

OH RADICALS VIA ATMOSPHERIC ^{14}C O

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ABSTRACT. Measurements of ^{14}C O in the lower troposphere show a well-defined seasonal variation between 11 ± 1 molecules cm^{-3} in summer and 25 ± 2 molecules cm^{-3} in winter at 51°N . The concentration at 27°N in summer is found to be 4.2 ± 0.7 molecules cm^{-3} . From these data and published ^{12}C O measurements, the average concentration of OH radicals in the troposphere is calculated to be $6.5 \pm 2.5 \times 10^5$ molecules cm^{-3} using a 2-D time-dependent model. The corresponding ^{12}C O lifetime is two months; the ^{14}C O lifetime is five months.

INTRODUCTION

McKay, Pandow, and Wolfgang (1963) demonstrated that at least 95 percent of the ^{14}C produced in the earth's atmosphere by cosmic ray neutrons reacts with O_2 immediately after the nuclear reaction to form ^{14}C O rather than $^{14}\text{CO}_2$. The same authors reported the first measurements of tropospheric ^{14}C O.

Weinstock (1969) and later, Weinstock and Niki (1972) used those measurements to calculate the atmospheric turnover time of CO, τ_{CO} , from the ^{14}C O and ^{12}C O balance to be on the order of one month. They also suggested that OH radicals might be responsible for the removal of CO from the atmosphere.

The relatively short CO lifetime derived from ^{14}C O was in substantial disagreement with estimates by Seiler (1974), who derived a lifetime of six months from the ^{12}C O cycle alone and argued that the ^{14}C O measurements made by McKay, Pandow, and Wolfgang might be too low, thus giving too short a lifetime. In this paper, new measurements of ^{14}C O in the lower troposphere are presented, which indeed show a higher ^{14}C O concentration than found previously. In addition, well-defined seasonal and latitudinal variations of ^{14}C O are observed.

EXPERIMENTAL TECHNIQUES

Carbon monoxide was separated quantitatively from 200m^3 of ambient air with the sampling apparatus shown schematically in figure 1. After compression to 4 bar by a viton diaphragm compressor, the air was pushed through the system at a flow rate of 50 l (STP)/min . Absorber I contained 5 l of a 5M NaOH solution and served to reduce the atmospheric CO_2 concentration of about 330ppmv to a level below 3ppbv. After the removal of CO_2 , carbon monoxide was quantitatively oxidized to carbon dioxide on a hot Pt-surface and collected in a second absorber II, which contained CO_2 -free NaOH solution. The total amount of air processed was measured with an integrating flow meter.

The carbon dioxide collected in absorber II was liberated in the laboratory by acidification and collected through a vacuum line into a trap chilled with liquid N_2 . After purification by low temperature distil-

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lation and gas chromatography on charcoal, the CO_2 was transferred into a proportional gas counter. The counter had a total volume of 55ml, a background counting rate of 0.30cpm and a sensitive volume of 42ml. The counting system was calibrated by counting CO_2 samples prepared from the ^{14}C -standard of the Institut für Umweltphysik, University of Heidelberg, West Germany.

The error of the $^{14}\text{C}/^{12}\text{C}$ determination employing a 4-day counting period was usually 3 to 5 percent. To calculate the error of the absolute concentration of ^{14}CO , the uncertainty introduced by contamination or losses during sample collection had to be taken into account. The latter were determined by simultaneous collection of an air sample whose CO concentration was measured by gas chromatography and compared to the CO concentration calculated from the amount of CO_2 collected in absorber II and the total amount of air processed. A more detailed discussion of the techniques and their uncertainties is given by Volz and others (1979).

RESULTS

The air samples were collected at a rural site near Jülich, West Germany (51°N) over a two-year period starting in May 1977. Additional samples were obtained at Miami, Florida (27°N) in September 1977 and during a cruise of *RV Knorr* (Woods Hole Oceanographic Institute) in the Mediterranean and Atlantic during April 1976. The measured ^{14}CO concentrations are summarized in table 1 together with the earlier results by McKay, Pandow, and Wolfgang (1963).

An examination of the ^{14}CO data in table 1 reveals a well-defined seasonal variation at 51°N with a maximum concentration of 25 ± 2 molecules cm^{-3} in winter and a minimum concentration of 11 ± 1 molecules cm^{-3} during summer. Details of the seasonal variation are shown

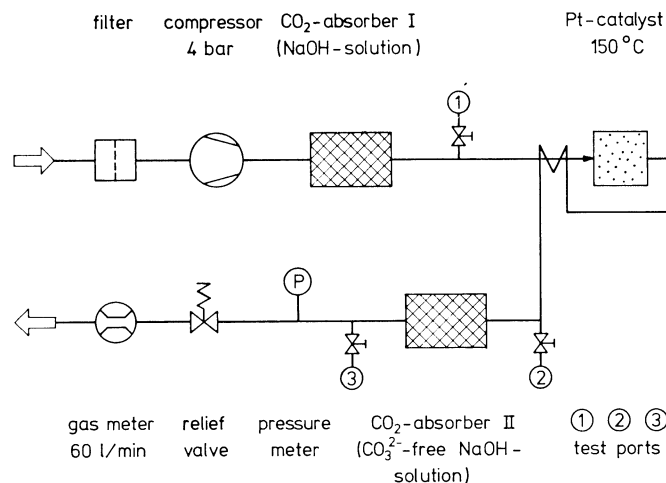


Fig 1. Schematic diagram of the apparatus for separation of carbon monoxide from ambient air.

TABLE I
Measurements of ^{14}CO at ground level

Date	Location	Latitude	$[^{14}\text{CO}] \pm \sigma$ molecules cm^{-3}
05/25/77	Jülich	51°N	13.8 ± 1.6
07/14/77	Jülich	51°N	9.4 ± 2.7
08/17/77	Jülich	51°N	10.8 ± 1.7
11/01/77	Jülich	51°N	16.8 ± 3.5
12/07/77	Jülich	51°N	23.3 ± 4.0
12/13/77	Jülich	51°N	20.9 ± 1.4
01/13/78	Jülich	51°N	29.0 ± 2.1
01/23/78	Jülich	51°N	22.9 ± 2.8
02/12/78	Jülich	51°N	24.2 ± 1.6
02/19/78	Jülich	51°N	23.8 ± 1.7
07/20/78	Jülich	51°N	12.1 ± 3.2
09/06/78	Jülich	51°N	10.5 ± 1.7
09/17/78	Jülich	51°N	12.4 ± 1.8
09/20/78	Jülich	51°N	12.8 ± 1.4
04/08/76	Mediterranean	36°N	14.7 ± 1.5
04/15/76	Atlantic	36°N	15.3 ± 2.0
04/22/76	Atlantic	43°N	19.1 ± 1.8
09/10/77	Miami	27°N	4.2 ± 0.7
09/12/77	Miami	27°N	
02/60 (McKay, Pandow, and Wolfgang, 1963)	Buffalo	43°N	8 (average of 3 samples)

more clearly by figure 2. The observations at different latitudes also indicate a marked latitudinal variation with higher ^{14}C O concentrations at higher latitudes and lower values in the tropics. Thus, the data from the *RV Knorr* cruise indicate a decrease from 19 molecules cm^{-3} at 43°N latitude to 15 molecules cm^{-3} at 36°N latitude during April 1976. An even larger effect is observed between Miami, with a ^{14}C O concentration of 4 molecules cm^{-3} at 27°N latitude, and Jülich, with 12 molecules cm^{-3} at 51°N latitude (*cf* fig 3). Both measurements were made in September.

The ^{14}C O concentrations reported here for winter at 51°N are about three times higher than the earlier measurements of McKay, Pandow, and Wolfgang (1963) at 43°N latitude. The difference in latitude can account only for a part of this discrepancy (*cf* fig 3). The major part seems to be due to the fact that McKay, Pandow, and Wolfgang (1963) could give only a crude value of the ^{12}C O mixing ratio. Although the $^{14}\text{C}/^{12}\text{C}$ ratio in carbon monoxide was measured precisely, only a rather uncertain value for the ^{14}C O mixing ratio or ^{14}C O concentration can be derived from their measurements. As Seiler (1974) already pointed out, the ^{12}C O mixing ratio of 0.3ppmv quoted by McKay, Pandow, and Wolfgang seems low in view of the mixing ratios around 1ppmv various authors have found in industrialized areas (*cf* Seiler and Zankl, 1976). Such mixing ratios would increase the ^{14}C O concentration derived from

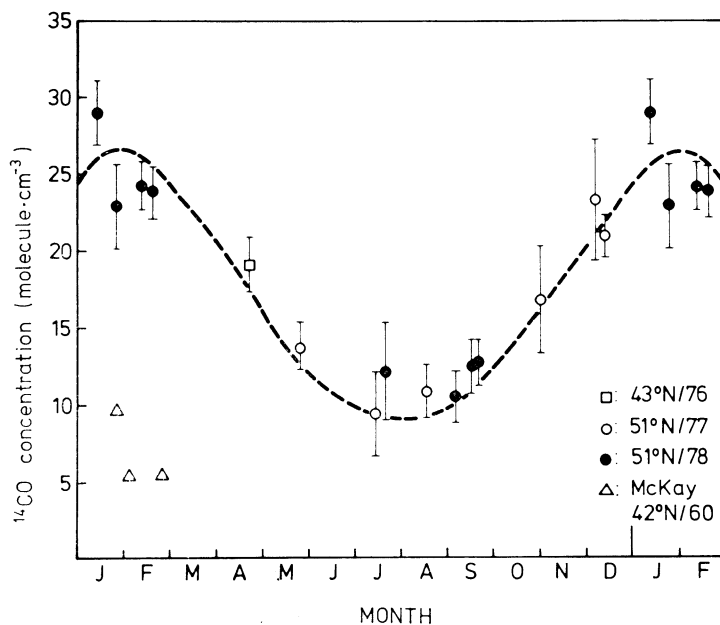


Fig 2. The measured seasonal variation of ^{14}C O at 51°N latitude. The early measurements by McKay, Pandow, and Wolfgang (1963) are also indicated. The dashed curve represents the computed seasonal variation for $[\text{OH}] = 6.5 \times 10^5$ molecules cm^{-3} and $P_{\text{bio}} = 1250 \times 10^{12}\text{g CO/yr}$.

the data of McKay, Pandow, and Wolfgang to a value more in line with the present study.

DISCUSSION

The observed seasonal variation of ^{14}CO can be described by the time dependent balance equation

$$\frac{d [^{14}\text{CO}]}{dt} = P - D + \text{div } \Phi, \quad (1)$$

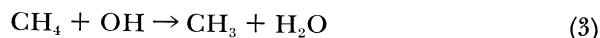
where $[^{14}\text{CO}]$ is the concentration of ^{14}CO , P , and D are the combined sources and sinks, and $\text{div } \Phi$ is the flux of ^{14}CO into the volume considered. In order to establish the source and sink terms, we discuss first the known sources and sinks of ^{12}CO :

P_{foss} : Emissions from fossil-fuel burning contribute about $640 \times 10^{12}\text{g } ^{12}\text{CO/yr}$ (Seiler, 1974).

P_{CH_4} : For each CH_4 molecule oxidized by OH radicals eventually one CO molecule is formed. Thus, the strength of this source is virtually equal to the CH_4 destruction rate:

$$P_{\text{CH}_4} = k_3 [\text{CH}_4][\text{OH}] \quad (2)$$

where k_3 is the temperature dependent rate coefficient of the reaction



P_{bio} : CO is also released from organic material either directly by incomplete combustion or indirectly by the emission of precursor gases (non-methane hydrocarbons), which are rapidly oxidized to CO in the atmo-

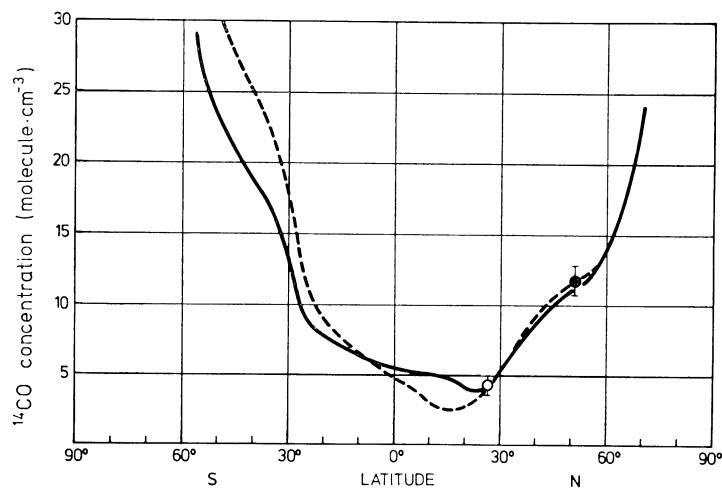


Fig 3. The calculated latitudinal distribution of ^{14}CO in the lower troposphere during September. The dashed curve was computed for $P_{\text{bio}} = 0$ and $[\text{OH}] = 4.8 \times 10^5$ molecules cm^{-3} , the full curve for $P_{\text{bio}} = 1250 \times 10^{12}\text{g CO/yr}$ and $[\text{OH}] = 6.5 \times 10^5$ molecules cm^{-3} . Open circle represents the measurements from Miami (27°N ; September 1977); full circle represents the average of three measurements at Jülich (51°N ; September 1978).

spheric boundary layer and can, therefore, be treated like a direct emission of CO (Zimmerman and others, 1978).

D_{OH} : Destruction by OH radicals is by far the most important sink of atmospheric CO



and we can write:

$$D_{\text{OH}} = k_4 [\text{CO}][\text{OH}] , \quad (5)$$

where k_4 is the (pressure-dependent) rate coefficient for reaction (4).

D_{soil} : CO is also removed by soil uptake. The uptake rate is proportional to the CO concentration above the soil and a deposition velocity v_s , which has been determined by Liebl and Seiler (1976) to average $0.04 \text{ cm} \cdot \text{s}^{-1}$.

Thus, we can write:

$$D_{\text{soil}} = [\text{CO}] \cdot v_s \quad (6)$$

Equation (1) then becomes for ^{12}CO :

$$\frac{d}{dt} [^{12}\text{CO}] = P_{\text{foss}} + k_3 [\text{CH}_4][\text{OH}] + P_{\text{bio}} - k_4 [^{12}\text{CO}][\text{OH}] - [^{12}\text{CO}] v_s + \text{div } \Phi \quad (7)$$

All natural sources of carbon monoxide contribute to the ^{14}CO budget and their relative source strength can be assessed by their specific $^{14}\text{C}/^{12}\text{C}$ ratio R . R_{foss} equals zero since all the ^{14}C originally present in fossil fuels has already decayed. R_{CH_4} has been redetermined recently to 1.2×10^{-12} by Levin (1978). For P_{bio} we adopt the isotopic ratio of recent organic material, which is 1.5×10^{-12} for the year 1977, when most of the ^{14}CO measurements were performed. However, the major source of ^{14}CO in the atmosphere is the production by cosmic ray neutrons. It is directly proportional to the ^{14}C production rate, which has been calculated by Lingenfelter (1963) as a function of height and geomagnetic latitude. The source strength is 2.0×10^{26} molecules/yr in the troposphere, which is about 70 percent of the total annual ^{14}CO production.

The corresponding balance equation for ^{14}CO is:

$$\frac{d}{dt} [^{14}\text{CO}] = P_{\text{cosm}} + R_{\text{bio}} P_{\text{bio}} +$$

$$R_{\text{CH}_4} \cdot k_3 [\text{CH}_4][\text{OH}] - k_4 [^{14}\text{CO}][\text{OH}] - [^{14}\text{CO}] v_s + \text{div } \Phi \quad (8)$$

Two parameters in the CO balance are poorly known: the tropospheric concentration of OH radicals and the magnitude of the biological sources. Using the ^{14}CO data presented here and the ^{12}CO data given by Seiler and Schmidt (1974), two relations can be established between P_{bio} and the average tropospheric OH concentration, $[\overline{\text{OH}}]$, from equations (7) and (8). For that purpose, both equations were to be solved using a 2-D time-dependent model. During the calculations, a 2-D OH field was adopted from the model itself (Derwent and Curtis, 1977) as a function of time of year. This field was then scaled at any given time, latitude, and altitude using a common scale factor f_{OH} . This scale factor was then optimized for various assumptions of P_{bio} until the deviations between

calculated and measured ^{14}CO and ^{12}CO data were minimized. The procedure ensured that during the calculation of the destruction terms the observed spatial and time variations of ^{14}CO , ^{12}CO , OH, etc, were taken into account. A 2-D model is sufficient because the longitudinal variations are minor. Integrating the scaled OH field over space and time, we were then able to extract the average tropospheric OH concentration required to balance either the ^{14}CO or the ^{12}CO budget as a function of P_{bio} . Thus, two independent relations between P_{bio} and $[\overline{\text{OH}}]$ were obtained. The intersection of the two relations eventually gave the unique solution for P_{bio} and $[\overline{\text{OH}}]$ which balances both the ^{14}CO and the ^{12}CO cycle. It was obtained for:

$$P_{\text{bio}} = (1250 \pm 800) \times 10^{12} \text{g } ^{12}\text{CO}/\text{yr}$$

and

$$[\overline{\text{OH}}] = (6.5 \pm 2.3) \times 10^5 \text{ molecules cm}^{-3}$$

The corresponding optimized calculations of the ^{14}CO seasonal and latitudinal variation are compared to the experimental data in figures 2 and 3 (for the ^{12}CO calculations, see Volz and others, 1979).

From the average destruction terms in equations (7) and (8), the tropospheric lifetimes of ^{14}CO and ^{12}CO can be calculated. They are:

$$\tau_{^{14}\text{CO}} = 5 \pm 1 \text{ months}$$

and

$$\tau_{^{12}\text{CO}} = 2 \pm \begin{matrix} 0.7 \\ 0.4 \end{matrix} \text{ months}$$

The errors given are caused by the source and sink terms in equations (7) and (8); they are discussed in detail by Volz and others (1979).

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