The cycle of atmospheric CO

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(Manuscript received June 20; revised version October 15, 1973)

ABSTRACT

New measurements of the CO-mixing ratio in the two hemispheres with the dissolved CO in surface seawater together with previous results are used to set up a detailed budget of CO in the atmosphere. It is shown that CO is produced by technological and by natural sources. The source strengths of both kinds of sources are of the same magnitude. The total CO-production rate is estimated to be 10×10^{14} g per year. The corresponding residence time is 0.5 years. From the observed latitudinal CO-distribution between the hemispheres the production of CO by the oxidation of methane in the troposphere is judged to be a minor source. CO is removed by microbiological processes at the soil surfaces, by photochemical consumption in the stratosphere, and probably also by reaction with OH radicals in the troposphere.

Introduction

Since carbon monoxide was first detected in the atmosphere by Migeotte (1949), the concept concerning the major cycle of CO in the troposphere has changed three times. Until 1969, anthropogenic CO production was considered the only important source with a rate of approx. 2×10^{14} g per year (Bates & Witherspoon, 1952; Robinson & Robbins, 1969). In 1969, Swinnerton et al. reported high supersaturations of CO in Atlantic ocean water with respect to air. Subsequent confirmation of this finding by Swinnerton et al. (1970), Seiler & Junge (1970), Lamontagne et al. (1971) and Seiler & Schmidt (1973), indicated that the world oceans serve as a source for atmospheric carbon monoxide. The associated source strength was estimated by Junge et al. (1971) to be approximately equal to the anthropogenic production on a global scale. Taking an average CO mixing ratio of 0.1 ppmv, these authors estimated a mean residence time of about 1 year.

A much shorter residence time, 0.1 year, was derived by Weinstock (1969) from the radiocarbon CO data by MacKay et al. (1963). Such a short residence time would imply the existence of sources much larger than had previously been recognized. Weinstock & Niki (1972), Levy (1973), Wofsy et al. (1972) and Stevens et al. (1972) considered as an additional source the oxidation of methane by OH radicals, this species being photochemically produced in the troposphere. The existence of OH radicals in the atmosphere leads to a simultaneous loss of carbon monoxide also by reaction with OH radicals.

The oxidation of methane was estimated to generate $20–40 \times 10^{14}$ g CO per year, about ten times the amount produced anthropogenically. The corresponding residence time of CO, 0.1 year, is in agreement with that given by Weinstock (1969) and Weinstock & Niki (1972).

In this paper new measurements of CO in air and in the surface water of the Atlantic ocean in both hemispheres are presented. Also reported are laboratory measurements on the uptake of CO by soil. The results and detailed budget considerations show quite clearly that the oxidation of methane in the troposphere cannot be the principal source of CO in the atmosphere.

Measurements and techniques

Since 1968 we have been involved in an extensive CO-measuring program covering the lower and the upper tropospheres of both hemispheres. Measurements in the lower stratosphere of the northern hemisphere have also

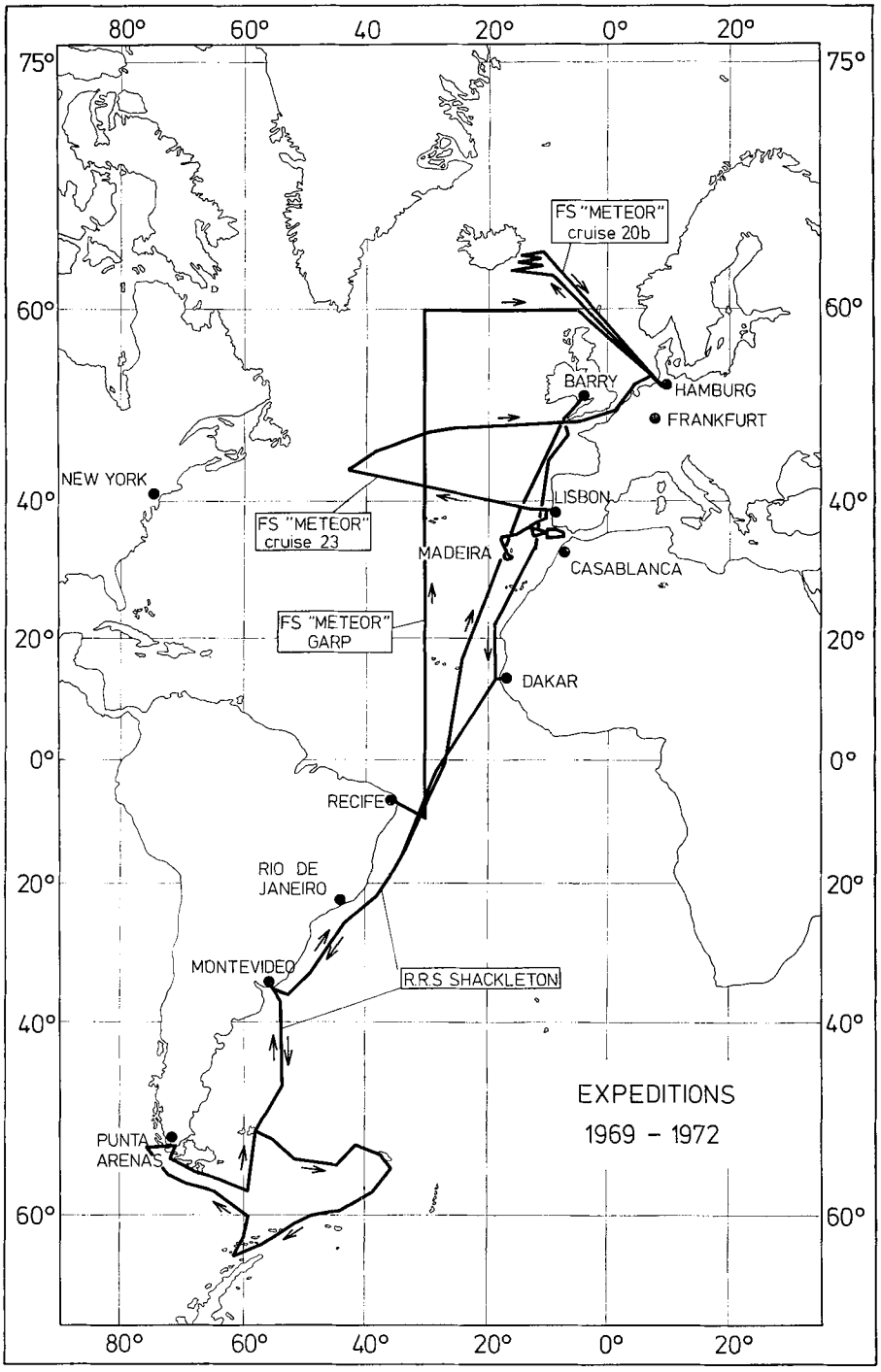

Fig. 1. Tracks of the cruises on board R. V. *Meteor* and R. R. S. *Schackleton* during which the CO-mixing ratio in surface air and the dissolved CO in surface water were measured.

been made. Surface data in unpolluted air masses were obtained over the Atlantic ocean on board the German research vessel *Meteor* during the GARP-expedition in 1969, expeditions No. 20b and No. 23, and more recently on board the British research ship *Shackleton* during the Atlantic cruise from November 1971 to April 1972. The latter cruise included parts of the Southern Pacific. Fig. 1 illustrates the routes of these expeditions.

On all expeditions, the atmospheric CO mixing ratio was continuously registered. On the last three expeditions also the CO contained in marine surface water (at 2 m depths) was measured continuously over a large period of time, whereas previously only batch samples were taken. Deep sea samples were obtained at several stations to determine the profile of CO-concentrations as a function of depth from the ocean's surface down to the bottom level (Seiler & Schmidt, 1973).

The CO-mixing ratio of the upper troposphere was measured continuously on board of aircrafts B 707 of the 'Deutsche Lufthansa' in the 8–10 km altitude region during several flights from Frankfort to Tokyo via Anchorage, from Frankfort to Johannesburg (South Africa), from Frankfort to Rio de Janeiro and from Frankfort to New York. During these flights the tropopause was penetrated several times so that data were obtained also in the lower stratosphere. The vertical distribution of CO mixing ratio in the vicinity of and above the tropopause was investigated separately over Western Europe by means of a chartered aircraft. The results of these missions have been reported previously (Seiler & Warneck, 1972; Warneck et al., 1973).

The CO-measurements were carried out using a set of continuous recording instruments based on the principle of HgO–Hg conversion by CO with subsequent detection of mercury by atomic absorption. The details of the instrumentation were described previously (Seiler & Junge, 1970). An automatic program routinely provides zero level checks once every hour and calibration against a standard every three hours. The standard error for a CO mixing ratio of 0.10 ppm is $\pm 3\%$. The lower limit of detection has recently been improved to 0.1 ppbv. Carbon monoxide dissolved in surface water and deep water samples is determined in a similar manner by two separate techniques developed and described by Seiler & Schmidt (1973). The accuracy of either techniques is approximately $\pm 10\%$. The lower detection limit is 0.5×10^{-6} cm^3 CO/l H_2O.

Compared with other known methods of CO-measurement with a similar sensitivity. (Swinnerton et al., 1968) our instruments have the advantage of continuous registration providing more information especially on short term fluctuations. Furthermore, errors in sampling, often inherent to discontinuous CO-instruments are minimized. Changes of the CO-mixing ratio due to physical and chemical processes in our instruments can be neglected due to the short residence time of only a few seconds for air passing the inlet system.

Results

(a) *CO-measurements in surface air over the northern and southern Atlantic*

Atmospheric mixing ratios of carbon monoxide observed during the GARP-expedition in 1969 and during the Antarctic expedition 1971/72 are shown in Fig. 2 as a function of latitude. Each data point represents an average of the CO-mixing ratios observed over 1° latitude. Fig. 2 includes also CO-data reported by Robinson & Robbins (1969) and Swinnerton et al. (1973) in air over the Pacific ocean. These investigations employed discontinuous sampling techniques. The data obtained during the GARP-expedition in 1969 and shown in Fig. 2 differ slightly from those published by Seiler & Junge (1970) owing to a recent improved laboratory calibration of our instruments.

The three sets of results obtained over the Atlantic ocean show a similar CO-distribution between the two hemispheres even though the measurements were made in different years and seasons. The similarity can hardly be accidental so that these north–south CO-mixing ratio profiles must represent the average CO-distribution in the lower troposphere over the Atlantic. The low maximum at 23° S is probably caused by polluted air masses from the South American continent. The most important feature displayed by these data is the difference of the CO-mixing ratios found in the two hemispheres. The CO-content in the northern hemisphere is higher than in the southern hemisphere. The highest CO-mixing ratios (0.2–0.3 ppm) were observed at middle latitudes over

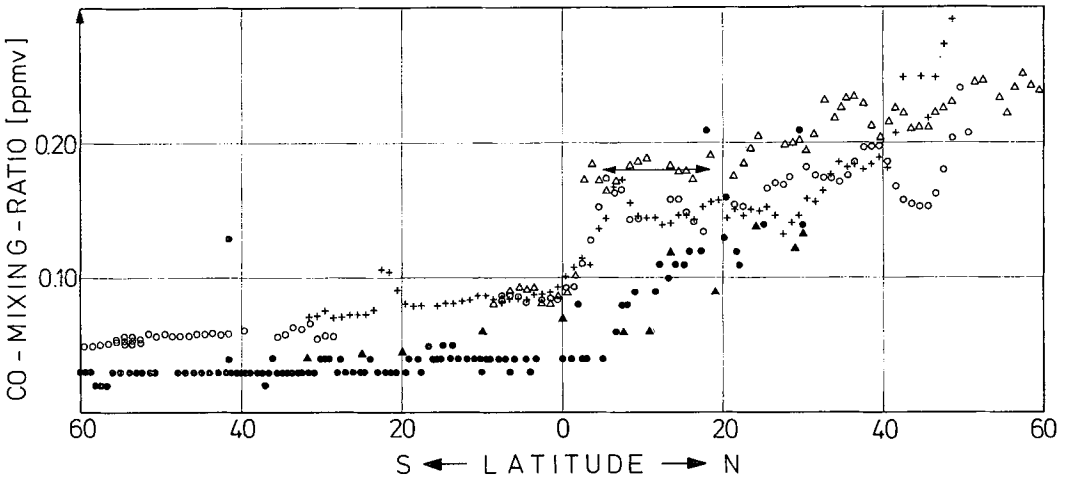

Fig. 2. CO-mixing ratios in marine air masses over the Atlantic and Pacific oceans. Full triangles represent the *Eltanin*-cruise No. 31 (1967) from San Francisco to New Zealand (Robinson & Robbins, 1969). The open triangles represent the GARP-expedition in 1969 from 10° S to 60° N along 30° W (Seiler & Junge, 1970) over the Atlantic ocean; the solid lines represent the average CO-mixing ratio found by Ripperton et al. (1972) in the Bomex-area over the Atlantic ocean; the open circles represent the "Shackleton" expedition in November 1971 over the Atlantic ocean; the crosses represent the "Shackleton" expedition in April 1972 over the Atlantic ocean and the points represent the cruise from the USA to the Antarctic (Swinnerton et al., 1973) over the Pacific ocean.

the northern Atlantic. The results from all expeditions show a decrease of the mixing ratios from about 0.20 ppm at 40° N to about 0.16 ppm at the intertropical convergence zone (ITC). Interestingly the CO-mixing ratios increase just north of ITC. During the Antarctic cruises the CO-mixing ratios increased from 0.14 to 0.17 ppm. Similar observations were made during the earlier expedition in 1969. South of the ITC the CO-mixing ratios dropped rather rapidly to 0.08 ppm, and then decreased slowly to 0.05 ppm at 60° S. CO-mixing ratios measured over a period of 4 weeks east of Iceland at 64° N during the expedition No. 20 b fluctuated between 0.14–0.30 ppm with an average of 0.18 ppm indicating that the CO-concentration decreases towards higher latitudes. During the expedition No. 23 between Lisboa and Newfoundland CO-variations between 0.14 and 0.20 ppm were observed. The average value of 0.16 ppm agrees with those data already mentioned above.

High CO-fluctuations were found only over the Northern Atlantic. During the expedition No. 23 the standard deviation of the continuous CO registration exceeded values of ±20% even in the middle of the Atlantic, where the direct influence of the continents can be excluded. Apparently, clouds of polluted air are transported from the North American continent by westerly winds into the middle of the Atlantic without attaining complete mixing with the surrounded air even over such long a distance. Observations made during flights from Frankfurt to New York at altitudes of 10 km showed a similar effect. In contrast to the results for the northern hemisphere the CO-mixing ratios in the southern hemisphere remained comparatively constant. The standard deviation of the continuous CO-registration during 3 months in an area 50°–65° S and 30°–80° W which includes parts of the south Pacific, was not more than ±3%. This value is identical with the accuracy of the instrument. Sometimes the deflection of the CO-instrument remained so constant over a period of several days that the instrument was presumed to have malfunctioned. Each time, the instrument was checked and was found to have its usual sensitivity. Diurnal variations of the CO-mixing ratio as reported by Lamontagne et al. (1971) have never been observed, even at days with a low temperature inversion and correspondingly small vertical mixing.

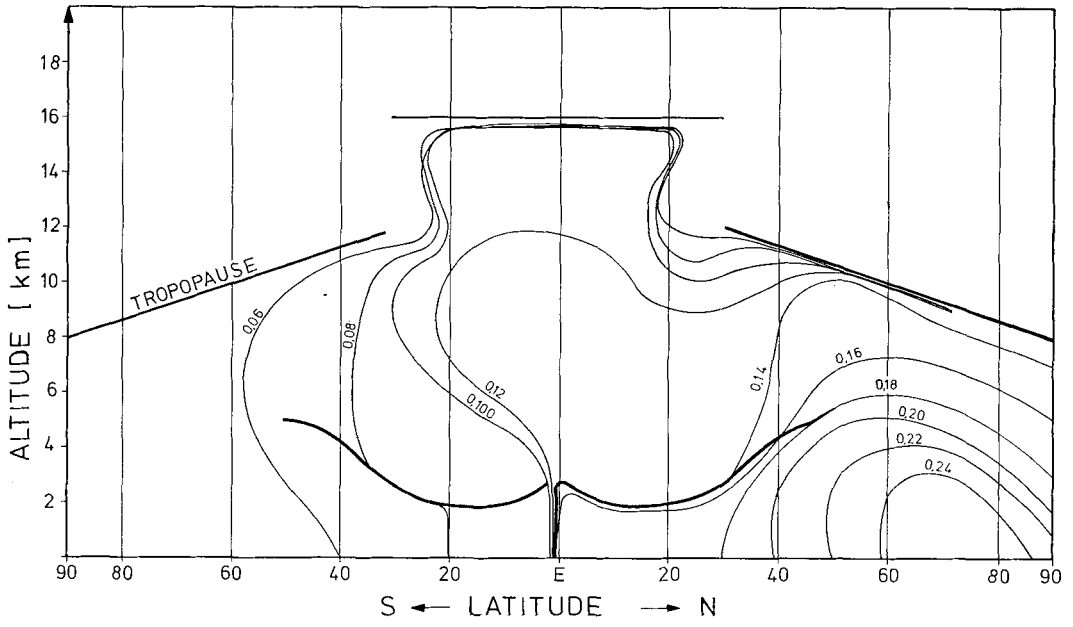

Fig. 3. General distribution of CO in marine air in the troposphere and lower stratosphere. Thick lines represent the tropopause and the trade wind inversion.

(b) CO-Measurements in the upper troposphere and the lower stratosphere

The measurements performed during flights in the upper troposphere show that the CO-mixing ratio is not as uniformly distributed in this atmospheric domain as has been assumed previously (Junge et al., 1971). Especially in the northern hemisphere at middle latitudes high CO-mixing ratios ranging from 0.12 to 0.22 ppm with an average of 0.15 ppm were observed during flights between Europe and the USA. The observation of considerable CO-fluctuations were not only restricted to areas near or over the continents but were also found at 40° W over the middle Atlantic Ocean. Together with the data from the ocean surface air measurements, the flight observations show that CO-rich air parcels are transported within the general circulation over long distances without a rapid mixing into air of a lesser CO-content. The same appears true for the upper troposphere over the northern Pacific Ocean where in a few short intervals CO-values up to 0.20 ppm were observed. The highest CO-mixing ratios, sometimes exceeding 0.50 ppm, were found over the continents. Lower values (0.07–0.10 ppm) than the normal background values were measured only in the vicinity of deep pressure systems and near the tropopause breaks where stratospheric air with a relative low CO-content enters the troposphere.

The latitudinal CO-distribution in the upper troposphere differs significantly from that found in surface air. Whereas a rapid decrease of the CO-mixing ratio occurs at the ITC at the surface, the CO-mixing ratio in the upper troposphere decreased more slowly at the same latitudes. During two flights in March 1972 the CO-mixing ratio decreased regularly from 0.15 ppm at 50° N to 0.08 ppm at 20° S, identical with the CO-concentration found in surface air at the same latitude. This value did not change during the descent of the airplane from a flight level of 11 km to an altitude of 1 km and increased only shortly before landing at the airport at Rio de Janeiro, most likely the result of local pollution. On the other hand, during two flights on the same route in November 1971, no difference of the CO-mixing ratio was found between the hemispheres. This observation agrees with results obtained earlier during flights from Frankfort to Johannesburg (Seiler & Junge, 1970). The constant CO-values

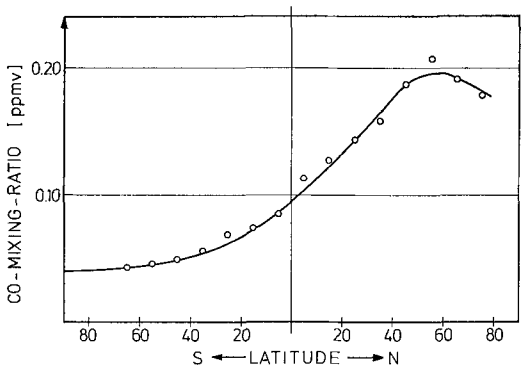

Fig. 4. Mean latitudinal CO-distribution in the troposphere. Each value represents the CO-mixing ratio averaged over 10° latitude and the total air column from surface to the tropopause.

in the upper troposphere between the two hemispheres during these flights indicate a vertical CO-gradient from the surface to the upper troposphere even at latitudes of 20° S. The vertical profile over Rio showed indeed higher CO-values only in the upper layer of the troposphere between 8 km and 12 km. Below 8 km the CO-mixing ratio decreased to values typical for surface air. One reasonable explanation for these observations is the transport of air from the northern hemisphere into the southern hemisphere in the uppermost layer of the troposphere. Indeed, Newell (1969) has shown that this layer is the chief interhemispheric mixing zone. In time periods with strong eddy mixing and correspondingly high air exchange rate between the hemispheres the interhemispheric gradient of the CO-mixing ratio is essentially eliminated in the upper troposphere.

Whenever the tropopause was penetrated, the CO-mixing ratio decreased very rapidly attaining a value of about 0.05 ppm at 1 km above the tropopause. This value remained constant with increasing altitude up to the maximum flight level of the aircraft. This behaviour is identical with that observed on board of a chartered airplane over western Europe (Seiler & Warneck, 1972). The same stratospheric CO-mixing ratio of about 0.05 ppm was observed in the northern hemisphere during the transatlantic and interhemispheric flights regardless of the season, the longitude, and the latitude. At present, no data are as yet available for the stratosphere of the southern hemisphere. However, because of the constancy of the stratospheric CO-mixing ratio in the northern hemisphere we shall assume that this value is representative also for the stratosphere of the southern hemisphere.

(c) CO-measurements in seawater

On all ship expeditions both surface water and deep sea water was sampled and analyzed for dissolved CO. Only the results concerning the surface layer will be treated here. Table 1 shows a summary of data presently at hand, both our own data and those of other investigators. At least for the Atlantic Ocean, a good coverage of all regions is now achieved as the second column of Table 1 illustrates. All the measurements indicate CO contents in excess of that expected from an equilibrium with the atmospheric CO content. The fourth column gives the atmospheric equilibrium value calculated on the basis of the observed CO content of surface seawater. The values are usually much higher than the actual atmospheric mixing ratios. The corresponding supersaturation factors sometimes exceed two orders of magnitude. Quite clearly, the oceans provide a substantial source of atmospheric CO.

Not all the data are useful for a calculation of the average degree of supersaturation which is required for an estimate of the total source strength. On all the earlier expeditions, including the 1969 GARP expedition, only batch samples were taken. These samples are biased, because they were obtained mainly during the daytime and during quiet weather conditions during which the supersaturation is normally very high. A much larger body of data and correspondingly more detailed information was obtained during the last three cruises entered in Table 1 due to the continuous sampling procedure and data registration over periods of approximately six weeks. The continuous sampling technique also avoids the change of a sample due to microbiologic activity during the period between sampling and processing. The results obtained in this manner show that the range of values for dissolved CO is quite similar in the various regions of the Atlantic ocean but that the fluctuations are considerable. As an example, the concentrations obtained in the South Atlantic (Table 1) varied from 0.2 to 21×10^{-5} ml/l and correspond to equilibrium values of 0.1–10.0 ppm. The lower

Table 1. *Summary of all data concerning the dissolved CO in seawater available at the present time*

Author	Location	Diss., CO in water (10^{-5} ml CO/l water)	Equilibrium value (ppm)	Mixing ratio in surface air (ppm)	Super-saturation factor	Number of samples
Swinnerton et al. (1969)	Tropical western Atlantic	2.0–5.0	1.0–3.0	0.10–0.25	10–30	8
Swinnerton et al. (1970)	Western Atlantic	1.0–10.0	0.5–5.0	0.09–0.15	5–50	26
Seiler & Junge (1970)	Middle and northern Atlantic	3.0–10.0	1.5–5.0	0.15–0.25	15–33	20
Lamontagne et al. (1971)	Western Atlantic	6.0–19.0	3.0–10.0	0.10–0.18	20–100	11
	Northern Pacific	2.0–14.0	1.0–7.0	0.08–0.16	10–60	52
Swinnerton (1973)	Northern Pacific	1.5–10.0	0.7–5.0	0.04–0.14	4–120	21
	Southern Pacific	1.0–31.0	0.5–15.0	0.03–0.08	13–500	94
Greese (1973)	Norwegian Sea (1970)	1.5–18.5 avg. 5.4	0.8–9.0 avg. 2.7	0.13–0.30 avg. 0.18	3–56 avg. 6.8	Continuously (6 weeks)
Seiler & Schmidt (1973)	Northern Atlantic (1971)	0.3–15.0 avg. 4.4	0.1–7.0 avg. 2.2	0.10–0.30 avg. 0.15	0.8–70 avg. 6.8	Cont. (6 weeks)
Seiler & Schmidt (1973)	Southern Atlantic (1971)	0.2–21.0 avg. 5.6	0.1–10.0 avg. 2.8	0.05–0.07 avg. 0.06	1–140 avg. 21	Cont. (6 weeks)

value was found during stormy weather with wind speeds greater than 50 kts. It corresponds to near equilibrium with CO in air indicating an efficient exchange of gases between seawater and the atmosphere. In normal weather, the surface was supersaturated with respect to the atmospheric CO-mixing ratio. The highest supersaturations were found in nutrient-rich water. Then supersaturation factors up to 140 were observed. Undoubtedly, the high supersaturations are due to a production of CO in seawater by microbiological processes. Laboratory experiments with bacteria and algae isolated from water samples from the Atlantic ocean showed that a number of species are active generators of CO (Junge et al., 1971, 1972). This is in agreement with independent knowledge on microbacterial activity (Wittenberg, 1960; Loewus & Delwiche, 1963; Pickwell et al., 1964; Chapman & Tocher, 1966). In seawater the production of CO must be partially balanced by a consumption, since the diurnal variation of dissolved CO in the euphotic zone exhibits a decrease in the afternoon too rapid to be explained by diffusion into neighbouring layers.

The net effect is nevertheless a release of CO from the surface water to the atmosphere on account of the *average* supersaturation. The average values of dissolved CO, the corresponding averages of the equilibrium values, and the average supersaturation factors deduced from the records obtained on the three cruises during which continuous sampling was performed are also entered in Table 2. The amounts of dissolved CO and the corresponding atmospheric equilibrium values thus obtained are fairly uniform in the various regions of the Atlantic ocean, about 5×10^{-5} ml/l and 2.5 ppm, respectively. These values will be used subsequently to estimate the source strength of the marine CO-production.

Table 2. *Summary of estimated annual CO-production and CO-consumption by anthropogenic and natural processes in the northern and southern hemispheres*

The emission rates are given in 10^{14} g per year

	Total	Northern Hemisphere	Southern Hemisphere
Sources $\times 10^{14}$ *g per year*			
Anthropogenic	6.4	5.4	1.0
Oceans	1.0	0.4	0.6
Rain water	Uncertain		
Bush- and forest-fires, burning of agricultural waste	0.6	0.4	0.2
Oxidation of hydrocarbons	0.6	0.4	0.2
Total CO-production	8.6	6.6	2.0
Oxidation of methane	15.0–40.0		
Sinks ($\times 10^{14}$ *g per year*)			
Uptake by soil	4.5	3.0	1.5
Flux into the stratosphere	1.1	0.9	0.2
Total CO-consumption	5.6	3.9	1.7
Oxidation by OH	19.4–50.0		

(d) *Laboratory measurements on the uptake of CO by soil*

In recent years we performed a number of detailed laboratory and field tests concerning the CO-uptake by soil. Preliminary results were reported by Seiler & Junge (1970). A detailed report has been given in the form of a thesis (Liebl, 1971) which unfortunately is not readily available. Hence, we summarize below the main results of this study.

The initial tests were made in the field using a glass box set over the natural soil surface and registering the CO-mixing ratio inside and outside of the box, as well as the soil temperature under the box. Fig. 5 shows a typical registration over loam. While the CO-mixing ratio in air remained nearly constant at a value of about 0.25 ppm, the CO-mixing ratio in the glass box showed marked diurnal variations with a maximum of 0.6 ppm around noon and an extended minimum during the night. The CO-mixing ratio in the glass box turned out to

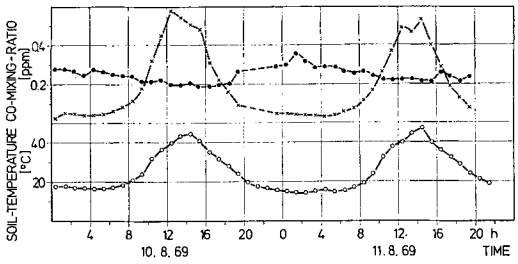

Fig. 5. Variations with time of the CO-mixing ratio in a closed glass box covering the soil surface. Crosses represent the CO-mixing ratio in the glass box; the filled circles represent the CO-mixing ratio in outside air; the open circles represent the soil temperature in the glass box, 2 mm below the soil surface.

be very sensitive to changes of the soil temperature. Natural or artificially produced variations of the soil temperature immediately caused a change of the CO-mixing ratio. The correlation between CO-mixing ratio and soil temperature is thought to derive from a balance of CO-destruction and CO-production by microbiological processes in the soil. Evidence for this behaviour was obtained more explicitly by a variety of laboratory measurements.

The laboratory tests employed a similar experimental set-up as described above, however with one important difference. Whereas the air in the glass box was not exchanged during the whole field studies, we replaced the air in the box during the laboratory experiments after each test by air with a constant CO-mixing ratio of 0.2–0.3 ppm which is equivalent to the normal CO-content of continental air in un-

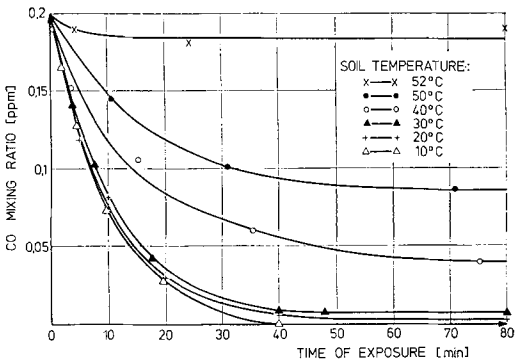

Fig. 6. CO-mixing ratio in a glass box over soil obtained from a greenhouse as a function of time and soil temperature.

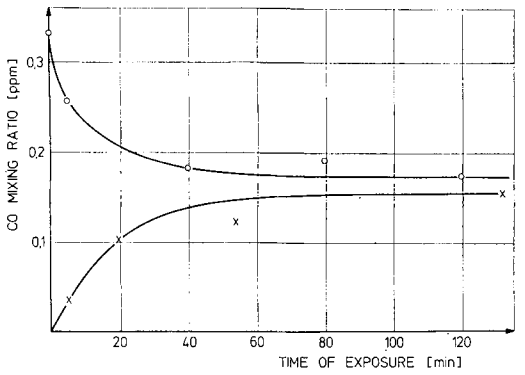

Fig. 7. CO-mixing ratio in a glass box over soil obtained from a greenhouse as a function of time starting with a CO-mixing ratio of 0.3 ppm (O—O) and less than 2 ppb (× — ×).

polluted areas. Fig. 6 shows the variations of the CO-mixing ratios with time in the glass box for soil obtained from a greenhouse. At soil temperatures below 20°C the CO-mixing ratio in the glass box decreased exponentially from 0.2 ppm to a value lower than 2 ppb. However, at soil temperatures above 30°C the CO-content reached after 40 minutes a final value which remained constant over a period of two days provided the soil temperature was kept constant. Evidently an equilibrium is set up between CO-production and CO-destruction. The CO equilibrium value increased with increasing temperature. Similar results were obtained for other types of soil.

When CO-free air was used as the test gas an increase of the CO-mixing ratio was observed, rising to the same equilibrium value as observed for that temperature when starting with CO rich air (Fig. 7). This result clearly demonstrates that soil does not only consume CO but has also a capacity for its production. On the basis of this result from these laboratory and field tests the CO-uptake rates of various types of soil were calculated as a function of temperature. The highest CO-uptake rates were found to occur at temperatures of 10°C over organic rich soil with values up to 2.5×10^{-11} g/cm² sec. At a temperature of 15°C which is a representative value for the mean soil temperature of the earth, the CO-uptake rates amount to 1.5×10^{-11} g/cm² sec, when averaged over all types of soil used in our tests.

Discussion of latitudinal distribution, sources, sinks, and residence time of CO

(a) *Latitudinal distribution*

Our data obtained over the northern Atlantic agree fairly well with CO-measurements by other institutes using completely different CO-measuring techniques, mainly gaschromatographic methods. Ripperton et al. (1972) found during the Bomex voyage in 1969 from Wilmington, USA, to the mouth of the Amazon river CO-mixing ratios between 0.06 ppm and 1.92 ppm with an average of 0.18 ppm. Only three samples of a total of 103 had a CO-mixing ratio greater than 1.00 ppm. It can be assumed that these samples are influenced by exhaust gases of the ship and do not represent the CO-mixing ratio in marine air masses. Unfortunately, the CO-data are not given as a function of latitude, so that only the average CO-value can be used in Fig. 2.

Further CO-measurements in the same Atlantic region at two stations (10° N 60° W, 13° N 59° W) by Swinnerton et al. (1970) show CO-fluctuations from 0.08 to 0.11 ppm and 0.10 to 0.18 ppm respectively. Slightly higher CO-values (0.09 to 0.22 ppm) were found by Swinnerton et al. (1969) during a cruise from 32° N to 23° N along 74° W. These CO-mixing ratios were confirmed by Lamontagne et al. (1971) during a cruise from Washington to the Panama Canal.

All CO-measurements including our data showed high short-term fluctuations of the CO-mixing ratios in marine air masses in the north Atlantic region. For example, Ripperton et al. (1972) found CO-mixing ratios which frequently exhibited differences of more than 50–100% of the lower samples between sequential samples, although the air samples were taken every 6 hours. In contrast to all CO-data from the Atlantic marine air masses, known at present, only Lamontagne et al. (1971) found marked diurnal variations of the CO-mixing ratio with a maximum during noon and a minimum during night. It is interesting to note that on the other hand the CH_4-mixing ratio measured in parallel during most of these cruises remained nearly constant with an average of about 1.3 ppm.

CO-measurements over the Pacific were carried out by Robinson & Robbins (1969) and by Swinnerton et al. (1974) during two different

north–south cross sections from 30° N to 70° S and during a cruise from the Panama Canal to Hawaii (Lamontagne et al., 1971). The results (Fig. 2) show a similar CO-distribution as already described over the Atlantic, with a sharp decrease of the CO-mixing ratio at the ITC from about 0.14 ppm at 30° N to 0.04 ppm south of the ITC. Over the northern Pacific between 30° and 70° N only a few CO-data are available. Robinson & Robbins (1969) found CO-values up to 0.24 ppm during a cruise from Bangkok to Seattle which indicates similar high CO-mixing ratios at the middle latitudes over the northern Pacific as over the northern Atlantic. However, the CO-mixing ratios obtained by Swinnerton et al. (1974) over the southern Pacific south of 50° S are different from our data over the southern Atlantic and the eastern, southern Pacific at the same latitudes. Whereas we found a very constant CO-mixing ratio of 0.05 ppm between 30° W and 80° W, 55° S, Swinnerton et al. (1974) observed a mixing ratio of 0.03 ppm. The constancy of the CO mixing ratio in both areas over several days even on days with different weather conditions strongly suggests that the southern hemisphere at these latitudes is well mixed with respect to CO and we should expect similar CO-mixing ratios. We assume, therefore, that the difference in the CO-data by these two groups is due to the different sampling methods and instrumentation, especially the different calibration systems. It is intended to check on this aspect by comparison of the measurements of the calibration gases employed in both laboratories.

With the data obtained over the Pacific and the Atlantic as well as our data in the upper troposphere a sufficient body of data is available to estimate the global distribution of CO in the troposphere and lower stratosphere which is illustrated in Fig. 3. Although only CO-data in marine air were considered, the highest CO-mixing ratios are evident in the middle northern latitudes in surface air. Here, the mixing ratios decrease with altitude from a mean value of 0.24 ppm at the surface to about 0.15 ppm just below the tropopause and then drop rapidly to a constant CO-value of 0.05 ppm in the lower stratosphere. Strong vertical CO-gradients were also observed at the trade wind inversion (Abel et al., 1969; Seiler & Junge, 1970) where the CO-mixing ratios decreased from 0.17 ppm below the inversion to 0.13–0.14 ppm above the inversion. In contrast to the northern hemisphere the CO-mixing ratio increases with altitude in the southern hemisphere from the equator to at least 20° S, due to the interhemispheric exchange in the upper troposphere and a corresponding flux of CO-rich air from the northern hemisphere into the southern hemisphere. This flux is illustrated by the bulbshaped extension of the isoline patterns in southern direction in the upper troposphere. Because of the constancy of the CO-mixing ratio in surface air at 50° S even during days with rapidly changing weather conditions and pronounced vertical and horizontal mixing, CO seems to be well mixed with little or no gradients in horizontal and vertical directions at these latitudes.

The pattern of the CO-distribution strongly indicates that CO is produced at the surface in middle northern latitudes and transported in southern and northern directions where it is destroyed. Similar information is obtained from the latitudinal distribution of the mean tropospheric CO-mixing ratio averaged over 10° latitudes which is shown in Fig. 4. In order to derive a representative average CO-mixing ratio for the whole troposphere, the data are corrected for the air densities at different altitudes and for the lengths of the latitudinal circles. As expected, the mean tropospheric CO-mixing ratio decreases from 0.19 ppm at middle latitudes in the northern hemisphere to 0.04 ppm at 65° S, with an overall average CO-mixing ratio of 0.11 ppm in the troposphere.

Only CO-data in marine air masses over the Atlantic and the Pacific were considered for the calculation of the latitudinal CO-distribution. If data from the continents will also be included in Fig. 4, we should expect a change in the latitudinal CO-distribution, especially in middle latitudes of the northern hemisphere where the anthropogenic sources of CO are concentrated resulting in considerable higher CO-mixing ratios over the continents than over the oceans. However, due to the lack of CO-data over the largest parts of the continents, e.g. Russia and China, it is not possible to provide a proper estimate. Unpublished calculations about the influence of the aerosol-production over land on the average aerosol-distribution by Junge (1973) indicate only a 10–20% higher tropospheric aerosol-concentra-

tion over land compared with that over the ocean, if an aerosol-life time of 200 days is assumed comparable with the estimated residence time of CO. Although this calculation includes a number of simplifications, it indicates fairly well that the latitudinal CO-distribution as given in Fig. 4 will not change dramatically.

The difference in the CO-mixing ratio between both hemispheres (Fig. 4) can only be explained either by the higher CO-sinks in the southern hemisphere or higher CO-sources in the northern hemisphere, or both. The suggestion of higher CO-sinks in the southern hemisphere must be rejected. From all presently known CO-sinks, the CO-uptake by soil, the CO-flux into the stratosphere, destruction by OH, as well as the uptake by plants, are more effective in the northern hemisphere due to the higher land masses and higher CO-mixing ratios in the northern hemisphere. As far as the photochemical reactions in the troposphere are concerned there are no indications for higher destruction rates in the southern hemisphere. The same should be true for a higher photochemical CO-production in the northern hemisphere so that the unsymmetrical CO-distribution must be caused by the additional CO-production in the northern hemisphere from anthropogenic and some smaller natural CO-sources like forest fires and oxidation of hydrocarbons. The important oceanic source is excluded due to higher CO-production in the southern hemisphere as a consequence of the larger ocean-surface.

In the following sections the individual sources and sinks are discussed in detail.

(b) *Sources for CO*

1. Anthropogenic CO-production

CO is produced by various anthropogenic processes, mainly by the incomplete combustion of carbonaceous fossil fuels used in motor vehicles, aircraft, and stationary sources, as well as by some industrial processings. The total annual anthropogenic CO emission was already estimated in 1952 by Bates & Witherspoon to be 2.1×10^{14} g. A more detailed estimate of 2.85×10^{14} g annually for the year 1966 was given by Robinson & Robbins (1969).

Recently, Jaffe (1972) reported a global CO-emission of approximately 4.1×10^{14} g for 1970, using the world wide usage of refined petroleum products, coal and lignite for combustion and CO emission factors known for several processes. Due to the increasing consumption of fossil fuel the total anthropogenic CO-emission for 1971 should be about 4.6×10^{14} g per year. A total of 70–80 % is contributed from automobil exhaust, whereas fuel combustion in stationary sources and industrial processes account for 20–30 %. The production by heating of homes using coal and fuel oil was estimated to be negligible compared with these sources.

There are several reasons why the total anthropogenic CO-production of 4.6×10^{14} g per year can be considered only as a lower limit. In a recent paper, Baum (1972) estimated the production of CO by home-heating in West Germany to be 2.5×10^{12} g per year or 30 % of the annual CO-production by motor vehicle in West Germany. Independent measurements of the CO-emission in Cologne, Germany (Emissionskataster, Köln, 1973), over a period from 1969 to 1971 indicate even similar annual production rates for both, motor vehicles and home-heating. If we assume that the ratio given by Baum (1972) is true also for other countries, the CO-generation by home-heating would contribute more than 1.0×10^{14} g per year and represent a larger portion as assumed before.

Furthermore, not all CO-producing industrial processes were considered in the estimates given above. As pointed out in the NATO/CCMS report No. 10, several additional industrial sources exist whose emission cannot be estimated because of the lack of published data on production, types of equipment and controls as well as emission factors. Some of these sources are ammonia and methanol reforming, synthetic gas manufacture, organic chemical manufacture and others.

Thirdly, most of the emission factors used in estimating the total anthropogenic CO-production were based on USA-data. Since this country is under pollution control it is likely that CO-emission factors are lower than the global average and consequently the total anthropogenic CO-production higher than the estimated given above.

We think that the additional CO-sources and the higher average CO-emission factors will contribute about 40 % so that the total anthropogenic CO-production would increase to 6.4×10^{14} g per year. Due to the uncertain-

ties involved in this estimation this number has an accuracy not better than ± 20–30 %. If we use the annual consumption of petrol in both hemispheres as an indicator for the anthropogenic CO-production, 85 % of this is produced in the northern hemisphere, mainly between 40° and 60° N.

2. CO-production in the oceans

The measurements of the dissolved CO in surface water of the oceans (Table 2) including our data from the northern and southern Atlantic as well as CO-data by Swinnerton et al. (1970, 1974) and Lamontagne et al. (1972) over the northern and southern Pacific, show significantly greater concentrations ($1–10 \times 10^{-5}$ ml CO/l H_2O) than could be accounted for by the equilibrium with the atmosphere. Small undersaturations were found only during short time periods (Seiler & Schmidt, 1973). All measurements made so far in the Atlantic and the Pacific show agreement with an average of about 5×10^{-5} ml/l, corresponding to an average equilibrium value of 2.5 ppm. The average CO-mixing ratio in air above the sea water, by contrast, varies between 0.04 to 0.20 ppm so that the seawater is supersaturated on the average by a factor of about 30. The flux of CO into the air resulting from this high supersaturation can be calculated (Seiler & Schmidt, 1973) by the expression

$$J = \frac{(E - M)\,\varphi\alpha DP}{z}$$

assuming that the flux density is determined by the molecular diffusion of CO through a laminar boundary layer at the water surface (Broecker & Peng, 1971).

E = equilibrium value in ppm
M = mixing ratio in surface air in ppm
φ = density of CO = 1.165×10^{-3} g/cm^3
α = solubility of CO = 0.022 cm^3 CO/cm^3 H_2O atm.
D = molecular diffusion coefficient = 2.3×10^{-5} cm^2/sec
P = barometric pressure $\approx$ 1 atm., and
z = thickness of the boundary layer.

With an average value of 2.5×10^{-3} cm (Broecker, 1973) for z in all oceans and an average CO-equilibrium value of 2.5 ppm, the net flux J is about 1.0×10^{14} g per year. This is higher than the estimated value of about 0.15×10^{14} g per year by Swinnerton et al. (1971), but lower than the value of 2.20×10^{14} g reported by Linnenbom et al. (1973), using a completely different model.

According to the distribution of the oceans between the hemispheres and the lower CO-mixing ratio in air in the southern hemisphere corresponding to a greater CO-gradient at the sea surface the oceanic CO-production in the southern hemisphere is larger. The annual CO-production of 0.6×10^{14} g in the southern hemisphere, compared with about 0.4×10^{14} g in the northern hemisphere, however, is too small to balance the additional anthropogenic CO-production in the northern hemisphere.

3. CO-production in rain water

In a recent paper Swinnerton et al. (1971) reported high supersaturations of dissolved CO in rain water relative to the CO mixing ratio in air. Measurements were made in regions with polluted air (Washington, D.C.) but also in unpolluted air over the Pacific and in Hawaii. The CO-concentrations varied during day-time between 6.0×10^{-5} ml CO/l water in Hawaii and 140×10^{-5} ml/l in Washington with an average of about 30×10^{-5} ml/l. During night-time the dissolved CO in rain droplets was lower by a factor of 1.1 to 2.0 but the rain water was still supersaturated by a factor of 16 to 105. Rain water samples taken in clouds in altitudes of 5 000 feet showed a slightly higher CO-concentration (33×10^{-5} ml/l) than those taken near sea level with a value of 20×10^{-5} ml/l, indicating only a small vertical gradient of CO-concentration in the water droplet. Swinnerton et al. (1971) therefore suggested the CO-production in droplets to occur mainly at altitudes where they were formed. They assumed a CO-production by oxidation of organic material in rain water, as shown by Wilson et al. (1970) or by electric discharge within clouds leading to dissociation of CO_2.

More recently Galbally (1972) postulated that photolysis of formaldehyde and higher aldehydes by UV light produces this excess of carbon monoxide in rain droplets. In a model he calculated the dissolved CO-amount in the droplet size using a mean formaldehyde concentration in rain water of 0.6 mg/l as given by Dhar & Ram (1933) and Shearer (1969). The predicted CO-concentration varied between

2 and 180×10^{-5} mg/l in fair agreement with the data found by Swinnerton et al. (1971). Using the same model, Galbally (1972) predicted also a supersaturation of H_2 in the rain water by a factor of 20–50.

The high mean supersaturation of CO in the droplet causes—as already shown in the previous section—a net flux of CO through the surface of the water droplet into the atmosphere. Unfortunately, no information concerning the total amount of rain droplets in the world is available at present. The amount used in the following calculation is estimated by the use of a global annual precipitation of 100 g cm^{-2} and an average droplet size of 100 μ. With the assumption of an average CO-concentration of 30×10^{-5} ml/l in all rain droplets during the average life time of the rain droplets of 1 h, the total CO-production would be about 3×10^{19} g per year, which is higher by a factor of 10^4 than all known sources together. Even if we assume that the CO-supersaturation in the droplet is present only during a period of 10 minutes—corresponding to the fall time of a droplet in a layer between 5 000 feet altitude and sea level (Beard & Pruppacher, 1969) where the CO-concentration in the droplet was found to decrease only slightly—the total CO-production does not decrease significantly. On the other hand, it may be pointed out here that the estimated value of 3×10^{19} g per year is only a lower limit of the total CO-production by rainwater for two reasons: Firstly, in the estimation only droplets which reach the earth's surface are considered. This amount, however, represents only a small portion of all droplets present in clouds and being active in the formation of CO. Secondly, the flux of CO through the surface of a sphere is greater than through a plain surface as used in this calculation.

Due to the extreme CO-flux from the droplet into the atmosphere, one has to expect a significantly higher CO-mixing ratio, especially in stable clouds like stratus. However, measurements in different cloud types including stratus over Germany in 1971/72 did not show any differences in CO-mixing ratios outside or inside the clouds. This was confirmed by Swinnerton (1973) by several flights near Florida, USA. Thus, we have to assume either lower CO-supersaturations in rain droplets as found by Swinnerton et al. (1971) or a lower flux of CO from the droplet into the atmosphere due to some unknown processes.

To solve this contradiction, we started in April 1973 CO-measurements in rainwater in Mainz, West Germany, after development of a new technique to be published elsewhere. All rainwater samples analysed up to 10 minutes after rainfall show only small amounts of dissolved CO (6×10^{-5} ml/l). The most surprising finding is the rapid increase of the dissolved CO in the rain water sample by a factor of more than 6 within one hour after sampling. Thus, we have to expect a CO-concentration in the rain droplets during rainfall lower than the measured one of 6×10^{-5} ml/l. It may be possible that the high supersaturation found by Swinnerton et al. (1971) were influenced by this process, especially in those rainwater samples not analysed immediately after rainfall.

Because of the short life time of a water droplet of about 1 hr and the high CO-supersaturations found during night-time by Swinnerton et al. (1971), photolysis of formaldehyde and photoxidation of organic material cannot be the only CO-producing mechanism in the droplet. We have to assume additional light-independent CO-production processes. One possibility is the activity of microorganisms which are transported with seaspray and dust into the atmosphere (Blanchard, 1970). Even during daytime photolysis of formaldehyde seems to be of minor importance in droplets because we could not find any supersaturation of H_2 in rainwater as to be expected by this process according to Galbally (1972).

All those considerations show that the CO-production by rainwater is certainly lower than the value given before. A more accurate estimation will be possible only if more data are available and the processes responsible for the CO-production in the rain droplet are understood.

4. Photochemical production of CO

In the last 3 years the chemistry of atmospheric trace gases in the troposphere has received considerable interest. As new and better reaction constants became available, photochemical models were developed and the altitude profiles as well as the total production of several minor tropospheric species calculated. Of particular interest is the oxidation of me-

thane by OH with formaldehyde as the major intermediate product of the oxidation path. All major removal mechanisms in the troposphere for formaldehyde seem to result in the production of CO so that the oxidation of methane by OH provides a source for CO. The annual CO-production by this process was calculated by several authors (McConnell et al., 1971; Levy, 1972; Wofsy et al., 1972) to $20-40 \times 10^{14}$ g, using similar photochemical models.

In a more detailed photochemical model Levy (1973) calculated a methane loss rate of 10.5×10^{14} g per year. Assuming that every CH_4-molecule destroyed by the reaction with OH leads to the formation of one CO-molecule, the annual CO-production would amount to 15×10^{14} g. This value is lower than those reported before, but nevertheless it is higher by a factor of 3 than the total anthropogenic CO-production so that the methane oxidation was assumed to be the dominant source in the troposphere. This assumption was confirmed by measurements of the O^{18}/O^{16} ratio and the C^{13}/C^{12} ratio in CO in both hemispheres by Stevens et al. (1972) who interprets his results by the CO-production of natural CO-sources, especially the oxidation of methane. Using his isotopic data, Stevens et al. estimated the CO-production of the latter process to more than 30×10^{14} g per year.

Warneck (1974) could show by considerations of the NO_3-budget that the OH-concentration in the troposphere seems to be less by a factor of five than those values given by Levy (1972) and Wofsy et al. (1972). This would result in a lower CO-production by the same factor assuming a 1:1 conversion of methane to CO. In this case the total CO-production by the methane oxidation would be less than the anthropogenic CO-production. Another argument against dominant CO-production by the methane oxidation is the latitudinal distribution of the CO-mixing ratio between the hemispheres which is discussed in detail in a later section.

5. Other natural CO-sources

Carbon monoxide is also produced by several different natural CO-sources, first of all the CO-production by forest fires and bush fires. Robinson & Robbins (1969) estimated the global annual CO-production by forest fires and bush fires to be 11×10^{12} g and 6.3×10^{12} g respectively. More recently the CO-production by wild and controlled forest fires was estimated to be 8.5×10^{12} g per year only for the USA (NATO/CCMS-report, 1972). In addition, 2.3×10^{14} g agricultural waste is burned each year in the USA resulting in an annual CO-emission of 8×10^{12} g. Assuming that this is only 25% of the global CO-emission (Robinson & Robbins, 1969), the world total CO-production by forest fires and open burning of agricultural waste is likely to be 34×10^{12} and 30×10^{12} g per year respectively (Table 1).

There are indications that CO is also produced by the biosphere, by photochemical oxidation of hydrocarbons in the atmosphere and by microbiological activity on the earth's surface. Wilks (1959) reported that green plants grown in closed illuminated systems liberate small quantities of CO, which he explained by the action of sun radiation on chlorophyll in the presence of O_2. Siegel et al. (1962) found CO-formation during the growth of cucumber seedling and seed germination of rye, cucumber and other species. Sometimes the CO-mixing ratio exceeded values of 6 000 ppm, in the test atmosphere. In contradiction to Wilks (1959), they showed that CO is also produced in dark and that neither sun radiation nor chlorophyll is required for CO-formation. At present the data available are insufficient to estimate the total CO-production by these processes.

CO seems to be produced also by photochemical oxidation of hydrocarbons, e.g. terpenes, which are found in measurable amounts of 2–20 ppb in various parts of the world (Rasmussen & Went, 1965). The total yearly production of volatile organic substances is suggested by Went (1966) to be 10^{15} g, which may result in a CO-production of about 60×10^{12} tons annually (Robinson & Robbins, 1969).

Furthermore, CO is produced in living animals and men probably by decomposition of hemoglobin (Coburn et al., 1964; Conkle et al., 1967). The production rates vary between 0.4 and 1.0 ml CO/man/h which is negligible compared with other natural sources.

(c) *Sinks for CO*

Until 1969 our knowledge of the removal processes in the troposphere and lower stratosphere was unsatisfactory. Jaffe (1968) and Robinson & Robbins (1969) have discussed pos-

sible sink mechanisms but could not find any of importance. In the meantime, several processes were reported which can decompose CO in significant amounts, first of all the consumption of CO on the soil surface by microorganisms and the reaction of OH with CO. Furthermore, the uptake by plants seems to be an important sink.

1. CO-uptake on the soil surface

Measurements by our group have shown that CO is consumed on the soil surface. Liebl (1971) determined an average uptake rate of 1.5×10^{-11} g/cm² sec over several types of soil and at a soil temperature of 15°C. In similar experiments Inman et al. (1971) found uptake rates between 6 and 50×10^{-11} g/cm² sec over various soils in the USA. They calculated an average uptake rate of 25×10^{-11} g/cm² sec, higher by a factor of 15 than the values given by Liebl (1971). This discrepancy is most likely caused by the different CO-concentrations used by these two groups. Whereas we used test atmospheres with a CO-mixing ratio of 0.20 ppm, comparable with the normal CO-mixing ratio in air over the continent, Inman et al. (1971) started their experiments with a CO-mixing ratio of 100 ppm. As the uptake mechanism can be characterized as a first order reaction, one has to expect higher CO-uptake rates by use of higher CO-mixing ratios. Therefore, the lower value found in our experiments seems to be more realistic with respect to global uptake of CO. With a mean uptake rate of 1.5×10^{-11} g/cm² sec and the assumption that this value is true for the land areas in the tropical and temperate zones, the global consumption by soil is estimated to be 4.5×10^{14} g per year equivalent to the total anthropogenic CO-production. According to the distribution of land masses between the hemispheres about 3.0×10^{14} g per year are consumed in the northern hemisphere with 1.5×10^{14} g per year in the southern hemisphere.

However, these values are only a crude estimation because of the relationship found between the CO-equilibrium value above the soil, the soil temperature and the type of soil. It may be possible that the uptake rates in heavy polluted regions where the CO-mixing ratios exceed values of a few ppm are considerably higher than the average value used above. On the other hand, the soil in the tropics may be a source rather than a sink for CO.

2. The stratosphere as a sink for tropospheric CO

As we have shown previously (Warneck et al., 1973), the behaviour of the CO-mixing ratio above the tropopause can be approximated by

$$m_z = [m_s + (m_0 - m_s) \exp(-az)]$$

where m_0 is the average CO-mixing ratio at the tropopause, m_s is the constant CO-mixing ratio in the stratosphere = 0.05 ppm, and z is the height above the tropopause. The scale height a was derived from our vertical CO-profiles in the northern hemisphere.

The corresponding flux of CO into the stratosphere is given by

$$F = -D \cdot \varphi_{CO} \frac{\partial m(z)}{\partial z}$$

$$= D\varphi_{CO}(m_0 - m_s)\, a$$

With average values of 3.0×10^{-4} g/cm³ for φ_{CO}, 3×10^3 cm²/sec for D, 1.6×10^{-5} cm^{-1} for a, 0.05 ppm for m_s and 0.13 ppm for m_0, corresponding to 1.1×10^{15} molecules/g air and 2.7×10^{15} molecules/g air respectively, the CO-flux into the stratosphere in the northern hemisphere amounts to 2.4×10^{10} molecules/cm² sec in agreement with estimations by Seiler & Warneck (1972). The corresponding size of the stratospheric sink in the northern hemisphere is 0.9×10^{14} g per year. The stratospheric sink in the southern hemisphere is considerably lower due to the lower CO-mixing ratio in the upper troposphere of the southern hemisphere of approximately 0.07 ppm. No data are available at the present time for m_s and a in the southern hemisphere. As already discussed CO seems to be uniformly distributed in the stratosphere of both hemispheres with an average of 0.05 pm. If we take for a the same value as obtained for the northern hemisphere, the flux of tropospheric CO into the stratosphere is reduced to 0.2×10^{14} g per year. The total stratospheric sink in both hemispheres would thus amount to 1.10×10^{14} g per year.

In addition to the CO-flux by eddy diffusion as discussed before, tropospheric air is transported into the stratosphere by mean vertical motion through the tropical tropopause. Because of the air mass balance between strato-

sphere and troposphere the same amount (3×10^{12} g/sec) enters the troposphere mainly in the middle latitudes. With an average CO-mixing ratio in the upper troposphere of the equatorial regions of 0.12 ppm, the net flux of tropospheric CO into the stratosphere amounts to 7×10^{12} g per year which is negligible compared with other CO-sinks.

3. CO-uptake by plants

At the present time several contradictory publications concerning the influence of plants on the CO-cycle exist. Only some of those should be mentioned here.

Krall & Tolbert (1957) could demonstrate that CO is consumed by higher plants, for example by leaves of barlay. The uptake mechanism was found to be light-dependent and resulted in a production of serine. In 1962 Chappelle reported the oxidation of CO by various types of algae. In contradiction to this, tests with a wide variety of plants by Ingersoll (1971) did not show any change in the test atmospheres even over 24-hours-test-periods. Thus he concluded that plants did not have the "slightest capacity" for a CO-uptake.

More recently, Bidwell & Fraser (1972) found an uptake of CO by bean leaves using C^{14}-labelled CO. In light, CO was converted mainly to succrose and protein, whereas in darkness CO was almost completely oxidized to CO_2. The uptake rates varied widely with species and were roughly proportional to the concentration of CO. As an example, the uptake rates varied at CO-mixing ratios of 1–360 ppm between 0.003 and 1.42 μ mole/dm^2 hour. Using the value for bean leaves (0.06 μ mole/dm^2 hour) at a CO-mixing ratio of 2 ppm, Bidwell & Fraser (1972) calculated the uptake rate of 12–120 kg/km^2 ground/day, which corresponds to a total uptake rate by plants of 6.5 to 65×10^{14} g per year. In this case the uptake by plants would represent the most important sink in the troposphere.

However, as shown by the following considerations this value is overestimated. The total amount of the uptake by both, plants and soil, would amount to $1\text{–}7 \times 10^{15}$ g per year, compared with an anthropogenic CO-production of 0.6×10^{15} g per year which represents the major source over the continents. Both, the removal mechanism and the anthropogenic CO-production, occur only over land. As the calculated uptake rates are higher by a factor of ten than the CO-sources over the continents, lower CO-mixing ratios should be expected over land compared with those found in marine air masses.

However, all measurements made so far always show higher CO-mixing ratios over land, even in country-like areas where the direct influence of anthropogenic sources is negligible. This strongly indicates that the uptake by both, plants and soil, must be lower than the total CO-production over land. Since the consumption rate of CO by soil is already comparable with this amount (as already discussed in a previous section), the uptake rate by plants seems to be relatively small in agreement with Ingersoll's (1971) data.

The high uptake rates found by several authors are probably influenced by the activity of microorganisms sitting on the leave surface. Similar to the uptake on the soil, these microorganisms can oxidize CO to CO_2 which is consumed by the plants by assimilation. Such processes would explain the conversion of CO to succrose during daytime when assimilation occurs and the oxidation to CO_2 in darkness.

4. Oxidation by OH

The oxidation of CO by OH in the troposphere is suggested to be the major CO-sink by several authors. Weinstock (1969) and Weinstock & Niki (1972) calculated an average CO-destruction of 5×10^{15} g per year. Similar values can be derived from OH-concentrations given by McConnell et al. (1971) and Wofsy et al. (1972). More recently, Levy (1973) published CO-loss rates as a function of altitudes and the CO-mixing ratio in the troposphere which result in an annual CO-destruction of 1.9×10^{15} g, assuming an average CO-mixing ratio of 0.11 ppm.

It is very important that all calculations concerning the photochemical production of CO and destruction by OH resulted in a higher CO-destruction. Using the data by Levy (1973) the ratio of the global photochemical CO-production Q and the global photochemical CO-destruction S is given by

$$\frac{S}{Q} = \frac{19.4 \times 10^8}{15.0 \times 10^8} = 1.29$$

This ratio depends only on the average CH_4-

and CO-mixing ratios as well as two reaction constants but not on the OH-concentration. Due to the different photochemical production rate and destruction rate, additional CO-sources in the troposphere are required to maintain steady state. Using the results by Levy (1973), the difference amounts to approximately 5×10^{14} g, identical with the anthropogenic CO-production.

However, as shown by Warneck (1974), the OH-concentrations and the corresponding CO-destruction seem to be less by a factor of approximately 5 which would reduce this CO-sink to about $4–10 \times 10^{14}$ g, comparable with the CO uptake by soil.

(d) Residence time of CO

The CO-sources and sinks as discussed above are summarized in Table 2. According to the uncertain effects of the photochemistry and correspondingly different production- and destruction-rates published, the total CO-production in the troposphere varies between 2.5 and 5.0×10^{15} g per year. Similar values are found for the total CO-destruction with $2.5–5.6 \times 10^{15}$ g per year so that the tropospheric CO-cycle appears to be balanced. Using these data and a mean tropospheric CO-mixing ratio of 0.11 ppm, the residence time of tropospheric CO is about 0.1–0.2 years which is short compared with values reported by Robinson & Robbins (1969) and Junge et al. (1971). It is very important that at least 70% of the global CO-production and 80% of the global CO-destruction is contributed by photochemistry. Changes of the estimated OH-number densities will therefore influence the residence time in about the same ratio.

A similar residence time, 0.1 years, was calculated by Weinstock (1969), using the C^{14}-production and the specific C^{14}-activity of CO in the troposphere. The production of C^{14} which is fixed as $C^{14}O$ (Pandow et al., 1960; McKay et al., 1963), is better known than the total $C^{12}O$-production. Unfortunately, only three values of the specific C^{14}-activity in CO are available at the present time, reported by McKay et al. (1963). These three values taken over a period of 3 months at Linde's South Buffalo plant in a heavily industrialized and populated area show high variations between -39.3, -4.3 and $+9.3 \pm 7.8$%, relative to 95% of NBS oxalic acid sample defined as zero age in 1955. McKay et al. (1963) explained the lack of constancy of the specific activity by high fluctuations of the CO-mixing ratio in polluted airmasses and correspondingly a dilution of normal specific activity in background CO by the C^{14}-free man-made CO. On this basis the highest specific activity approaches the specific activity in clean air but is still less because of the higher CO-mixing ratios over continents due to pollution. Adopting an average CO-value of 0.6 ppm in polluted air and using the highest measured specific activity one obtains a residence time of 0.5 years. McKay et al. (1963) did not state if their published value of 0.3 ppm for Buffalo air which was used for the determination of the specific activity of C^{14} in CO was measured or only estimated. The average CO-mixing ratio of 0.6 ppm used in our calculation was derived from continuous CO-registrations over a time period of several months in the outskirts of Mainz (Germany), with a population of 150.000 people.

Because of the inaccuracy of the C^{14}-data and the uncertainty of the CO-mixing ratio in Buffalo air during the air sampling the calculated residence time of 0.5 years is not very reliable but seems to be more likely as the short residence time of 0.1 year as reported by Weinstock (1969).

In a recent paper Weinstock & Niki (1972) pointed out that the residence time of 0.1 year should be taken only as a lower limit which agrees with our considerations. This estimated residence time of approximately 0.5 years results in a reduction of the global CO-production and -destruction. In steady state conditions the total tropospheric CO-production has to be reduced to about 10×10^{14} g per year. As shown in the previous discussions the anthropogenic and oceanic CO-production as given in Table 2 is reasonably well established with an annual total CO-production of 7.4×10^{14} g. Highly uncertain are the production rates by bush- and forest-fires and by the oxidation of hydrocarbon. The CO-production by these sources was assumed to be 1.2×10^{14} g per year with an inaccuracy factor of at least 2. Even if we neglect the CO-production by these sources, the CO-generation by the methane oxidation has to be reduced to 2.6×10^{14} g per year, considerably lower than estimated before. Similar results are obtained for the CO-destruction by the photochemical oxidation of CO by OH.

This process would contribute about 5.0×10^{14} g or 50% of the total CO-destruction. These results are in reasonable agreement with data by Warneck (1974) who postulated an OH number density in the troposphere less by a factor of 5 compared with those used in the previous estimation of the photochemical CO-production and -destruction. Unfortunately, no method is available at the present time to measure the OH number densities in the troposphere so that the OH-concentration and correspondingly the photochemical CO-production and -destruction can only be estimated from budget considerations of those gases in which the OH radicals are involved.

A very important point is the observed interhemispheric difference of the CO-distribution with an average CO-mixing ratio of 0.15 ppm in the northern and 0.06 ppm in the southern hemisphere, resulting in a flux of CO from the northern into the southern hemisphere. This information together with the interhemispheric distribution of the known sources and sinks as given in Table 2 was used to estimate the global photochemical CO-production and -destruction, using the interhemispheric exchange model by Czeplak & Junge (1973). These calculations will be published separately. However, two preliminary results should be mentioned here already: First, the photochemical CO-production and CO-destruction seem to be small compared with other known CO-sources and CO-sinks in the troposphere, suggesting lower OH number densities in the troposphere as given by Levy (1973) and others. Second, the CO-production in the northern hemisphere relative to that in the southern hemisphere should be higher than listed in Table 2 to balance the flux of CO into the southern hemisphere. On the other hand, hemispheric balance considerations appear to be very sensitive to the accuracy of the input data so that it is difficult to draw definite conclusions.

Summary

In this paper the distribution as well as the sources and sinks of carbon monoxide in the troposphere are discussed. It could be shown that the average tropospheric CO-mixing ratios differ between the two hemispheres with 0.15 ppm in the northern and 0.06 ppm in the southern hemisphere. Whereas fluctuations of the CO-mixing ratio exceeded values of ±30% in the northern hemisphere, the CO-mixing ratio in the southern hemisphere appears to be surprisingly constant. This is in agreement with the difference in the large scale hemispheric distribution. CO is produced by several natural and technological sources, the source strengths of which are listed in Table 2. There are several reasons for including calculations using the interhemispheric exchange model by Czeplak & Junge (1973) which seem to indicate that the photochemical CO-production and CO-destruction in the troposphere are lower than estimated before (Levy, 1973; McConnell et al., 1971; Wofsy et al., 1972). In contrast to the troposphere, these processes seem to be dominant in the lower stratosphere. The total CO-production in the troposphere is estimated to be approximately 10×10^{14} g per year, corresponding to a residence time of 0.5 years.

CO is removed by microbiological processes at the soil surface and by OH-destruction. A smaller part is transported by eddy diffusion into the stratosphere where CO is oxidized by OH.

It is clear from the discussion that the CO-cycle presented in this paper is still uncertain. The estimations of the CO-sources and -sinks given in Table 2 are still unreliable due to incomplete data. Corrections of the CO-budget will therefore become necessary as new data, especially about the influence of the biosphere and about the CO-production in rain water, will become available. It would be most important to obtain data about the specific C^{14} activity of CO in unpolluted air masses. As shown by Weinstock (1969) and Junge et al. (1971) these data can be used to calculate the CO-residence time in the troposphere with a high accuracy.

Acknowledgements

I am indebted to Professor Dr C. Junge for many discussions and general support; to U. Schmidt for cooperation and assistance; to Mrs C. Tonn, Miss I. Schüler and Mr K. H. Liebl for temporarily operating the instruments on board the R. V. *Meteor* and general help; to the Bundes-Verkehrsministerium, the Deutsche Lufthansa and the Conti-Flug for cooperation in performing the flights. I also thank the National Environmental Research Council

of Great Britain (NERC) for the invitation to participate in the Antarctic cruise on board the R. R. S. *Shackleton*, and Mr P. F. Barker, University of Birmingham and Mr R. J. Wade, University of Southampton, for their help.

This work was performed as part of the program of the Sonderforschungsbereich 73 "Atmospheric Trace Components", receiving partial funds through the Deutsche Forschungsgemeinschaft.

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ЦИКЛ АТМОСФЕРНОГО CO

Для определения детального бюджета CO в атмосфере используются новые измерения отношения смеси CO в обеих полусферах с учетом растворенного в поверхностях водах в CO и с учетом уже известных данных. Показано, что CO производится технологическими и естественными источниками. Мощность источников обоих сортов одного порядка величины. Общее производство CO оценивается в 10^{15} граммов в год. Соответствующее время пребывания газа в атмосфере равно 0,5 года. Из наблюдаемого распределения CO по широте найдено, что производство CO путем окисления метана в тропосфере является несущественным источником. CO удаляется путем микробиологических процессов на поверхности почвы, фотохимическими реакциями в стратосфере и, возможно, реакцией с радикалом OH в тропосфере.