbon monoxide production in seawater was mainly due to photooxidation of dissolved organic matter. Photobiological and microbial CO production processes were of minor importance. Carbon monoxide destruction was due to a light-independent microbial metabolism. Based on average CO saturation factors of 30 ± 20 in the surface water of the ocean, the total source strength for atmospheric CO is calculated to 10–180 Tg yr^{-1}.

INTRODUCTION

Measurements carried out by *Swinnerton and Lamontagne* [1974], *Swinnerton et al.*, [1970], *Seiler and Junge* [1970], *Seiler and Schmidt* [1974, 1976], and *Seiler* [1978] have shown that the surface water of the Atlantic and Pacific oceans is generally supersaturated with respect to the atmospheric CO mixing ratios, indicating that CO is produced in ocean water. Since the CO concentrations correlated closely with phytoplancton, particulate carbon, primary productivity, and chlorophyll a [*Swinnerton et al.*, 1977], it was assumed that CO is produced by metabolic processes, e.g., algae. Observations of CO production in filtered, poisoned, and boiled seawater, however, showed that nonbiological CO-forming processes must also exist in ocean water [*Wilson et al.*, 1970; *Conrad and Seiler*, 1980; *Bullister et al.*, 1982]. On the other hand, it has been demonstrated that dissolved CO is also consumed, most likely by microorganisms [*Seiler*, 1978; *Conrad and Seiler*, 1980], so that the CO concentration in the surface water of the oceans must be controlled by simultaneously occurring production and destruction processes.

The supersaturation of CO in the surface water of the oceans results in a flux of CO from the ocean into the atmosphere that has been estimated by several investigators to be in the order of 10–220 Tg yr^{-1} [*Linnenbom et al.*, 1973; *Seiler and Schmidt*, 1974; *Liss and Slater*, 1974; *Seiler*, 1978; *Logan et al.*, 1981]. The individual estimates are based on a limited number of discontinuous measurements of dissolved CO that were carried out mainly in the northern Atlantic and Pacific oceans. In this paper we present results of semicontinuous measurements of dissolved CO in surface water (4-m depth) and discontinuous measurements in water samples taken in depths between surface and 4000 m. The results were obtained during three ship expeditions between Hamburg and Buenos Aires/Montevideo, covering large parts of the northern and southern Atlantic Ocean. If averaged over 1

hour, the semicontinuous CO measurements result in a total of approximately 8000 data points, which represent the largest data pool hitherto published in the literature. In addition we have carried out laboratory experiments on board the research vessels to study the processes responsible for the CO production and destruction. The results of measurements and laboratory experiments show that CO is predominantly produced by nonbiological processes, most likely by photooxidation of dissolved organic matter, and is consumed in the water by microorganisms. The total net flux of CO from the ocean into the atmosphere is calculated to range between 10 and 180 Tg yr^{-1}.

ITINERARY

The measurements and laboratory experiments were carried out on board the German research vessels *FFS Walther Herwig* and *FS Meteor* during three expeditions in the northern and southern Atlantic Ocean. The routes of the individual expeditions are illustrated in Figure 1. The first continuous CO measurements via the equilibration technique were obtained on board the *Walter Herwig* during an expedition from Mar del Plata (Argentina) to Hamburg in November/December 1978. Because of instrument failure, data are only available between the equator and Hamburg. Further CO measurements in surface water and deep ocean water were carried out on board *Meteor* in January/February 1979. This expedition allowed the semicontinuous record of CO in the surface water of a small ocean area (2°S to 5°N along 22°W) over a 3-week period and gave interesting results on the temporal variations of the amount of dissolved CO. Data on the spatial distribution of CO in surface water were obtained during the third expedition of *Meteor* in October/November 1980.

EXPERIMENT TECHNIQUE

The schematic of the technique for semicontinuous measurements of dissolved CO in surface water is illustrated in Figure 2. The technique employs an upright 1.5-m-long glass cylinder that has a total volume of 7 l. Approximately 90% of this volume was filled with seawater, which was replaced continuously by a water flow of more than 400 l h^{-1}, so that
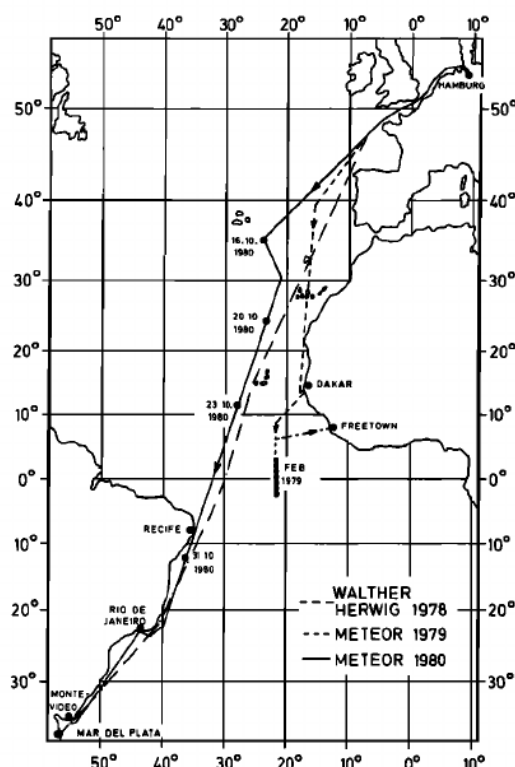
Fig. 1. Routes of the *FFS Walther Herwig* between Mar del Plata (Argentina) and Hamburg and the *FS Meteor* between Hamburg and Freetown (Sierra Leone) as well as Hamburg and Montevideo (Uruguay). Stations for deep water sampling are indicated by (●).

started with CO-free oxygen/nitrogen (20/80) as recycled air. The given response time was determined by measuring the dissolved CO in the seawater outflow of the gas cylinder and the CO mixing ratio of the recycled air, which increased with time after starting the experiments and remained constant after 5 min. After this time the concentration of dissolved CO in the seawater outflow of the glass cylinder was identical with that in the seawater inflow, and the CO mixing ratio of the recycled air coincided with the value calculated via Henry's law from the concentration of dissolved CO. With a response time of 5 min, even short-term fluctuations of the dissolved CO in seawater could be detected.

To determine the CO mixing ratios of the recycled air, the described system was connected to a second loop, which was constantly flushed with a flow rate of 0.3 l min^{-1}. The air was dried by using a refrigerator kept at a constant temperature of $-70°C$; it was then passed through the automatic sampling device and finally recycled into the main system. Samples ($V = 7$ cm^3) were taken once every 10 min and were injected into the CO detector for analysis. The sample volume was replaced by CO-free synthetic air, which was used in the CO detector as the carrier gas to keep the pressure in the air-recycling system constant at ambient pressure. After four analyses, the sampling device was provided with a calibration standard by opening the selenoid valves S2 and closing the valve S1. In general, two samples of calibration standard stored under high pressure in steel tanks were analyzed before the system was switched back to normal operation.

The whole system worked completely automatically, providing four individual data points per hour. The cooling trap was exchanged once a day outside the tropics and twice a day inside the tropics when the water temperature reached 28°C. Data points obtained within 20 min after the exchange of the cooling trap were not considered in the following discussion. Interferences of the CO measurements by parts of the equilibration system, such as pumps, stainless-steel tubing, selenoid valves, glass cylinders, cooling traps, etc., were not observed. The glass cylinder had to be kept in darkness to prevent photooxidative production of CO in the water column. Because of the high flow rate, the temperature of the seawater at the inlet and the outlet of the glass cylinder did not differ by more than 0.2°C, which had no

the residence time of seawater in the cylinder was in the order of ≤ 0.7 min. The water column was flushed with air that was recycled at a high flow rate (≥ 5 l min^{-1}) to establish a relatively long contact time between the seawater and the recycled air and thus ensure equilibrium between CO in the liquid and the gas phases. Because of the high flow rate of seawater through the glass cylinder and the small volume of recycled air, the equilibrium was reached after a relatively short time period of about 5 min, when the experiment was
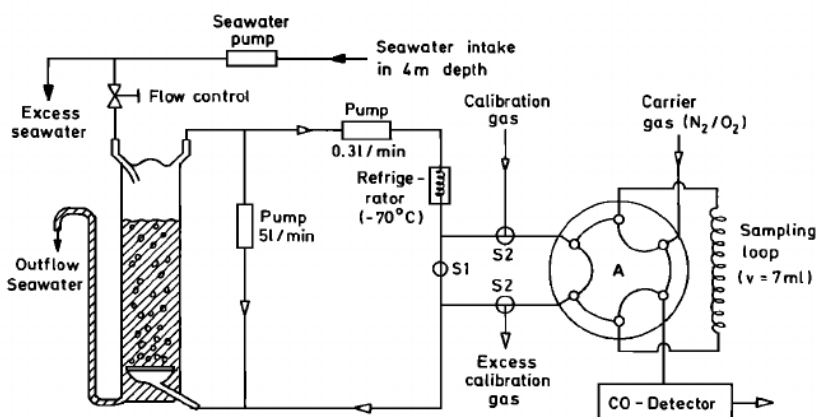

Fig. 2. Schematic of the equilibration and continuous CO analysis system. Valve A is a six-port gas-sampling valve; S1 and S2 are selenoid valves.

significant influence on the accuracy of the obtained CO data.

The seawater was pumped in through a hose near the bow of the ship from a depth of approximately 4 m. It was then pumped at a flow rate of 1500 l h^{-1} into the laboratory, where part of it was used for the continuous measurement of dissolved CO. Comparisons of results obtained by the continuous system and by discontinuous measurements of water sample in the same depth by hydrocasts (Niskin) did not show any significant differences of the dissolved CO, indicating that the CO data obtained by the described continuous system were not significantly influenced by the seawater pump or the conducting pipe. This conclusion is not valid for hydrogen, whose concentration in the continuous system was more than one order of magnitude higher than that found by the discontinuous measurements taken by using hydrocasts. Obviously, H$_2$ was produced in significant amounts by hydrolysis of water, which was caused by the electrodes mounted at the ship's wall and the intake pipe to prevent corrosion.

The CO mixing ratio in the recycled air was measured by using the mercury oxide to mercury vapor conversion

$$HgO + CO \xrightarrow{210°C} Hg + CO_2$$
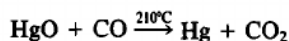
described by *Seiler et al.* [1980]. Hydrogen, as the only interfering gas, was quantitatively separated from CO on a column consisting of stainless-steel tubing ($\phi = \frac{1}{4}''$, length = 60 cm) filled with molecular sieve 13× (45–60 mesh). The lower detection limit of the applied CO instrument during operation on board ship was about 4 ppb, which corresponds to a CO concentration in seawater of $\leqq 0.1$ nl per liter water, assuming equilibrium between gas and liquid phase in the glass cylinder. The detection limit was at least one order of magnitude lower than the expected CO concentration in surface seawater when the dissolved CO is in equilibrium with the atmospheric CO. As an example, Figure 3 shows a section of the CO record obtained on Oct. 19, 1980, between 10 A.M. and 2 P.M. The calibration of the CO instrument via the use of a calibration standard of 0.8 ppm CO is denoted by C, and the seawater analyses are denoted by A. The chromatogram of each analysis consists of two peaks; the first is caused by the H$_2$, and the second by the CO content of the sample. Figure 3 demonstrates the increase of dissolved CO with values of 1.6 ppm in the morning and 2.4 ppm in the early afternoon. Compared to the CO mixing ratios in the air above the sea surface, which are about 120 ppb CO, the seawater in this example is supersaturated by factors of 13 and 20, respectively. Figure 3 also demonstrates the good stability of the CO calibration, which did not change by more than 10% during the cruise.

Whenever the ship stopped, vertical profiles of dissolved CO from the surface down to 250–4000 m were measured. Water samples in depths deeper than 1–2 m were taken by hydrocasts (niskin 10-l samplers). Once on board, the water samples were immediately transferred from the Niskin samplers into 100-ml glass bottles, which were then stored in darkness at room temperature until analysis. Great care was taken that the storage time of the samples did not exceed half an hour so as to prevent possible changes of the CO concentration in the samples as the result of microbial activities, etc. Water samples from the ocean surface layer between surface and 1-m depth were taken from a rubber raft

at a distance of at least 100–200 m from the ship, avoiding disturbances of the vertical CO structure by turbulent mixing caused, for example, by the ship's propeller. The water was sampled in 100-ml glass bottles via a technique already described by *Seiler* [1978].

For analysis of the dissolved CO, about half of the water sample in the glass bottle was replaced by CO-free synthetic air. The glass bottle was then shaken vigorously by hand for approximately 30 s, which was found to be sufficient for the two phases in the glass bottle to equilibrate. A gas sample was then taken from the glass bottle and injected into a second CO instrument for analysis. From the measured CO mixing ratio m and the solubility α of CO in seawater, and from the volumes V_w of the water and V_g of the gas phase in the bottle, the dissolved CO concentration C is calculated by

$$C = m\,(V_g/V_w) + \alpha m$$

Because of the low solubility of CO in seawater, more than 97% of the dissolved CO is found in the gas phase, so that the term αm can be neglected. The lower detection limit of this technique is $\leqq 0.5$ nl CO per liter water. For comparison, the dissolved CO amounts to about 2 nl l^{-1}, when the seawater is in equilibrium with an atmospheric CO mixing ratio of 100 ppb. The overall accuracy of the discontinuous determination of dissolved CO in water samples is better than ±20% for operation on board ships.

Simultaneous CO measurements in air were conducted by means of an automatic CO instrument, described by *Seiler et al.* [1980]. This instrument provides a continuous record of CO mixing ratios in air and has a lower detection limit of 0.1 ppb. The response time is in the range of a few seconds, so that short-term variations of the CO mixing ratios are detected. The instrument was automatically calibrated once
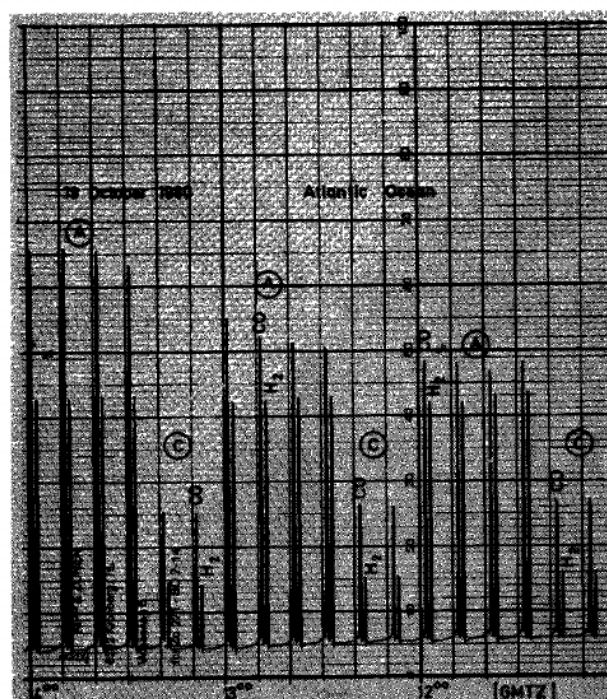
Fig. 3. Section of a continuous record of CO dissolved in surface seawater (4-m depth) with the calibration (C) and the seawater analysis (A). The second peak of each chromatogram is due to CO.
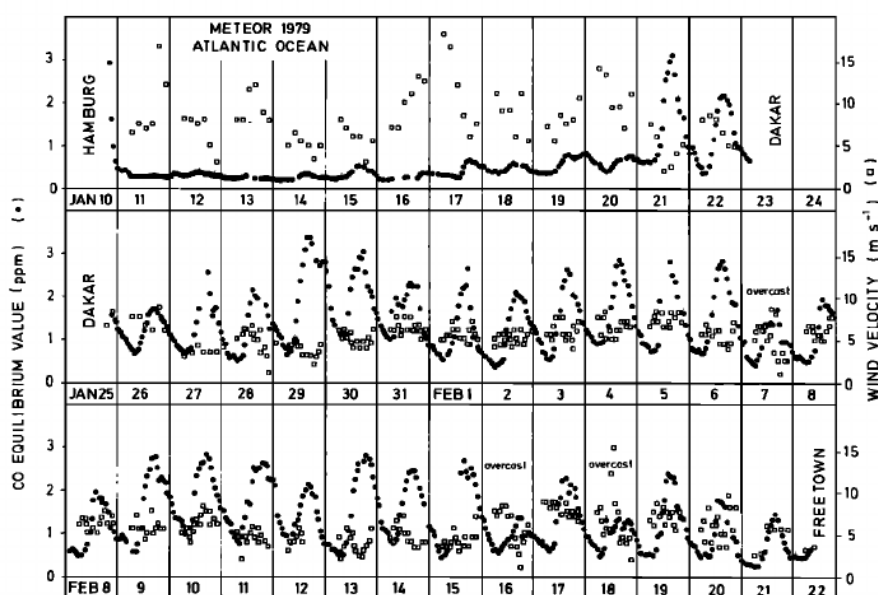
Fig. 4. CO equilibrium values observed in surface water (4-m depth) during *Meteor* cruise 1979. Each data point (●) represents the hourly average CO value. The time is given in GMTZ. Wind speed (□) was measured at 20-m height.

every hour via a CO calibration standard in the ppb range. The linearity of the calibration curve was checked repeatedly during the cruise and was found to remain stable, even under rough sea conditions. The ambient air was drawn in by a metal-bellows pump on the uppermost deck, approximately 20 m above sea surface; it was then pumped into the laboratory at high flow rates, which resulted in short residence times in the conducting pipe. Before analysis, the air was dried at a temperature of −70°C and passed through molecular sieve 13× to avoid possible interferences of the CO record by water vapor and hydrocarbons. Contaminations of the ambient air, for example, by ship exhausts during periods with low wind speed, were perceptible by the strong scattering variations of the CO mixing ratios. Gradients of the CO mixing ratios within the lower 20–30 m of the atmosphere have not been detected, so that the values observed at 20-m height can be assumed to be representative for the CO mixing ratios just above the sea surface.

The light intensity was measured continuously on board ship by using a solarimeter, type CM5 (Kipp und Zonen, Germany). Data on wind velocity, wind direction, and air temperature were taken from the meteorological observations carried out routinely by the meteorological observer present on the research vessels. The chlorophyll a data were provided by Dr. Boje (Kiel, Germany) for the *Meteor* cruise 1979 and by M. Andreae (Tallahassee, Florida) for the *Meteor* cruise 1980.

Laboratory experiments were carried out on board the research vessels to avoid changes in the chemical and microbial composition caused by transport from the ship to the main laboratory. Water samples were incubated in 100-ml glass bottles that were kept in darkness or exposed to daylight. The temperature was kept at ambient values of the ocean surface water by using a water bath. Experiments with the water included boiling for 10 min, poisoning with a concentration of 50 μg ml^{-1} of NaN$_3$, and filtration through Nucleopore filters of 3.0 or 0.2 μm pore size.

RESULTS AND DISCUSSION

CO Dissolved in Surface Water

Figures 4 and 5 summarize the data on dissolved CO in surface water (4-m depth) obtained during the *Meteor* cruises of 1979 and 1980, respectively. Each data point represents the hourly average of the semicontinuous CO record and is given in terms of equilibrium value. The corresponding amounts of dissolved CO are calculated by $C = E\alpha$, with E = equilibrium value and α = solubility of CO in seawater. The short interruptions of the CO record on Oct. 26, 27, and 31 and on Nov. 1, 1980 (Fig. 5), were due to instrument failures or checks of the equilibrator system. Figures 4 and 5 include data on wind velocity, measured at 20-m height, which—following the logarithmic wind law— have to be divided by a factor of about 2 to obtain the wind speed at the sea surface. Figure 5 includes, in addition, the hourly average light intensity and the chlorophyll a concentrations obtained from individual measurements of seawater taken by the ship pump in 4-m depth.

The dissolved CO in surface water (Figures 4 and 5) shows large variations, with maximum values of 4–5 ppm and minimum values of 0.07–0.10 ppm. The corresponding saturation factors calculated by $S = E/M = C/\alpha M$, with M = mixing ratio in the air above the sea surface, varied between a value of 50, indicating high supersaturation of the ocean with respect to atmospheric CO, and a value of 1, indicating equilibrium between the ocean and the atmosphere. Slight undersaturations have been found only during one short time period of several hours in the British Channel on Oct. 11, 1980 (Figure 5), when the CO equilibrium value varied between 80 and 100 ppb, compared to 120 and 150 ppb in the atmosphere. The rest of the ocean water has always been found to be supersaturated with CO.

Dissolved CO as Function of Light
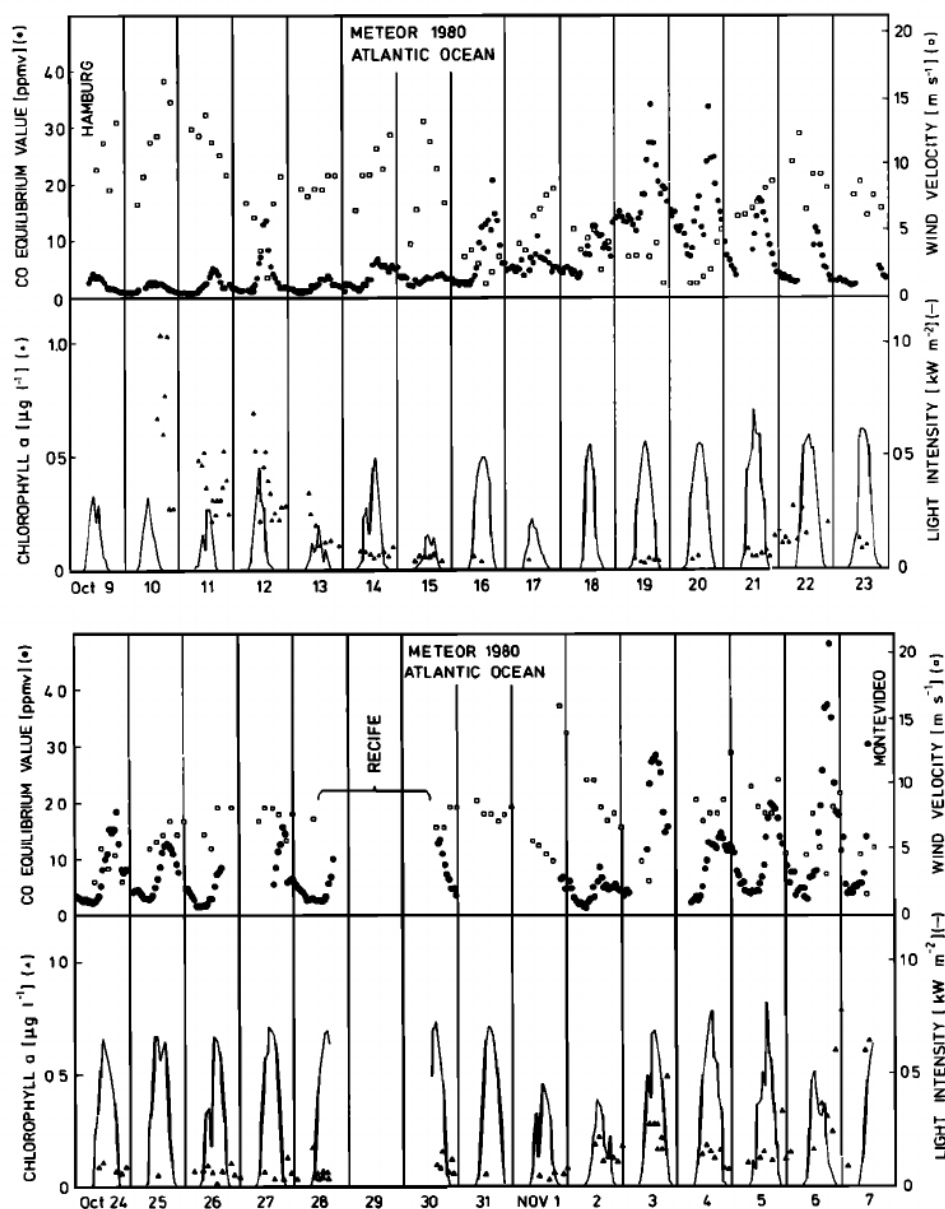
The amount of CO dissolved in surface water showed

Fig. 5. CO equilibrium values observed in surface water (4-m depth) during *Meteor* cruise 1980. Each data point (●) represents the hourly average CO value. The time is given in GMTZ. Wind speed (□) and light intensity (−) was measured at 20-m height. Chlorophyll a (▲) was analyzed in water samples from 4-m depth.

significant diurnal variations, indicating that the CO saturation factor in surface seawater is dependent on light intensity. An excellent example is the semicontinuous record obtained during the *Meteor* cruise 1979 (Figure 4) between Jan. 29 and Feb. 21, 1979, when the ship stayed in a narrow ocean area between 5°N and 2°S along 22°W with almost constant meteorological conditions. Nevertheless, the dissolved CO showed periodic variations, with maximum values in the early afternoon and minimum values in the early morning. Similar diurnal variations were observed during the *Meteor* cruise 1980 in the northern and southern Atlantic Ocean (Figure 5) and have also been reported by other investigators in the Pacific Ocean [*Lamontagne et al.*, 1971; *Swinnerton et al.*, 1974] and other parts of the Atlantic Ocean [*Seiler and Schmidt*, 1974]. The highest amplitudes of

the diurnal variations were observed on sunny days. On rainy days with low light intensities the dissolved CO showed lower amplitudes or remained almost constant. The rapidly changing CO concentrations observed on cloudy days with rapidly changing cloud cover (e.g., Feb. 18, 1979; Figure 4) and consequently changing light intensities are indicative of a relatively short residence time of CO in the ocean surface water.

The daily average CO saturation factors were directly proportional to the daily average light intensities (Figure 6). The scatter of the individual data is due to different wind speeds and different chlorophyll a concentrations on these individual days. The lowest values were generally accompanied by high wind speeds and low chlorophyll a concentrations, whereas the highest values were accompanied by low
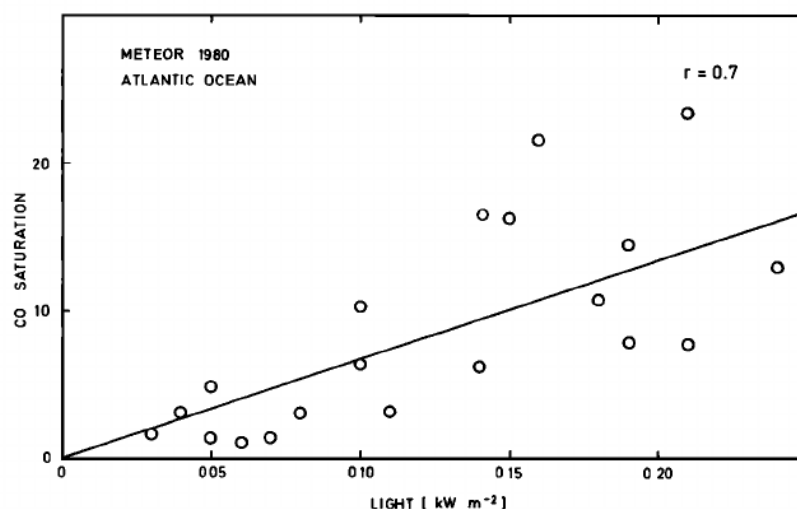
Fig. 6. CO saturation in surface water as function of light intensity. The data points represent average daily values of the continuous measurements of CO and light intensity during *Meteor* cruise 1980. Days with interruptions in the semicontinuous measurement of dissolved CO were disregarded.

wind speed and high chlorophyll a concentrations. Other unmeasured parameters might also be important in explaining local variability of dissolved CO. Despite the scatter of the individual data points, a linear increase of the CO saturation factor with increasing light intensity is obvious. The linear regression indicates a doubling of CO saturation with doubling of light intensity.

Interestingly, there was a time lag of approximately 2–3 hours between the maximum light intensity and the maximum CO concentration in water (Figure 5). The same phase shift was obtained, regardless of whether the semicontinuous CO record of dissolved CO or the discontinuous analysis of surface water samples were used (Figure 13). Therefore, the observed time lag cannot be due to instrumental problems. The increase of dissolved CO during the morning hours and the observed time lag relatively to the light intensity may be explained by a reaction mechanism of CO production in which the reaction is initiated by light and subsequently releases CO over a time period of several hours. A possible process would be the photooxidative CO production by photosensitized reactions involving oxygen radicals. The existence of photosensitized reactions is consistent with laboratory experiments by *Conrad and Seiler* [1980], who found continuing CO production in seawater over several hours, even after the light had been switched off. It is worthwhile to mention that a time lag relative to light intensity has also been observed during studies of CO production by higher plants [*Bauer et al.*, 1979], which had been explained by photooxidation of cellular material involving reactive oxygen species [*Bauer et al.*, 1980].

Dissolved CO as Function of Chlorophyll a Concentration

The highest CO saturation factors were found in nutrient-rich water, e.g., during Jan. 21–22, 1979, when the ship was under the influence of water originating from the upwelling area northwest of Africa (Figure 4). Similar observations were made during the same cruise, when the ship was close to the equator, e.g., during Jan. 29–31 and during February 1979, when the ship crossed the equator several times along

22°W. In the equator region, both the daily maximum and the daily minimum values of the CO concentration in surface water were significantly higher in comparison to the values found outside this region (Figure 7). The relatively high CO saturation in the equator region is most probably due to nutrient-rich water from the equatorial undercurrent that is mixed into the surface water by turbulent mixing processes [*Katz et al.*, 1979; *Voituriez and Herbland*, 1979]. The observed high CO saturation in nutrient-rich water was accompanied by high chlorophyll a concentrations, they being an indicator for biological activities and biomass. Parallelism between dissolved CO and chlorophyll a was also reported by *Swinnerton et al.* [1977] in near-shore oceanic water.

Using the data obtained in the open ocean during *Meteor* cruise 1980, a positive correlation between the daily aver-
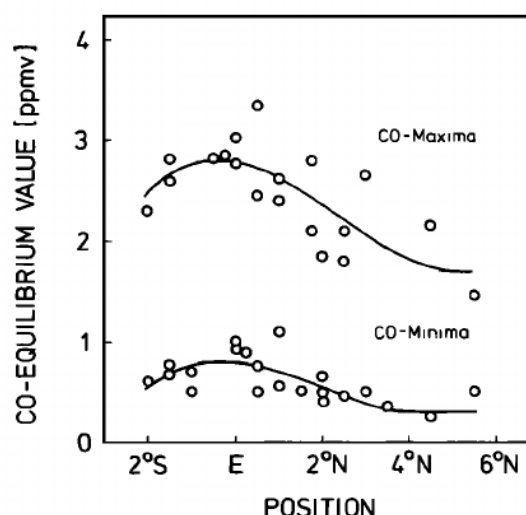

Fig. 7. Daily maximum and minimum CO equilibrium values as a function of latitude; from the semicontinuous analysis of surface seawater (4-m depth) during *Meteor* cruise 1979.
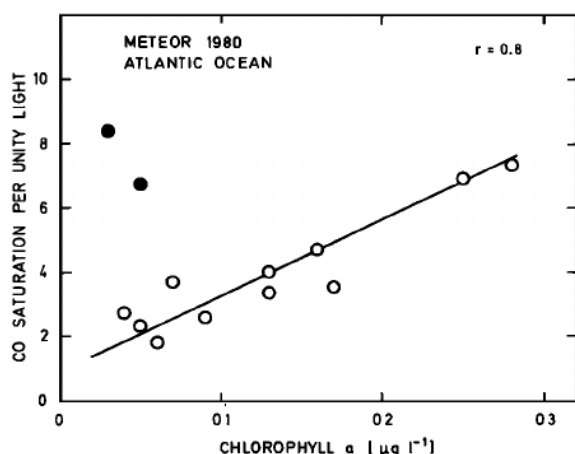
Fig. 8. CO saturation in surface seawater as a function of the chlorophyll a concentration measured in 4-m depth. Data obtained in the British Channel or on days with less than two chlorophyll a data points were disregarded. Daily average values given with open circles (O) were obtained at high wind speeds (5–9 m s^{-1}), those given with closed circles (●) at low wind speeds (2–3 m s^{-1}). The closed circles were disregarded for calculation of the correlation coefficient r.

high values were obtained on days with a wind speed of 2–3 m s^{-1}, whereas the rest of the values were obtained on days with wind speeds of 5–9 m s^{-1}. If we take into account that the amount of CO dissolved in surface water is indirectly dependent on wind speed (see later), and if we use the relationship as given in Figure 15, the two values obtained at low wind speed must be reduced by a factor of 3–4 for normalization to a wind speed of 5–9 m s^{-1}. Then, the corrected values agree well with the other values. Unfortunately, similar considerations cannot be made for the CO and chlorophyll a data obtained during the *Walther Herwig* cruise 1978 and the *Meteor* cruise 1979 because of the lack of continuous measurements of light intensities necessary for the normalization of the CO saturation to a constant light intensity.

In contrast to the observations in surface water, the vertical distribution of dissolved CO and chlorophyll a in the upper 200 m of the ocean do not correlate. This is illustrated in Figure 9, which summarizes the vertical profiles measured at different stations during *Meteor* cruise 1979 between 3°N and 2°S along 22°W. As already observed by *Seiler and Schmidt* [1974] and *Seiler* [1978], the amount of dissolved CO increased with decreasing water depth, reaching maximum values in the surface water. In contrast to CO, the chlorophyll a concentration showed a distinct maximum near the thermocline in depth between 40 and 70 m, as should be expected from the vertical distribution of phytoplancton and its specific chlorophyll a content in tropical oceanic waters [*Riley and Chester*, 1971; *Meyerhöfer*, 1980]. The lacking correlation between CO concentration and chlorophyll a concentration in vertical profiles is explained by the light regime in the water column. While photosynthesis and accumulation of heavily pigmented phytoplancton in the tropical ocean is optimal in the depth with light intensities of
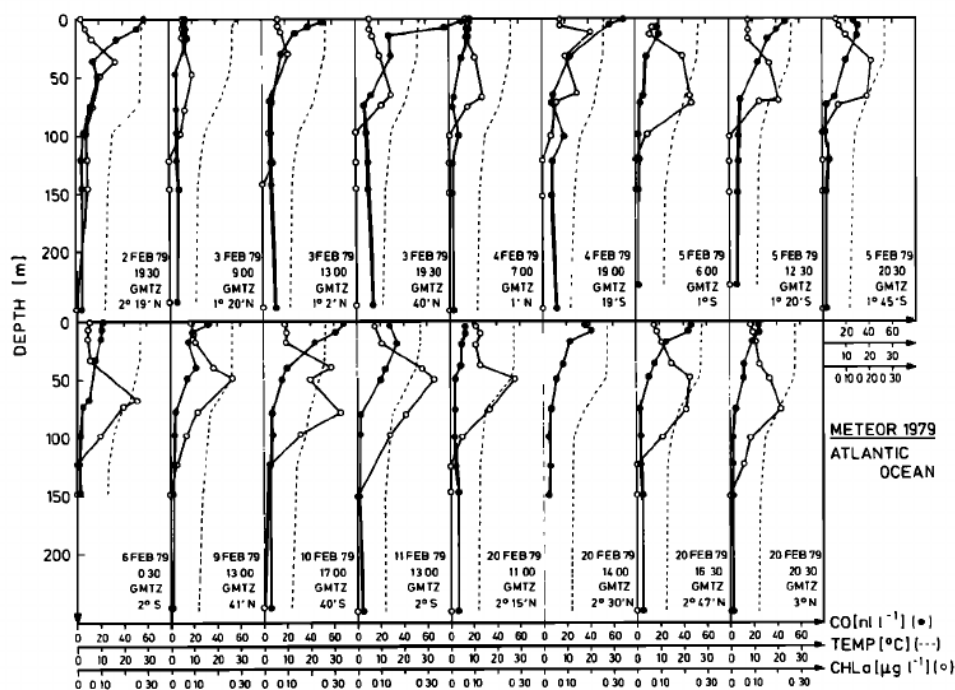
aged chlorophyll a concentrations and the CO saturation was observed (Figure 8). Normalized to a daily average light intensity of 0.1 kW m^{-2} the CO saturation increases linearly with increasing chlorophyll a concentration from a saturation factor of 2 at 0.05 μg l^{-1} chlorophyll a to a value of 8 at 3 μg l^{-1}. Exceptions are shown in Figure 8 as the two closed circles that show CO saturations of 6.5 and 8.3 at chlorophyll a concentrations of $\leqq$0.05 μg l^{-1}. These two exceptionally

Fig. 9. Vertical distribution of CO (●) and chlorophyll a (O) measured during *Meteor* cruise 1979 between 3°N and 2°S along the 22°W meridian.
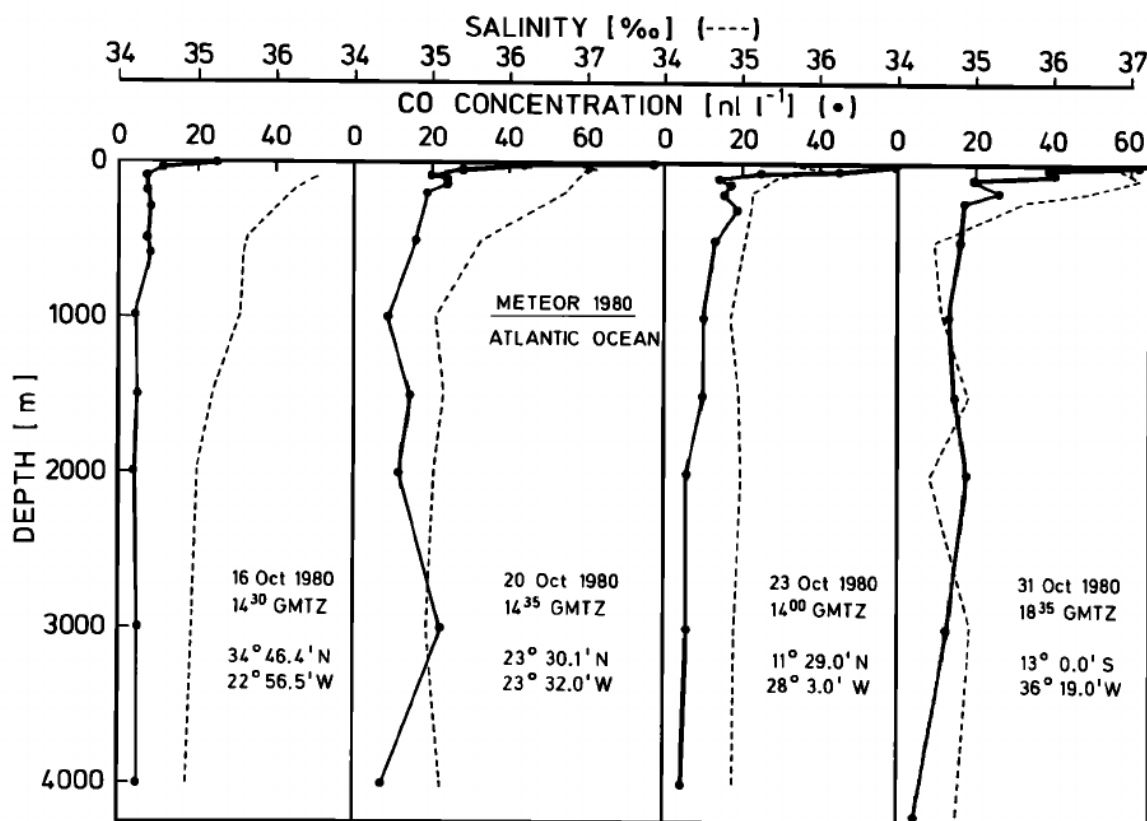
Fig. 10. Vertical distribution of CO in the Atlantic Ocean between the surface (1–4 m depth) and 4000-m depth, as measured during *Meteor* cruise 1980.

30–50% and 10%, respectively [*Meyerhöfer*, 1980], CO production increases linearly with light intensity. The lowest amounts of CO were found below the euphotic zone in depths beyond 100 m, where the CO concentrations varied between 1–12 nl l^{-1} water. Using CO solubility coefficients published by *Schmidt* [1979], the corresponding equilibrium values are calculated to 40–500 ppb, indicating that the ocean water in these depths is often undersaturated with respect to atmospheric CO. Other vertical profiles, e.g., those obtained during *Meteor* cruise 1980, showed CO concentrations higher than 10 nl l^{-1} in depths below 100 m (Figure 10). Sometimes even slight CO maxima were observed [see also *Seiler and Schmidt*, 1974]. Carbon monoxide supersaturation in the dark zone of the ocean water body is explained by dark, CO production processes resulting from CO-producing microorganisms [*Junge et al.*, 1971, 1972].

CO Production Processes in Ocean Water

It has usually been assumed that CO production in seawater is due to photobiological processes, e.g., CO production by algae [*Swinnerton et al.*, 1977]. Based on laboratory experiments with seawater, *Conrad and Seiler* [1980] proposed the existence of photooxidative CO production processes in ocean surface water with dissolved organic material as the main substrate for the photooxidation [see also *Wilson et al.*, 1971; *Bullister et al.*, 1982]. This conclusion was confirmed by further experiments carried out on board *Meteor* during the cruise in 1980. During these experiments,

surface water samples were degassed using CO-free synthetic air. Aliquots were then filtered through 3.0- and 0.2-μm filters to remove algae and bacteria. Subsamples were incubated in daylight and analyzed after different time periods (Figure 11). While the CO concentration of a dark control
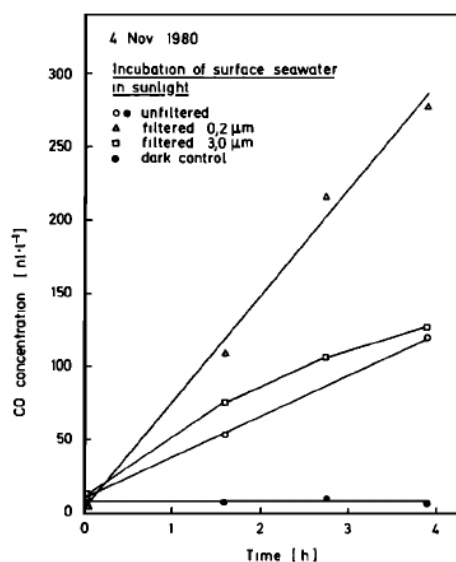

Fig. 11. Increase of CO concentration in filtered and unfiltered surface seawater upon incubation in daylight.
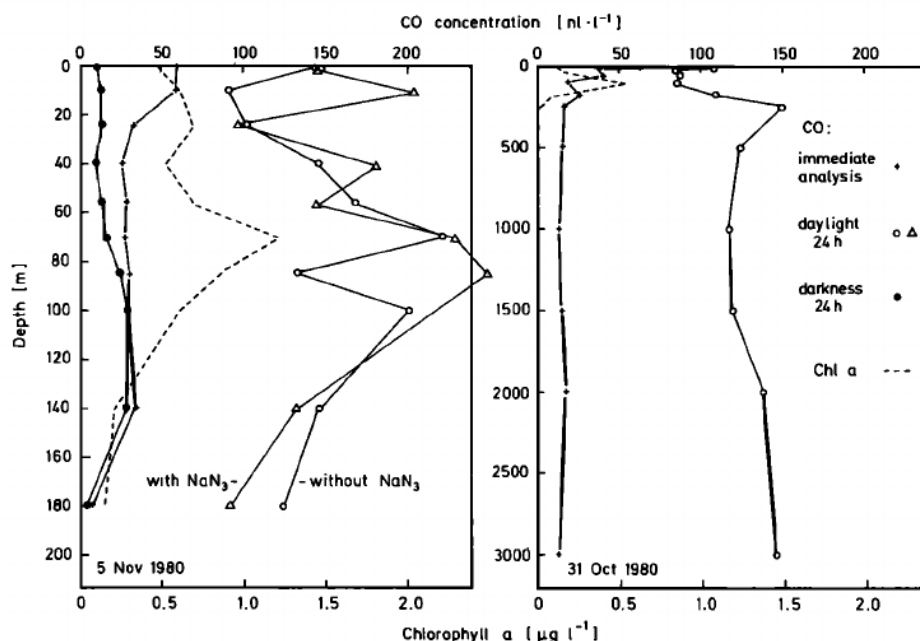
CO concentration [nl · l⁻¹]

Fig. 12. Change of CO concentration in seawater samples from different depths upon incubation in daylight and darkness.

remained at a constant low level of 10 nl CO per liter water, CO increased rapidly when the seawater was exposed to light. The rate of CO production was somewhat higher when the seawater was filtered through a 3-μm filter, which removes the algae and other large particles. When the seawater was filtered through a 0.2-μm filter, which removes, in addition, the bacteria, the CO production rate increased by a factor of 3. This observation demonstrates that CO is produced in sterile, particle-free ($\geqq 0.2$ μm) seawater by a light-dependent process. The relatively low CO production rate in unsterile seawater (3.0 μm, filtered or unfiltered) is indicative of the presence of CO destruction processes caused by the activities of bacteria (see next chapter). The substrates for the CO-producing photooxidative reactions must be dissolved organic substances, which are released from organisms or are solubilized from dead biomass or particulate organic matter. Therefore, the correlation between CO saturation and chlorophyll a concentration, as well as phytoplancton or particulate organic matter as observed in surface seawater [Figure 8; *Swinnerton et al.*, 1977], must be of an indirect nature. We assume that parameters like chlorophyll a, which stand for biomass and biological activity, are also indicators for dissolved organic matter serving as substrate for photooxidative CO production.

The assumption of a major role for photooxidative processes in the production of CO in seawater is in good agreement with the observed vertical distribution of CO in the ocean water. The difference in the vertical profiles of dissolved CO and chlorophyll a (Figure 9) or photosynthesis [*Meyerhöfer*, 1980] indicates that CO production is not due to algal metabolism. Direct evidence for the photooxidative nature of CO production came from incubation experiments carried out during the *Meteor* cruise 1980. In these experiments, seawater samples from different depths were incubated under daylight conditions (Figure 12). After 24 hours of incubation, the CO concentration in the water samples had increased markedly, independent of the depth from which the water was taken. This result demonstrates that the in situ concentration of CO is limited by the light regime in the different water depths. As soon as a water sample was exposed to full sunlight intensity, whether taken from 5- to 3000-m depth, its CO concentration increased. This general potential of seawater for a light-dependent CO production excludes a major importance of photobiological processes. Organisms with a potential ability for photobiological CO production are located exclusively within the euphotic zone and therefore cannot have caused the observed light-dependent CO production in samples from deeper water. Photobiological CO production is also excluded by the experiments in which light-dependent CO production occurred in water samples from within the euphotic zone, even when treated with azide as a metabolic inhibitor (Figure 12).

Vertical profiles show that deep ocean water below 100-m depth sometimes is supersaturated with respect to atmospheric CO [Figure 10; *Seiler and Schmidt*, 1974]. Such relatively high CO concentrations in the dark zone of the ocean water body are usually explained by the existence of bacteria capable of producing some CO in darkness, e.g., those bacteria described by *Junge et al.* [1972] that belong to the genera *Alginomonas*, *Brevibacterium*, and *Agrobacterium*. During our incubation experiments with water from different depths, a significant CO production in darkness could not be observed within an incubation period of 24 hours (Figure 12). Therefore, we have to assume that dark CO production by microorganisms is a slow process and does not contribute significantly to the establishment of the CO concentrations observed in the upper 100 m of the ocean.

CO Destruction in Ocean Water

The diurnal variation of CO, which was observed in the whole euphotic ocean layer, clearly indicates that CO is not
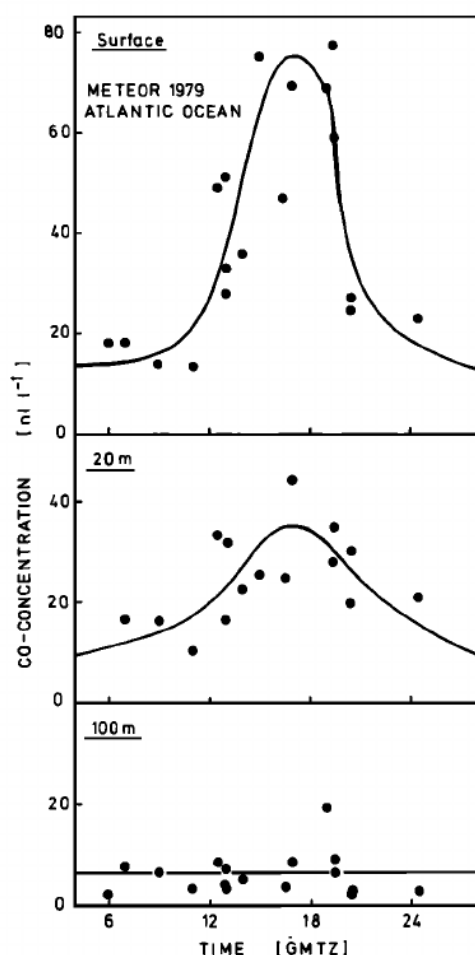
Fig. 13. Diurnal variation of CO dissolved in water measured at the surface (1–4 m depth) and at 20- and 100-m depth. The data were obtained during *Meteor* cruise 1979, at stations between 3°N and 2°S along 22°W.

ocean into the atmosphere, since the highest slopes of decreasing CO concentration in the afternoon were observed during sunny days with low wind speeds, when the lowest CO exchange rates at the air-sea interface should exist. Consequently, we have to assume that the CO decrease must be due to destruction processes occurring in the euphotic layer. This assumption is consistent with results shown in Figure 12, where dark incubation of seawater samples from the surface down to 70-m depth resulted in a decrease of the dissolved CO.

The possible CO destruction processes were studied via laboratory experiments on board *Meteor* during the cruise in 1980. The results of an incubation experiment with surface water are shown in Figure 14. A surface water sample was degassed with CO-free synthetic air. Aliquots were then filtered through 3.0- and 0.2-μm filters to retain algae and bacteria. After reastablishing a CO concentration of 120–140 nl l^{-1} by adding sterile seawater enriched with CO, the aliquots, including those with unfiltered seawater, were incubated in darkness and successively analyzed after different incubation periods up to 13 hours. As shown in Figure 14, the CO concentration in the unfiltered seawater decreased with a rate of 7 nl h^{-1}. Carbon monoxide consumption was also observed in those water samples with only the algae, but not the bacteria, removed (3.0 μm filtered), although the CO consumption rate of 5 nl h^{-1} was a little smaller than in unfiltered water. The CO concentration in the bacteria-free seawater samples (0.2 μm filtered), however, did not decrease with time (sometimes they even increased slightly), as in the case of the example shown in Figure 14. Similarly, CO destruction was abolished when unfiltered

only produced but also consumed in the water, either by microbial or by chemical processes. Physical processes, such as transport of dissolved CO from the main production area near the surface into the deeper ocean, can be ruled out. This is demonstrated in Figure 13, which summarizes the CO concentrations observed in the surface water as well as those in depths of 20 and 100 m. The individual data points were taken from 18 vertical profiles measured during the *Meteor* cruise 1979 in the equatorial Atlantic Ocean (Figure 9). The scatter of the individual data points is due to different weather conditions and consequently different light intensities. Nevertheless, it is easily seen that the diurnal variation of dissolved CO occurred in the entire euphotic zone, with decreasing amplitudes in greater depths reflecting the decreasing light intensities. A phase lag of the diurnal variations within the euphotic zone—indicative of vertical CO transport—is lacking. In contrast to the situation in the euphotic zone, the CO concentration remained constant with time in water below 100 m (Figure 13), indicating that the net exchange of CO between the euphotic zone and the underlying deeper ocean water is very small and cannot account for the observed diurnal variation in the euphotic zone. The same conclusion is obtained for the transport of CO from the
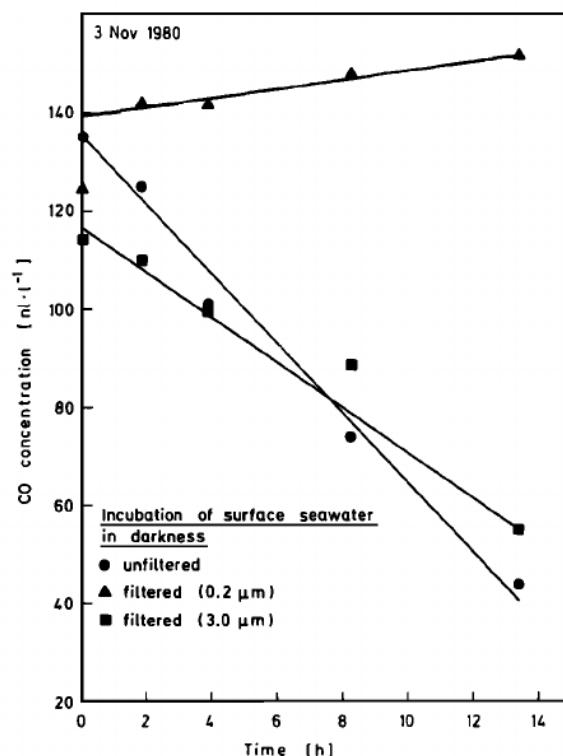

Fig. 14. Decrease of CO concentration in filtered and unfiltered surface seawater upon incubation in darkness.

seawater was boiled or poisoned with azide (50 μg ml^{-1}), indicating that the consumption of CO in seawater must be due to microbial metabolism and not to chemical processes. The species of microorganisms responsible for the observed CO consumption are not known presently. From other experiments [*Conrad and Seiler*, 1982] we known that the CO consumption follows Michaelis-Menten kinetics

$$v = \frac{V_{max}C}{K_m + C}$$

with v = CO consumption rate (nl l^{-1} h^{-1}), V_{max} = maximum CO consumption rate (nl l^{-1} h^{-1}), C = CO concentration in seawater (nl l^{-1}) and the K_m value (nl l^{-1}).

The K_m value is a constant for a particular microbial population and gives a measure for the affinity of the microbes for CO. Since V_{max} is proportional to the size of the population, the rate of CO consumption in seawater is dependent on the type and the amount of CO-consuming microorganisms. Thus we should expect the highest CO consumption rates in ocean areas with high biological activities and consequently high microbial population densities. If we take into account that these areas usually show the highest CO saturation factors, it is very likely that most of the CO produced in the euphotic ocean layer is directly consumed by microbial activities. In this case the flux of CO from the ocean into the atmosphere would represent only a small fraction of the total CO produced in the ocean water. This conclusion is in agreement with the lack of a phase shift between the diurnal variations of CO observed in different water depths and the fact that the highest amplitudes of the diurnal variations were found in areas with high biological activities and calm seas. From the shape of the diurnal variations of dissolved CO we conclude that the residence time of CO in seawater must be in the order of less than 3–4 hours.

Dissolved CO as Function of Wind Speed

The CO concentration in surface seawater was found to be strongly correlated with the wind velocity. The correlation is well documented in Figure 5, particularly during the beginning of *Meteor* cruise 1980, between Oct. 9 and 14, 1980, when the CO concentration in the surface water remained almost constant during periods of high wind speeds but increased by a factor of 10 on Oct. 12, 1980, as soon as the wind speed dropped to about 2 m s^{-1} for a short period of hours. As the light intensities observed during these particular days are comparable, the change of the CO concentration on Oct. 12, 1980, must have been caused by the change of the wind speed. Similar observations were made between Oct. 19 and 22, 1980, when the daily average light intensities were similar. The CO concentration, however, changed from daily average values of about 1.6 ppm to less than 0.8 ppm between Oct. 20 and 21, 1980, when the wind speed increased from 3 to about 8 m s^{-1}.

As the CO concentration in surface seawater is dependent on the light intensity, and as days with high wind speeds are often accompanied by bad weather conditions, one might argue that the observed relationship between CO saturation and wind speed is caused mainly by the different light intensities during sunny and calm or cloudy and windy days. That this is not the case is illustrated in Figure 15, in which the daily average CO saturations observed during *Meteor*

cruise 1980 and normalized to a constant daily average light intensity of 0.1 kW m^{-2} are plotted against the daily average wind speeds. Corresponding CO data obtained during *Meteor* cruise 1979 and the *Walther Herwig* expedition 1978 cannot be used because of the lack of continuous record of light intensities. The normalized CO saturations decreased with increasing wind speeds, thus indicating that the wind speed has a significant influence on the CO concentrations in surface water. This might be attributed to a decreased penetration of light through a rough sea surface. A more likely explanation, however, is the increased CO exchange rate at the air-sea interface under rough sea conditions. Based on the limited number of CO data given in Figure 15, the CO exchange rate seems to be roughly proportional to the square of the wind speed. This would be in agreement with results of wind tunnel experiments by *Kanwisher* [1963], *Deacon* [1977], and *Jaehne et al.* [1979] and considerations by *Liss* [1973] and *Hoover and Berkshire* [1969]. If we assume steady state conditions for the CO saturation in surface water, the saturation factors decrease by a factor of 4 when the wind speed obtained in 20-m height increases from 4 to 10 m s^{-1}—equivalent to values of about 2 to 5 m s^{-1} at the surface. Interestingly, a similar ratio has been observed most recently during wind tunnel experiments by *Merlivat* [1981], where N$_2$O was the gas exchanged between the gas and liquid phases. Our observations, however, are in disagreement with the observations by *Peng et al.* [1979], who—based on their radon measurements in the ocean mixed layer—did not find a direct relationship between the gas exchange at the air-sea interface and the wind speed. The different results obtained by these groups may be explained by the different vertical distribution of CO and radon in the ocean. While CO has the highest concentration at the sea surface, radon is more or less uniformly distributed in the whole mixed layer between surface and thermocline. The smaller CO reservoir and its concentration toward the sea surface results in a considerably lower CO residence time in the mixed ocean layer than that of radon. Consequently, changes in the exchange rates at the air-sea interface, e.g., by changing wind speed, will have a much more rapid effect on the CO concentration than on the radon concentration.
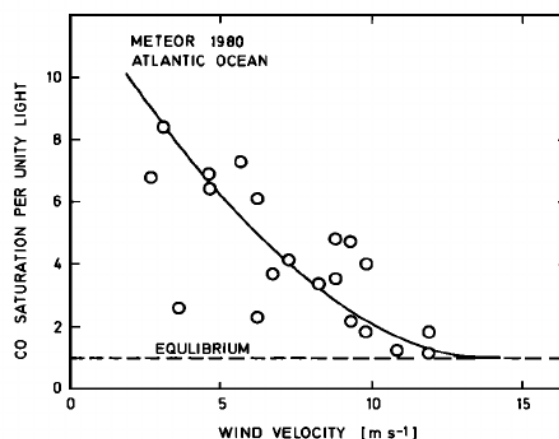

Fig. 15. Daily average CO saturation normalized to a daily average light intensity of 0.1 kW m^{-2} as function of the daily average wind speed observed at 20-m height.
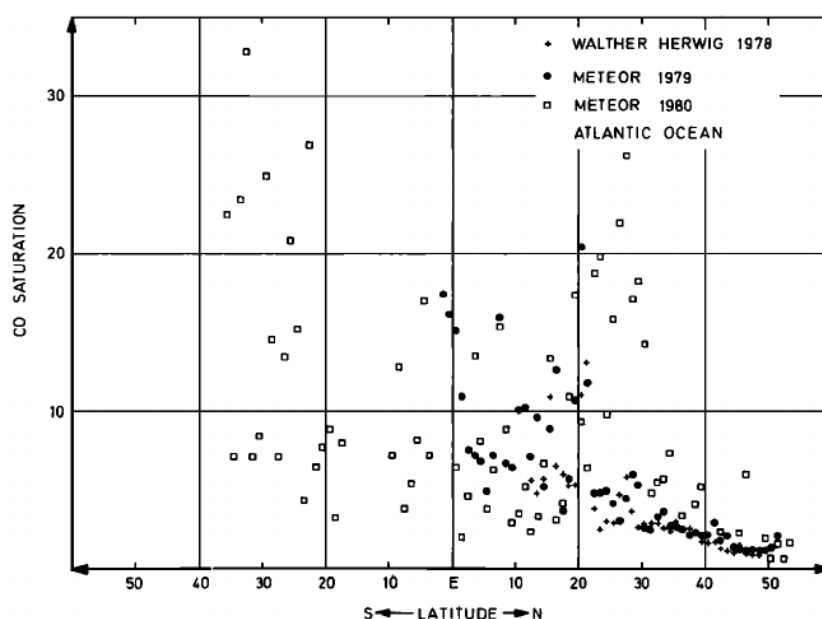
Fig. 16. Zonal distribution of dissolved CO in surface seawater (4-m depth). Each data point represents a CO value averaged over 1° latitude.

Flux of CO Into the Atmosphere

As shown in the previous chapters, the ocean surface water is usually supersaturated with respect to the atmospheric CO mixing ratios. From the 8000 individual CO analyses obtained during the *Walther Herwig* and *Meteor* cruises in the Atlantic Ocean, only a minor fraction of 10–20 data points show slight undersaturations ($S \approx 0.8$), so that the ocean must act as a source for atmospheric CO. The source strength can be calculated by using the classical stagnant film model, which, according to *Broecker and Peng* [1974], provides an adequate first-order approximation of the much more complex processes actually taking place. The stagnant film model assumes that the gas exchange rate between air and water is controlled by molecular diffusion through a hypothetical laminar boundary layer at the water surface. The flux depends on the difference of the partial pressure in the liquid and the gas phase and the thickness of the laminar boundary layer. The model furthermore assumes that the air above the water surface and the water below the boundary layer are well mixed and that the difference of the partial pressures at the boundary layer is not influenced by the flux through this layer. In the stagnant film model, the global flux rate is given by

$$ F = \frac{DAP\rho}{z}(C - \alpha M) $$

with D = molecular diffusion coefficient of CO (2.3×10^{-5} cm²s⁻¹), A = ocean surface area (361×10^6 km²), P = barometric pressure (≈ 1), ρ = density of CO (1.2 mg cm⁻³), z thickness of the laminar boundary layer, C = CO concentration in seawater at the base of the laminar boundary layer, α = solubility of CO in seawater (0.02 cm³ cm⁻³) and M = CO mixing ratio in the air.

The zonal distribution of dissolved CO measured continuously in 4-m depth and averaged over 1° latitude is shown in Figure 16. This diagram shows a great scatter of the individ-

ual data points as the result of the dependency of CO concentration on light intensity, amount of dissolved organic matter and wind speed. The lowest saturations of CO were observed north of 40°N, where the measurements were generally carried out at wind speeds higher than 10 m s⁻¹. The highest CO concentrations were found in the ocean areas between 15° and 30° latitudes of both hemispheres, which are influenced by the downward-directed Headley circulation, resulting in clear sky and calm sea. In the equator region, particularly near the intertropical convergence zone (ITCZ), the CO concentrations seemed to be generally lower, which most likely is due to the high cloud cover. The distribution of dissolved CO, as shown in Figure 16, may be somewhat influenced by the routes of the cruises, particularly in the Southern Hemisphere, where the measurements were carried out at distances less than 100 km from the continent, so that the high values found at 30°S may not be representative of the open ocean at this latitude. In addition we have to take into account that the cruises took place in late fall and early winter in the northern hemisphere, which might explain the generally higher CO values in the southern hemisphere relative to those observed at the same latitudes in the northern hemisphere. Normalized to the actual ocean area at the different latitudes, the Atlantic Ocean water taken from a depth of 4 m is, on the average, saturated by a factor of 10, as compared to the atmospheric CO mixing ratios.

The concentration of dissolved CO at the base of the laminar boundary layer may be considerably higher than the values found in 4-m depth because of the exponential increase of CO toward the surface, as observed in all vertical profiles taken during daytime (Figures 9 and 10). However, these measurements did not give information on the vertical distribution of CO in the upper few meters of the ocean because of the large size of the hydrocasts and also because of the influence of the ship, e.g., by turbulent mixing of the water, which disturbs the vertical structure of the water
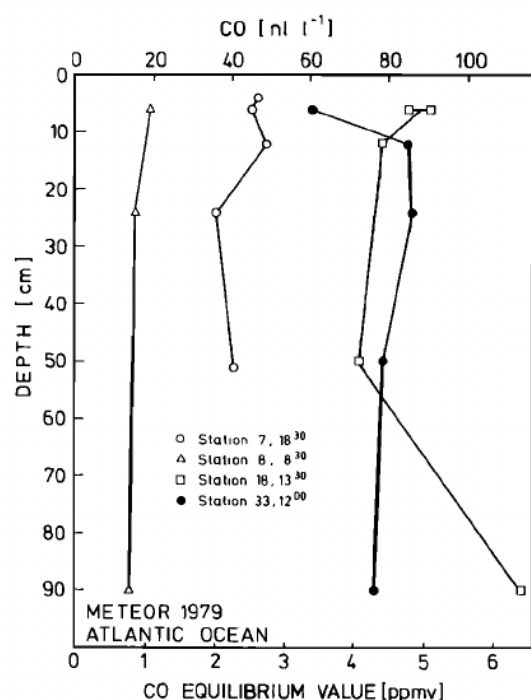
CO [nl l^{-1}]

Fig. 17. Vertical distribution of CO in the uppermost ocean layer.

body. Therefore, water samples were also taken from depths between 5 and 100 cm and at a distance of at least 100 m from the ship. Surprisingly, these profiles (Figure 17) show an almost constant CO concentration, indicating that the exponential increase of CO does not continue when one approaches the uppermost surface layer. Apparently, the vertical mixing in the surface layer is strong enough to prevent the establishment of a strong vertical gradient in the uppermost surface layer, which should be expected if one considers the dependency of CO production on light intensity. The CO concentration in this upper ocean layer was generally a factor of 2 higher than the values found at 4 m depth. At present we do not know whether or not this value is identical with the CO concentration at the base of the laminar boundary layer at the sea surface. Individual measurements reported by *Seiler* [1978] show CO concentrations at the sea surface of as high as 4000 nl l^{-1}—equivalent to a saturation factor of 200. Such high CO concentrations may be due to the existence of an organic surface film, as observed over large areas of the ocean, and to the consequently high CO production rates in the surface water. Therefore, a globally and seasonally averaged CO saturation of 30 ± 20, as derived from our observations reported in this paper, may not completely cover the possible range of CO saturations at the base of the stagnant film layer. This figure will remain uncertain until appropriate methods for continuous measurements of CO in the uppermost surface layer of the ocean are available.

A crucial parameter for the determination of the CO flux at the air-sea interface is the thickness of the hypothetical stagnant film layer. Individual estimates of z reported by different authors differ substantially, depending on the location of measurements, type of method applied, etc., so that reliable air-sea exchange rates for any given time and area of

the ocean cannot be given. Presently, it even remains uncertain whether or not the exchange rates of gases at the air-sea interface are dependent on wind speed. Our field observations, reported in this paper, support the conclusions from wind tunnel experiments, which predict a strong dependency of the gas exchange rate on the wind speed. However, our data do not allow the estimation of a quantitative relationship between CO exchange rate and wind speed, particularly because of the unknown contribution of microbial CO consumption.

In order to calculate CO flux rates from the ocean into the atmosphere we must use a likely range of film thickness values as first approximations. A global average film thickness was estimated by using the vertical distribution of natural and bomb-produced ^{14}C in the ocean, resulting in z values of 30 ± 10 and 30 ± 25 μm, respectively [*Broecker and Peng*, 1974]. Based on radon measurements, a similar value (36 ± 21 μm) was estimated by *Peng et al.* [1979]. Recently, *Broecker et al.* [1978] and *Merlivat* [1981] reported on wind tunnel experiments that had gas transfer rates of 0.7–0.8 × 10^{-2} cm s^{-1}, which allow the calculation of film thickness values of 20–30 μm. Therefore, we applied values of 10–50 μm as a likely range of film thickness for our flux calculations. By using average CO saturation factors of 30 ± 20 as representative of the conditions at the base of the stagnant film, the oceanic source strength is calculated to 10–180 Tg yr^{-1}. Considering the uncertainties involved in CO flux calculations, this figure agrees well with earlier estimates by *Linnenbom et al.* [1973], *Seiler and Schmidt* [1974], and *Seiler* [1978], who reported values of 220, 70, and 10–120 Tg yr^{-1}, respectively. Based on these figures, the ocean may contribute as much as 7% to the global atmospheric CO budget, which is estimated to be 2700 Tg yr^{-1} [*Logan et al.*, 1981]. The contribution of the ocean can be substantially higher when the assumption of CO production in the organic film on the ocean surface turns out to be correct. In this case the produced CO is more or less directly emitted into the atmosphere and therefore is not dependent on the stagnant film thickness and is less affected by microbial CO consumption. Further experiments are necessary to clarify this point. Finally, we have to point out that because of the simultaneous production and destruction of CO in the water the given oceanic source strength of 10–180 Tg yr^{-1} represents the net flux of CO from the water into the atmosphere. The individual gross fluxes at the air-sea interface may be considerably higher.

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