Atmospheric carbon dioxide variations at Mauna Loa Observatory, Hawaii

By CHARLES D. KEELING, ROBERT B. BACASTOW, ARNOLD E. BAINBRIDGE, CARL A. EKDAHL, JR, PETER R. GUENTHER, and LEE S. WATERMAN, *Scripps Institution of Oceanography, University of California at San Diego, La Jolla, California, USA* and JOHN F. S. CHIN, *National Oceanic and Atmospheric Administration, Mauna Loa Observatory, Hawaii*

ABSTRACT

The concentration of atmospheric carbon dioxide at Mauna Loa Observatory, Hawaii is reported for eight years (1964–1971) of a long term program to document the effects of the combustion of coal, petroleum, and natural gas on the distribution of CO_2 in the atmosphere. The new data, when combined with earlier data, indicate that the annual average CO_2 concentration rose 3.4 % between 1959 and 1971. The rate of rise, however, has not been steady. In the mid-1960's it declined. Recently it has accelerated. Similar changes in rate have been observed at the South Pole and are evidently a global phenomenon.

Introduction

In conjunction with the Antarctic study of atmospheric carbon dioxide discussed in the preceding paper (Keeling et al., 1976), a nearly uninterrupted series of CO_2 measurements has been obtained with a continuously recording nondispersive infrared gas analyzer over a period of fourteen years at the Mauna Loa high altitude observatory on the island of Hawaii. The sampled air at the station, as shown by Pales & Keeling (1965), is approximately representative of air above the North Pacific trade wind inversion between 15° and 25° N.

Two major features of the data are a seasonal oscillation and a long term increase.

The seasonal oscillation, with little doubt, reflects the integrated uptake and release of CO_2 by land plants and soil (Junge & Czeplak, 1968). The amplitude of the seasonal oscillation is maximum in the Arctic (Kelley, 1969) and decreases southward until low values are reached in the mid-southern hemisphere (Bolin & Keeling, 1963). The amplitude also decreases with height above ground and is barely observable in the lower stratosphere (Bolin &

Bischof, 1970; Bischof, 1973). The greater amplitude in the northern hemisphere is explained by the greater extent of boreal as compared with austral forests and grasslands. The decrease with height occurs because the seasonal oscillation, produced at ground level, is progressively attenuated upward by mixing.

Both the Antarctic and Mauna Loa data show an annual increase in CO_2 concentration of the order of 1 ppm (parts per million of dry air). This increase reflects the retention in the air of about half of the CO_2 produced by combustion of fossil fuels (Keeling, 1973). The rate of increase has not been strictly proportional to the rate of combustion of fossil fuels in either hemisphere.

Observing site

Mauna Loa Observatory is located 3 400 meters above sea level on an extensive lava flow on the north slope of the largest active volcano in the Hawaiian Islands. The observing site and its meteorological milieu have been described by Price & Pales (1959), Pales &

Keeling (1965), Mendonca & Iwaoka (1969), and Mendonca (1969). Some detectable CO_2 emanates from volcanic sources upslope. Extensive land plants, 30 km to the east and beyond, also produce observable changes in CO_2 concentration at the observatory.

Until July 21, 1967, electrical power was obtained from a local, diesel engine-driven generator. Thereafter, a transmission line has supplied municipal power. This change has nearly eliminated local production of CO_2 by the station itself, but, with the completion of a paved public road to the station in July, 1969, daytime automobile pollution has become a problem.

Sampling program

Continuous measurements of atmospheric CO_2 relative to dry air were made with an Applied Physics Corporation dual detector infrared analyzer, as described by Smith (1953). This analyzer registered the concentration (mixing ratio) of CO_2 in a stream of air flowing at approximately 0.5 1 min^{-1}. Every 20 min the flow was replaced for 10 min by a stream of calibrating gas called a "working reference gas", and every few days this and additional reference gases were mutually compared to determine the instrument sensitivity and to check for possible contamination in the air handling system. These reference gases, stored in size 3A stainless steel cylinders, were themselves calibrated against specific standard gases for which the CO_2 concentration had been determined manometrically, as discussed below. The experimental procedure in all essential details has remained as described by Pales & Keeling (1965).

Reference gas calibration

The concentration of atmospheric CO_2 deduced from the infrared measurements at Mauna Loa depends directly on the concentration of CO_2 attributed to the reference gases used to calibrate the analyzer. For this reason, considerable effort has been taken to suppress both random and systematic errors arising from use of these gases.

Each working reference gas used at the ob-

servatory in the determination of CO_2 in air was routinely compared twenty or thirty times during its period of use with semipermanent standard reference gases kept at the observatory and thirty times with similar semi-permanent standards kept at the Scripps central laboratory. The comparisons at Scripps were made partially before and partially after use at the observatory to assure detection of any significant long term drift in working gas concentration. Also, the semipermanent standards held at the observatory were compared with the semipermanent standard gases at Scripps at least fifty times before and fifty times after use in the field. Certain semipermanent standards at Scripps in turn were closely compared (at least 150 times) with a special set of manometrically calibrated standard gases also kept at the Scripps laboratory.

The infrared analyzer data involved in these calibrations were obtained as pen traces on a strip chart recorder. The differences between successive traces in recorder chart ordinates were read where the trace registered a change in concentration between the two gas mixtures being compared. All comparisons were brought to a common scale proportional to instrument response by arbitrarily assigning a magnitude to two reference gases at the beginning of the investigation in 1957. The resulting scale has been informally called the "Scripps index" scale. In 1959, a provisional manometric investigation was carried out. From this study, a linear relation between index and the mole fraction of CO_2 in nitrogen was determined in the narrow range of atmospheric CO_2 concentration variation where linearity in instrument response could be reasonably assumed, i.e. from approximately 310 to 330 ppm (parts per million of dry air). This approximate mole fraction scale will be designated the "adjusted CO_2 index" scale because, as in the case of the previous scale, it is linearly related to instrument response.

All published data which depend on the Scripps reference gases as a basis for comparison, have, as far as we know, been expressed in the units of this adjusted index scale.

Ekdahl et al. (1971) estimated that the standard deviation of an individual comparison of atmospheric CO_2 concentration in air with that of a reference gas of nearly the same CO_2 concentration is approximately 0.3 ppm

Table 1. *Apparent downward shift in CO_2 mole fraction (in ppm) as measured by applied Physics Model 70 Infrared Analyzer when nitrogen is substituted for carrier gas as specified*

Method	Adjusted CO_2 index	Carrier gas		
		79.1 % N_2 20.9 % O_2	99.07 % N_2 0.93 % A	CO_2-free air
Analysis	310	3.50	.20[a]	3.70
Synthesis		3.44	.24	3.68[b]
Analysis	320	3.68	.21[a]	3.89
Synthesis		3.63	.25	3.88[b]
Analysis	330	3.87	.23[a]	4.10
Synthesis		3.82	.26	4.08[b]

[a] Determined by difference.
[b] Determined by sum.

for the analyzer at Mauna Loa Observatory. The standard deviation for an individual comparison between two reference gases in the range 200 to 450 ppm has been found to be approximately 0.5 ppm for the analyzer at the Scripps laboratory. It follows that the daily means obtained routinely for Mauna Loa are imprecise with respect to the Scripps manometric standard gases by less than 0.1 ppm (1 standard deviation in the mean).

The inaccuracy of the manometric standard gases is more difficult to establish than the imprecision in the infrared comparisons because no procedure can prove the absence of undetected systematic errors. We have employed two related manometric methods of calibration to establish the mole fraction of CO_2 in reference gases: (1) *analysis* in which the CO_2 from aliquots taken from a cylinder of reference gas is separated from the carrier gas using a liquid nitrogen trap freeze-out technique as described by Keeling (1958), and (2) *synthesis* in which CO_2 is mixed with carrier gas in accurately determined proportions and the mixtures compared with reference gases by infrared analysis. The carrier gases used in these studies have included pure nitrogen, oxygen, and argon, and various proportions of oxygen in nitrogen. The analysis method has also been applied to compressed air with a correction for N_2O which appears in the liquid nitrogen sublimate along with CO_2 (Craig & Keeling, 1963).

Provisional manometric analyses were carried out in 1959, 1961, 1970, and 1972, and an exhaustive set of analyses was made during 1974. From these results we have established that the system of semi-permanent standard reference gases at the Scripps laboratory has drifted downward almost linearly at a rate of 0.060 ppm per year with an imprecision (1 standard deviation) in this estimate of 0.007 ppm per year. We further have found that the substitution of pure nitrogen for CO_2-free dry air as the carrier gas results in a decrease in infrared analyzer response. For a gas with a concentration of 320 ppm, the decrease at sea level is equivalent to a reduction in CO_2 mole fraction for air of 3.89 ppm with an imprecision of 0.04 ppm.

The apparent reduction in CO_2 concentration was found, within experimental precision, to be linear with oxygen mole fraction and could be expressed as a constant factor applied to the infrared response. The effect was determined both by analysis of compressed air and reference gases containing pure nitrogen, and approximately 20, 40, and 60 % oxygen in nitrogen, and by synthesis of mixtures containing pure nitrogen, oxygen, or argon. The results, after smoothing the data, are summarized in Table 1.

The carrier gas effect just discussed was found to increase with decreasing total gas pressure in the measuring cell of the infrared analyzer. Measurements in the Scripps laboratory during 1974, using compressed air and pure nitrogen as a carrier gas, indicated that an upward adjustment of the Mauna Loa data of 0.44 ppm should also be applied to the infrared data in addition to the upward adjustment appropriate to sea level. In these experiments,

Table 2. *Comparison between adjusted CO_2 index and CO_2 mole fraction (both in ppm) based on the 1974 manometric scale for CO_2 in air*

Adjusted CO_2 index	1974 manometric scale	
	Measurement on July 1, 1960	Measurement on July 1, 1970
At sea level		
310	312.50	313.11
320	322.67	323.29
330	333.05	333.69
At elevation of Mauna Loa Observatory		
310	312.93	313.54
320	323.12	323.74
330	333.52	334.15

the cell pressure was controlled with a cartesian diver manostat. This estimated pressure correction, referred to an adjusted index of 320 ppm, is imprecise to only 0.02 ppm if we assume that the effect is proportional to oxygen mole fraction in the carrier gas and we include measurements made with 40% and 60% oxygen. A second set of direct measurements were carried out at Mauna Loa Observatory using most of the same gas mixtures. These measurements indicated an adjustment of 0.37 ppm, with an imprecision of 0.07 ppm.

In summary, we have computed the mole fraction of CO_2 in dry air from the infrared data by the following series of equations based principally on the manometric studies of 1974:

1. Correction for drift:

$$J_d = J - 1.050 + 0.060t \tag{1}$$

where t denotes the time of analysis in years since January 1, 1957, and J denotes the adjusted CO_2 index in ppm.

2. Correction for 20.9% oxygen and 0.93% argon in the carrier gas:

$$J_c = J_d \times 1.01201\,[1.003157 - 2.237 \times 10^{-4}P$$

$$-2.522 \times 10^{-9}P^2] \tag{2}$$

where P is the total gas pressure in mmHg within the infrared measuring chamber, and the terms within brackets sum to unity for $P = 760$. For Mauna Loa Observatory we substituted for P a mean station pressure of 569.9

mmHg. For gases containing pure nitrogen as the carrier gas, $J_c = J_d$.

3. Conversion to 1974 manometric mole fraction scale, X, in ppm of CO_2 in dry air:

$$X = \sum_{n=0}^{3} C_n J_c^n \tag{3}$$

where $C_0 = 76.582$, $C_1 = 0.584910$, $C_2 = 3.1151 \times 10^{-4}$, and $C_3 = 7.3225 \times 10^{-7}$.

A condensed form of these expressions is given by Keeling et al. (1976).

The mole fraction scale, X, is approximately 3 ppm higher than the adjusted index, J, as can be seen from Table 2.

To provide continuity with previously reported data we have expressed tabular results, Figs. 1 through 4*h*, and Figs. 6 through 8 in terms of adjusted CO_2 index values.

Local influence on carbon dioxide concentration

The CO_2 concentration at Mauna Loa shows a persistent diurnal variation. Normally, during the night, especially after midnight, air of low humidity blows downslope. The concentration of CO_2 is typically steady, but on some nights is disturbed for as much as several hours by irregular bursts of higher concentration. During the morning hours an upslope wind developes, and on most days the humidity rises as moist air originally below the trade wind temperature inversion reaches the observatory. Meanwhile, the CO_2 concentration typically rises for one to two hours to a "midday peak" and then falls until a minimum in CO_2 and a maximum in humidity are reached near 1800 hr. The decline from noon maximum to afternoon minimum averages about 1 ppm; the largest decline, occurring always in summer, is about 5 ppm. Soon after 1800 hr the wind reverses direction. The CO_2 concentration rises and the humidity falls until, after several hours, both attain steady values typical of night time downslope airflow.

The nocturnal bursts we attribute to the release of volcanic CO_2 from a line of vents situated about 4 km upslope from the observatory. These bursts appear as highly variable recorder traces suggestive of imperfect atmospheric mixing of CO_2 from a nearby source.

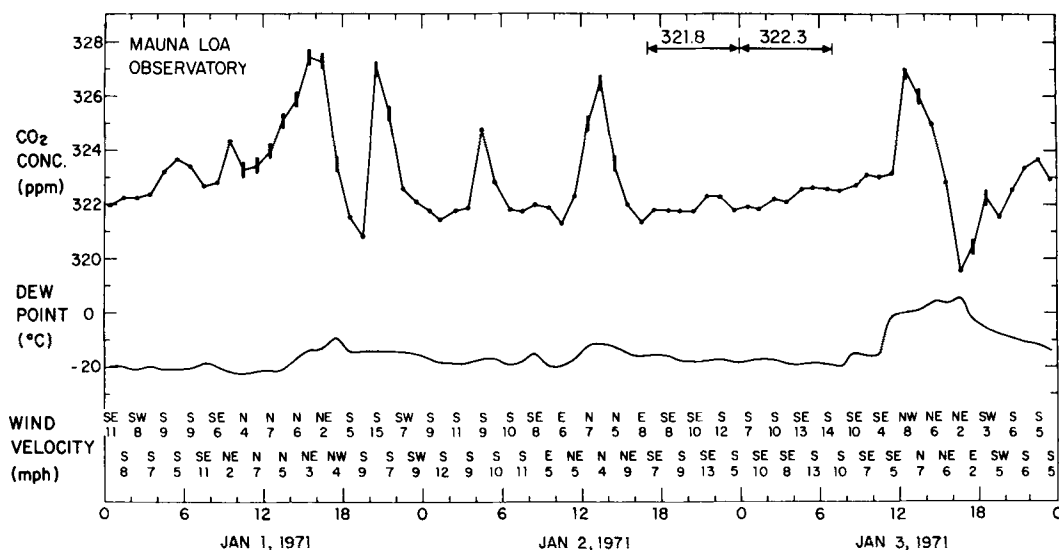*Fig. 1.* Hourly average atmospheric CO_2 concentration at Mauna Loa Observatory versus time during the first three days of 1971. Concentrations are plotted on the adjusted CO_2 index scale. Vertical bars indicate periods during which the record trace was variable, indicating local contamination. Horizontal arrows indicate periods of steady concentration. The average concentration for each steady period is indicated above the arrow.

They are routinely eliminated from further consideration in processing the data.

The origin of the midday peak is less obvious. The peak may be due in part to volcanic CO_2 from some distant source downslope, but its persistence suggests a more uniform source such as vegetation. Because the dip in concentration which usually follows the peak is almost surely a result of the passage of air over the forested lower slopes during periods of photosynthetic uptake, we propose that the peak is at least in part due to the arrival of air from downslope which contains CO_2 released by vegetation and soil during the previous night. Some contribution to the peak is, however, clearly from man-made sources, especially automobilies on the mountain itself. The shift from nighttime downslope to daytime upslope wind usually involves a period of light variable wind, when locally produced CO_2 from combustion has maximum probability of being admitted into the sampling system.

As an example of a series of midday peaks almost surely related to automobile combustion, we show in Fig. 1 the diurnal course of CO_2 at the observatory during the first three days of January 1971, when numerous visitors attended an on-site "open-house". The afternoon dips (typically small in January) are clearly less prominent than the high midday values. The persistence of a peak is evident in the diurnal course of all data (variable traces included) for an entire month, centered on this event (Fig. 2).

From an examination of all midday peaks from 1964 to 1970, we find that 38 % of those having maxima 1.5 ppm or greater than the estimated daily trend were attended by variable recorder traces, compared with 13 % of those with amplitudes less than 1.5 ppm, as
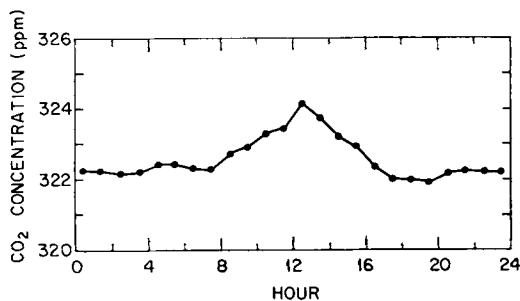
Fig. 2. The average diurnal course of atmospheric CO_2 at Mauna Loa, December 22, 1970 through January 17, 1971. Period averages for each hour on the adjusted CO_2 index scale are plotted versus time.
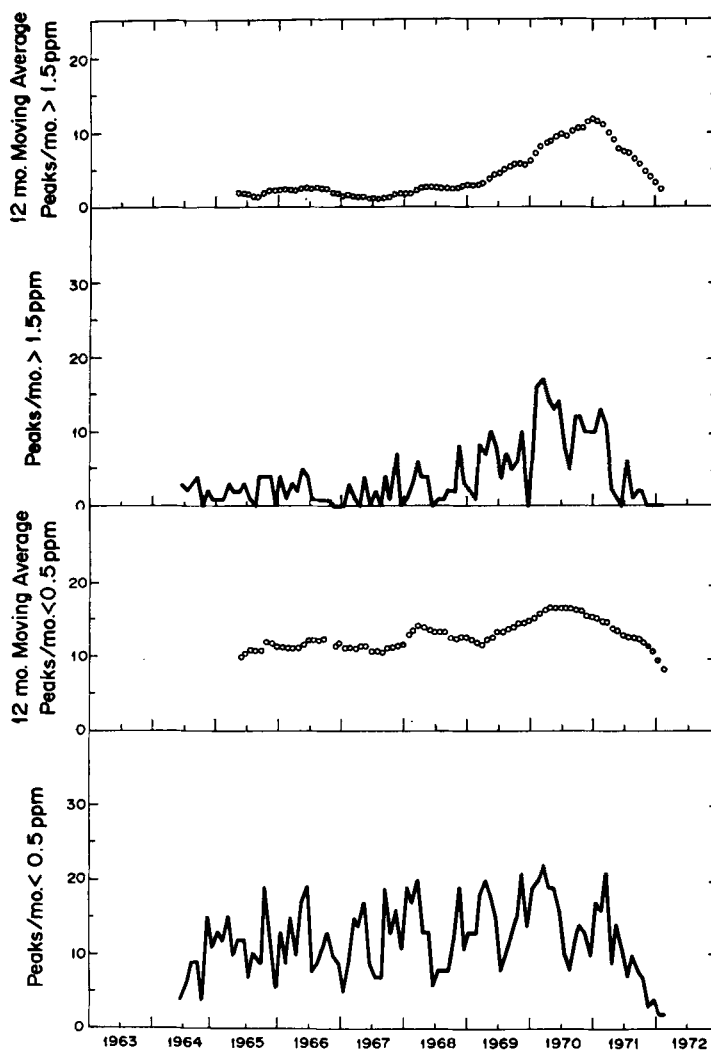
Fig. 3. Frequency of midday peaks plotted on the adjusted CO_2 index scale versus time. Two categories are shown: peaks with maximum amplitude greater than 1.5 ppm (top); and less than 0.5 ppm (bottom). In addition to monthly means, 12 month moving averages are shown. These are plotted versus the twelfth month of the appropriate 12-month interval so that abrupt changes in the original record first appear in the moving average at their original time of occurrence.

though the larger peaks, more often than the smaller, were associated with very local sources of CO_2, but that the principal source is distant. This hypothesis is also supported by comparing the long term trends in frequency of peaks having maxima greater than 1.5 ppm and less than 0.5 ppm, respectively (Fig. 3). The latter trend, except for a seasonal variation more obvious after 1966, shows only a moderate change from year to year, whereas the former shows a

striking rise near the time of completion of the paved road. Still more dramatic is the decrease in frequency of large peaks after March 1971 when a locked chain gate was erected across the road to the observatory 0.5 km from the CO_2 intakes. The smaller peaks also decreased in frequency during 1971, but more gradually.

The erection of the gate happens almost to coincide with the cessation of a prolonged period of volcanic activity which commenced in No-
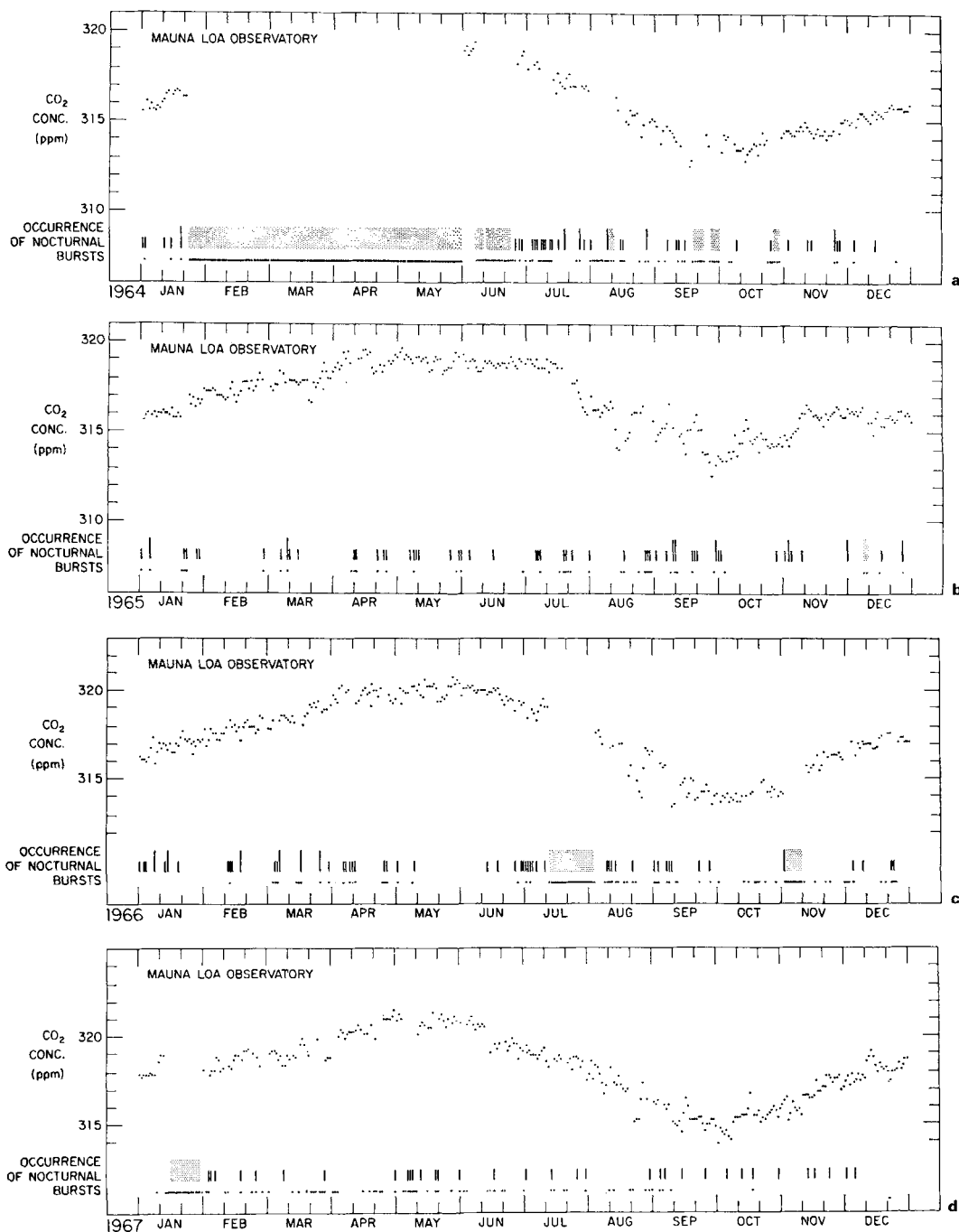
Fig. 4a–h. The daily average concentration of atmospheric CO_2 versus time at Mauna Loa Observatory for periods of steady concentration. Values, expressed on the adjusted CO_2 index scale, are shown by unconnected points. If no value was determined on a given day, a point appears below the main plot as a reading aid. Vertical lines denote days in which nocturnal bursts occurred within a 24-hour period commencing 12 hours before the calendar day. The approximate intensity of the maximum burst is indicated by the length of the line: shorter lines denote 0 to 5 ppm; longer lines, 5 to 10 ppm. Shaded areas represent periods when the analyzer was shut down for 48 hours or more.
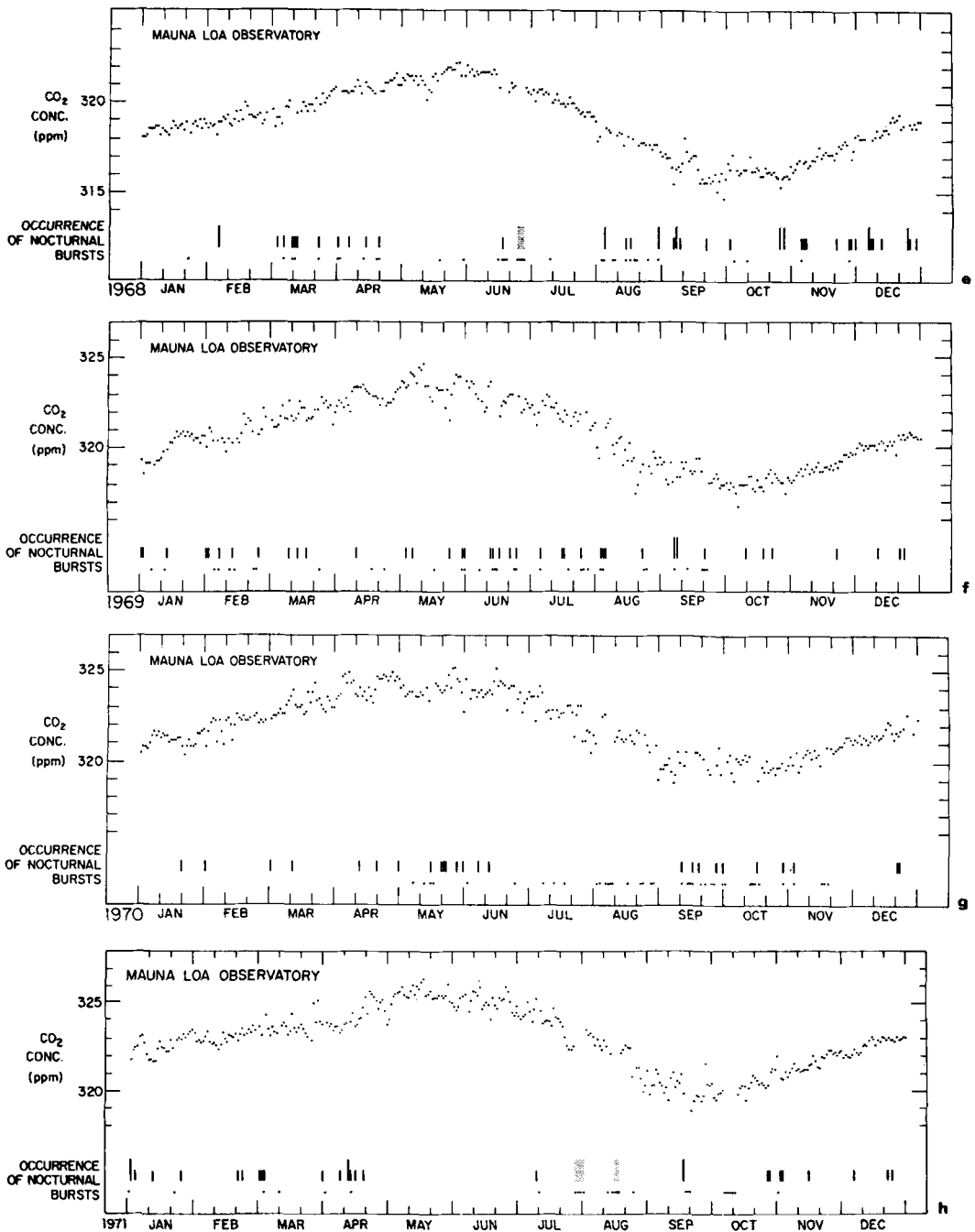
vember 1967 on the mountain of Kilauea. First, lava erupted for eight months in the main caldera, and then, after a short break, for twenty-three months more in the East Rift Zone. The smaller CO_2 peaks at Mauna Loa are more frequent during this volcanic activity, but they are sufficiently frequent earlier to imply that enrichment by vegetation is likely to have caused most of them.
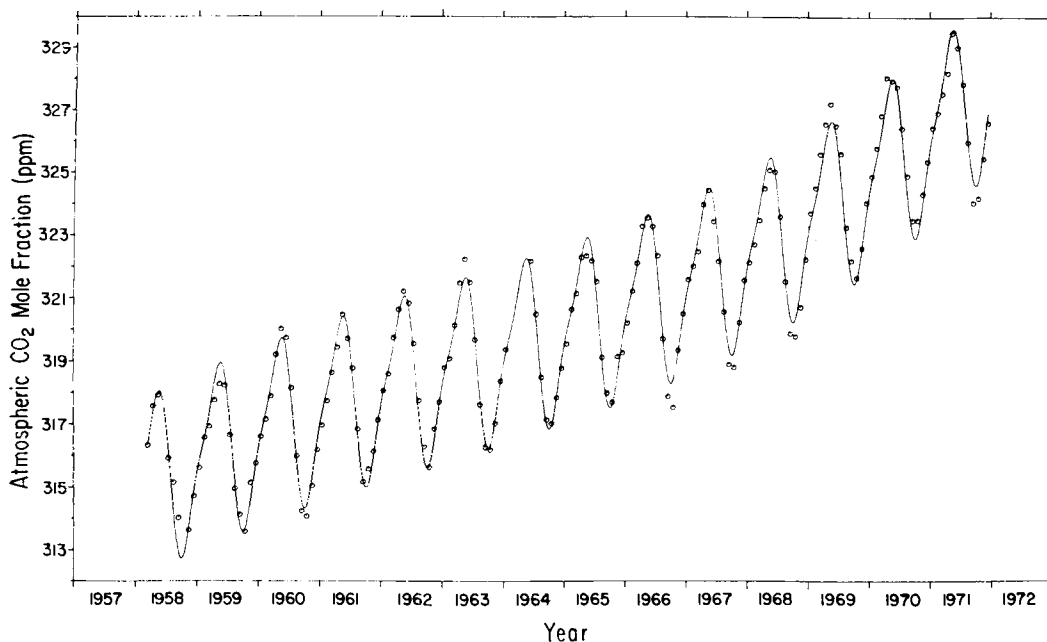
Fig. 5. Long term variation in the concentration of atmospheric CO_2 at Mauna Loa Observatory. The circles indicate the observed monthly average concentration. The oscillatory curve is a least squares fit to these averages of an empirical equation containing 6 and 12 month cyclic terms and a cubic trend function, chosen to contain powers of time up to the third. Concentrations are plotted as the CO_2 mole fraction of dry air in ppm.

Description of data

Continuous data. Daily averages of atmospheric CO_2 concentrations, based solely on

steady portions of the hourly record, are plotted in Figs. 4a to 4h for 1964 to 1971. These values, which approximately reflect the CO_2 in undisturbed Pacific Ocean air, were derived by

Table 3. *Monthly average concentration of atmospheric carbon dioxide (ppm) at Mauna Loa Observatory based on steady sata*

Month	1964		1965		1966		1967		1968	
	No. of days	Adjusted CO_2 index	No. of days	Adjusted CO_2 index	No. of days	Adjusted CO_2 index	No. of days	Adjusted CO_2 index	No. of days	Adjusted CO_2 index
January	18	316.13	26	316.25	31	316.84	11	318.13	30	318.60
February		316.67[a]	27	317.32	27	317.82	20	318.54	28	319.16
March		317.13[a]	29	317.80	23	318.69	20	318.99	26	319.91
April		318.34[a]	25	318.92	23	319.83	20	320.45	25	320.89
May		318.93[a]	28	318.96	29	320.08	18	320.89	28	321.46
June	9	318.86	29	318.80	29	319.81	23	319.91	22	321.40
July	20	317.20	23	318.15	9	318.90	25	318.67	30	320.00
August	14	315.23	24	315.80	18	316.31	24	317.09	21	317.98
September	14	313.90	25	314.68	21	314.52	27	315.46	30	316.57
October	23	313.78	30	314.39	23	314.17	30	315.36	28	316.27
November	28	314.58	30	315.81	16	315.95	30	316.75	28	317.17
December	29	315.50	27	315.92	23	317.07	31	318.06	25	318.65

[a] Estimated from oscillating power function (eq. (3)).

the same procedure used earlier by Pales & Keeling (1965). A minor association with regional weather patterns is suggested by short period oscillations of the daily averages, but the principal feature is a seasonal oscillation which repeats with remarkable regularity from year to year. This latter oscillation shows up clearly in monthly averages of the daily values as plotted in Fig. 5, and listed in Table 3.

In Table 4, column 2, are listed annual values of the steady data expressed on the adjusted CO_2 index scale. In column 3 of the same table are shown averages of the full data excepting only those values (about 4% of the total) which were evidently contaminated locally as shown by variable recorder traces. The full data (which we have also examined on a daily and monthly basis) hardly differ from the steady data because low values during afternoon dips tend to cancel with high values during midday peaks. Additional columns show the data reexpressed as CO_2 mole fractions.

Supplementary data. The individual reference gas calibrations and daily average atmospheric air measurements are too extensive to reproduce here. Those for 1964 through 1970 have been summarized in a detailed report (Ekdahl et al., 1971) and deposited with the National Auxiliary Publications Service of the American Society for Information Science.[1] All relevant calculations and supporting data are reported. A similar report of the measurements for 1971 will be prepared in conjunction with a subsequent article.

Table 4. *Seasonally adjusted concentration of atmospheric CO_2 (in ppm) at Mauna Loa Observatory*

	Adjusted CO_2 index		CO_2 mole fraction	
Year (1)	Annual average[a] of steady data (2)	Annual average of full data (3)	Annual average of steady data (4)	From trend equation[b] (5)
1958	Incomplete			
1959	313.23	—	316.14	316.30
1960	314.04	—	317.03	317.06
1961	314.66	—	317.71	317.74
1962	315.43	—	318.57	318.37
1963	315.83	—	319.03	318.98
1964	316.35[c]	—	319.63[c]	319.60
1965	316.90	316.92	320.25	320.27
1966	317.50	317.60	320.92	321.02
1967	318.19	318.14	321.70	321.88
1968	318.99	318.92	322.58	322.88
1969	320.77	320.85	324.47	324.06
1970	321.98	322.20	325.79	325.45
1971	322.93	322.94	326.83	327.08

[a] Annual averages for 1959 to 1963 are derived from Table 1 of Pales & Keeling (1965), for 1964 to 1971 from Table 3 of this paper.
[b] Smoothed values of steady data, for 1 July of each year, as derived from the last four terms of eq. (6).
[c] Partially estimated according to values listed in Table 3.

1969		1970		1971	
No. of days	Adjusted CO_2 index	No. of days	Adjusted CO_2 index	No. of days	Adjusted CO_2 index
29	320.08	31	321.16	29	322.60
22	320.85	27	322.03	28	323.05
30	321.90	31	323.03	29	323.65
28	322.82	30	324.20	28	324.29
28	323.45	27	324.09	30	325.51
24	322.76	28	323.90	29	325.06
26	321.89	28	322.61	25	323.93
27	319.61	20	321.14	23	322.12
25	318.56	21	319.75	27	320.24
31	318.03	25	319.75	25	320.37
30	318.94	26	320.56	30	321.60
31	320.35	27	321.57	31	322.70

Secular increase in CO_2

Two methods have been employed to separate the annual increase of about 0.8 ppm from the 6 ppm seasonal variation found in the Mauna Loa record. In the first method, monthly average adjusted CO_2 index values were fit to a function in time containing both a power series and Fourier harmonic terms. The harmonic frequencies were established by spectral analysis of the daily averages. The second meth-

[1] This information has been deposited with ASIS as NAPS document no. 02890. Order from ASIS-NAPS, c/o Microfiche Publications, 440 Park Avenue South, New York, New York 10016. Remit in advance for each NAPS accession number. Make check payable to Microfiche Publications. Photocopies are $87.25. Microfiches are $3.00. Outside the United States and Canada, postage is $4.00 for a photocopy or $1.00 for a fiche.

od filtered out the dominant harmonic terms with a moving average.

In the first approach the dominant frequencies in the daily average record of steady data from June 1964 through June 1971 were estimated from a discrete Fourier transform using the transform algorithm of Cooley & Tukey (1965). Transform terms were weighted to correspond to the cosine bell data window of Hann (Blackman & Tukey, 1959, pp. 14–15, 98; Hinnich & Clay, 1968), and afterwards converted to a power spectrum. Since the algorithm requires 2^N equally spaced data, days with no data were assigned values by linear interpolation of contiguous data, and spectra were obtained from both the first and last 2048 of the 2587 data points. The average of these two spectra is shown in Fig. 6. Since days without data are unclustered (see Figs. 4a through 4h) and constitute only 17% of the record, errors from interpolation have little effect on the analysis. The only significant harmonic contributions to the long term data record are the fundamental annual cycle and its first (6 months) harmonic.

To verify that very little information is contained in higher harmonics, monthly averages of the adjusted CO_2 index values were fit by the method of least squares to several trial functions consisting of power series of varying degree combined with a varying number of harmonic terms. For a given power series polynomial, the significance of the fundamental cyclic variation in combination with higher cyclic variations of 1/2 year, 1/3 year, 1/4 year, etc. was tested with the function:
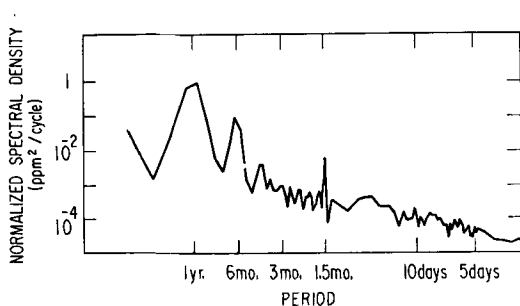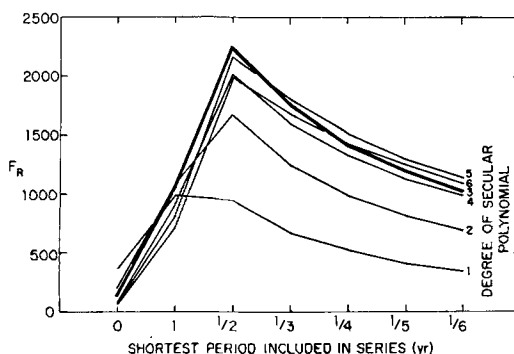

Fig. 7. The statistic F_R plotted versus varying numbers of harmonic terms, added to secular trend polynomials of varying degree as shown.

$$F_R = (R^2/n)/[(1 - R^2)/(N - n - 1)] \qquad (4)$$

where R, the multiple correlation coefficient, tends toward unity as the "goodness of fit" increases; n is the number of parameters determined by the least squares fit; and N is the number of data. The statistic F_R, which follows the F distribution (Bevington, 1969, p. 199), was found to be maximized when only the fundamental and its first harmonic were included in the trial function (Fig. 7). Also, F_R was maximized when the secular trend included powers of time up through the third.

Accordingly, the monthly average adjusted CO_2 index values were corrected to the CO_2 mole fraction scale and then fit with the function:

$$X(t) = Q_1 \sin 2\pi t + Q_2 \cos 2\pi t + Q_3 \sin 4\pi t$$
$$+ Q_4 \cos 4\pi t + Q_5 + Q_6 t + C_7 t^2 + Q_8 t^3 \qquad (5)$$

where X denotes the CO_2 mole fraction of dry air in ppm, t is the elapsed time, in years, relative to the first of January, 1958, and

$$\left. \begin{array}{ll} Q_1 = 2.339 \text{ ppm} & Q_5 = 313.802 \text{ ppm} \\ Q_2 = -1.065 \text{ ppm} & Q_6 = 1.213 \text{ ppm/yr} \\ Q_3 = -0.343 & Q_7 = -0.100 \text{ ppm/yr}^2 \\ Q_4 = 0.583 \text{ ppm} & Q_8 = 0.00545 \text{ ppm/yr}^3 \end{array} \right\} \qquad (6)$$

Fig. 6. Power spectrum of daily average concentrations of atmospheric CO_2 at Mauna Loa for the interval June, 1964 through June, 1971. The spectrum has been normalized to the maximum contribution from the one year cycle.

The standard deviation of the monthly averages with respect to this function is 0.27 ppm. The secular trend, which we seek, is given by the last four terms of eq. (6), as shown by the
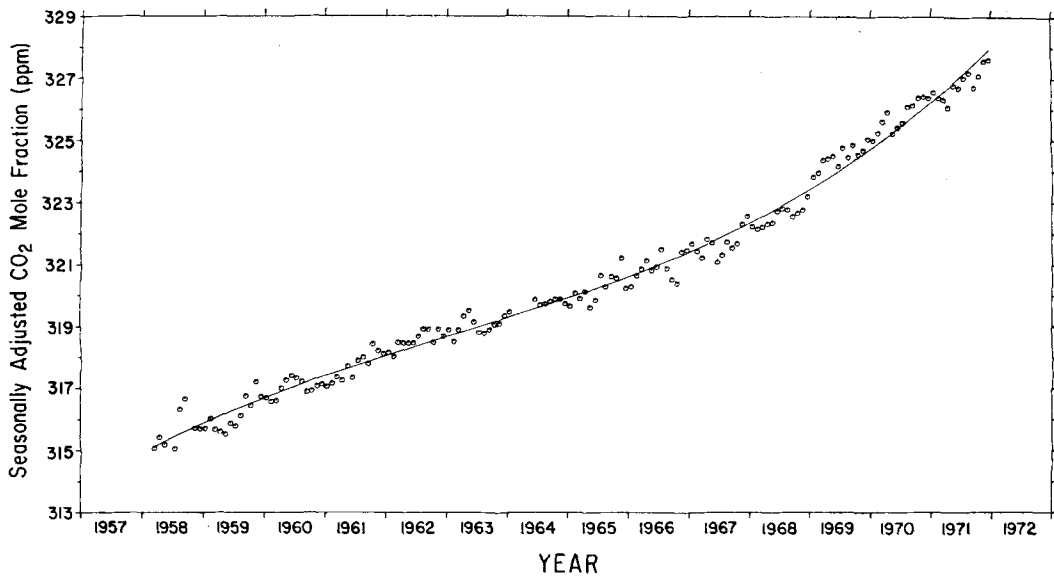
Fig. 8. Secular trend of atmospheric CO_2 mole fraction at Mauna Loa Observatory, based on a cubic trend function. Circles denote seasonally adjusted monthly averages. Concentrations are expressed as the CO_2 mole fraction of dry air in ppm.

curve in Fig. 8. Values of the trend for 1 July of each year are listed on the mole fraction scale in Table 4, column 5. The relative increase in concentration from 1959 to 1971 is 3.4 %.

This increase agrees closely with 3.1 % found for the South Pole for the same time interval (Keeling et al., 1976).

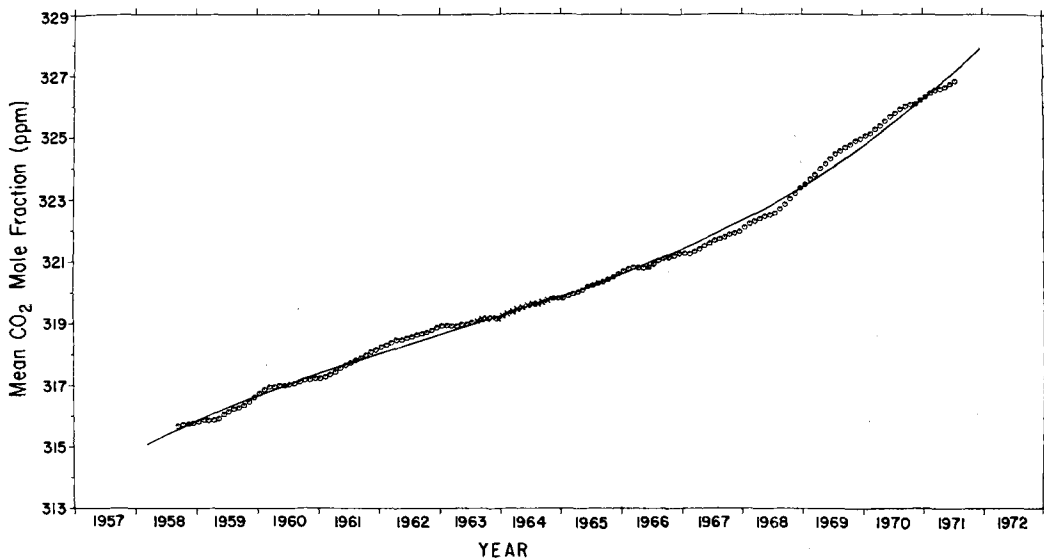To provide an independent estimate of the

Fig. 9. Twelve month moving average of atmospheric CO_2 mole fraction at Mauna Loa Observatory. Circles: means plotted versus the seventh month of the appropriate 12 month interval. Crosses: means which include concentration estimates calculated from the oscillating power function for the period February, 1964 through May, 1964. Full curve: secular trend based on cubic trend function.

secular trend, the monthly averages were filtered with a simple twelve months moving average (Fig. 9) as was done by Pales & Keeling (1965). We have examined the extent to which this moving average distorts the long term trend by computing its continuous analogue for the cubic trend function. Using the parameters Q_5 to Q_8 of eq. (6), the maximum error, incurred at the end of the record, is entirely negligible (less than 0.02 ppm).

As already noted by Pales & Keeling (1965) for the period before 1964, the moving average suggests a weak two year cycle. The data record is of insufficient length to expect such a cycle to be evident in a spectral analysis (Fig. 6), but the possibility was tested for using the F_R statistic described above. We found that no subharmonic of the annual cycle (2 to 6 years were tested) possesses a large enough signal to noise level to render it detectable.

The moving average filter removes completely the one year cycle and its harmonics from the estimate of the secular trend. Other variability within any year of record is also attenuated, but random variations which persist over several months, such as unusually low summer or high winter means, are only moderately attenuated. In contrast, the cubic trend function (last four terms of eq. (6)) greatly attenuates not only the two dominant frequencies, but also all random variations with periods less than approximately 10 years; it thus produces a smoother estimate of the secular trend than does the moving average. Furthermore, the trend for all years is changed each time the length of record is altered, for example, by the accession of new data. At the other extreme, the succession of seasonally adjusted monthly averages (circles in Fig. 8) indicate the secular trend without suppressing any frequencies except the two dominant ones.

The data could, of course, be reprocessed using still other filters, but salient features are almost surely revealed using the three filters just discussed. The three versions of the trend so obtained have one striking feature in common: An apparent decline in the rate of increase of CO_2 during the early 1960's, followed by an increasing rate after 1967.

Confronted with the break in record in 1964, we are reluctant to rule out the possibility that the decline is at least partly an instrumental artifact. Unfortunately, no second record of

atmospheric CO_2 concentrations in the northern hemisphere exists which can help us decide whether this decline is real or not. A possible slower rate of increase is not inconsistent with data of Bolin & Bischof (1970) based on aircraft samples collected over a broad region of the polar northern hemisphere, but as these authors point out, the irregularities of their sampling schedule (see their Table 2, p. 433) "hardly permit a search for possible secular variations in the annual increase".

If we disregard the temporary decline in rate during the early 1960's, the change in rate roughly approximates that of fossil fuel combustion which was 60 % higher in 1971 than in 1959.

Conclusions

In extending the previously published five year record of atmospheric CO_2 concentrations at Mauna Loa Observatory by eight additional years, new features of CO_2 in air near the Hawaiian Islands are revealed, and previously noted features more precisely defined. Statistical analysis of daily and monthly averages of the original continuous data establish a seasonal oscillation described by annual and semiannual harmonic oscillations about a long term trend. This latter trend, obtained by subtracting the average seasonal oscillation from each of the original 14 years of record, is a rising function of time and is described, within the precision of the data, by either a cubic power series, a 12 month moving average, or a set of seasonally adjusted monthly averages.

The air at Mauna Loa Observatory may be slightly influenced by local processes which cannot be expunged from the record, but the observed long term trend of rising CO_2 appears clearly to be in response to increasing amounts of industrial CO_2 in the air on a global scale. We are thus convinced of the observatory's suitability to monitor global changes in atmospheric CO_2 concentration.

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ВАРИАЦИИ ДВУОКИСИ УГЛЕРОДА В АТМОСФЕРЕ НА ОБСЕРВАТОРИИ МАУНА ЛОА, ГАВАЙИ

Сообщаются данные о концентрации в атмосфере двуокиси углерода на Обсерватории Мауна Лоа, Гавайи, для восьми лет (1964–1971 гг.) долговременной программы, направленной на изучение влияния сжигания угля, нефти и естественного газа на распределение CO_2 в атмосфере. Новые данные при учете более старых указывают, что среднегодовая концентрация CO_2 росла на 3,4 % в год между 1959 и 1971 гг. Скорость роста, однако, не была постоянной. В середине 1960-х гг. она уменьшилась, а недавно ускорилась. Аналогичные изменения в скорости роста наблюдались и на Южном полюсе и, очевидно, являются глобальным явлением.