Atmospheric carbon dioxide variations at the South Pole

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ABSTRACT

Duplicate measurements of 749 discrete samples of air collected at the South Pole indicate that the seasonally adjusted concentration of atmospheric carbon dioxide in the polar southern hemisphere rose 3.7 % between 1957 and 1971. The rise, mostly attributable to the burning of fossil fuels, has not been steady. In the mid-1960's, possibly as a result of wide-spread cooling of surface ocean water, it slackened for several years; recently it has accelerated. Similar changes in rate have also been observed at Mauna Loa Observatory, Hawaii, in the northern hemisphere and are evidently a global phenomenon.

Introduction

The discovery that coal, petroleum, and natural gas readily supply more energy to man than wood and water power has initiated an era of unprecedented exploitation of these fossil fuels. The outcome of this exploitation is not yet in sight. Wood and water are perpetually available, and their prudent use produces no far-ranging effects on the environment. Fossil fuels, however, are not renewable. They were formed from inorganic carbon by the action of photosynthesis over geologic eons at a rate infinitesimally slow compared to their present rate of reconversion to inorganic carbon. Because rapid fossil fuel consumption has begun only recently, man's past experience offers no guide for judging the consequences.

Atomic or nuclear fuels or solar power may some day provide abundant alternative sources of energy, but their rates of utilization are not likely to be soon sufficient to promote a large reduction in fossil fuel consumption. As long as industrial growth continues on a world-wide basis, and the choice of fuels rests solely on deciding which produces energy at the lowest production cost, it is probable that fossil fuel consumption will continue to increase at several per cent per annum until high grade sources are substantially depleted.

The choice of fuels should, ideally, take into acount all costs attending their use. Most costs, including those related to undesirable side effects, are regarded as local or regional problems to be dealt with according to the judgment of citizens and magistrates directly affected. The ultimate by-product of fossil fuels, however, is a gas whose accumulation may disturb the earth's environment globally, although it is scarcely noticeable near the source. This gas, carbon dioxide, is now being introduced into the earth's atmosphere so rapidly that its concentration in non-urban air is everywhere rising.

Whether this rise is harmful on a global scale, especially whether it will produce climatic change, is an unanswered question (SMIC, 1971; Manabe & Wetherald, 1975). The experimental program reported here and in the next paper, if continued (or better still, if augmented), will furnish an essential part of the direct observational data needed to establish whether any harm to the environment can be attributed to the production of carbon dioxide from fossil fuel.

History of the sampling program

Collections of air in glass flasks were first made during the International Geophysical Year at three Antarctic Stations: Little America, Byrd Station, and at the South Pole (Fritz et al., 1959). In 1957 and 1958 samples were taken at each station only four times per year because the supply of flasks was limited and retrograde shipping difficult. After 1958, sampling continued only at the South Pole station, but stepped up to twice monthly pairs.

From 1960 through 1963 CO_2 was also continuously monitored at the South Pole, and flask sampling became principally a check on the performance of the on site gas analyzer. From 1960 through 1962, the check was not very satisfactory, however, because the flasks, after exposure to air, were hung on a wall and repacked only when a dozen had accumulated. Photo-oxidation of the hydrocarbon stopcock grease occurred in the hanging flasks and rendered useless all but the last pair of each dozen. In 1963, with a return to the storage procedure used before 1960, agreement between flasks and continuous analyzer became close (Brown & Keeling, 1965, p. 6083).

Both flask collecting and continuous analysis were discontinued in 1964 to reduce the financial cost of the overall CO_2 monitoring program. In retrospect this was a mistake because during much of that year the only remaining global monitor at Mauna Loa Observatory, also owing to financial restrictions, was either shut down or performed poorly. We possess no satisfactory record of atmospheric CO_2 for 1964.

Twice monthly flask collections were resumed at the South Pole early in 1965 and have continued since without interruption.

Except for a brief report covering 1957 to 1959 (Keeling, 1960), and a full set of data for 1963 (Brown & Keeling, 1965), the South Pole flask data are reported here for the first time. Taken altogether, these constitute the longest modern record of CO_2 air concentrations at any single station. Because of the complete absence of local upwind contamination, the data are of higher quality than any other series so far obtained using flasks. As the only long record of CO_2 variations in the southern hemisphere, they contribute significantly to an understanding of the global distribution of atmospheric CO_2.

Experimental procedure

Five liter spherical glass flasks, previously evacuated to a pressure below one micrometer of mercury, were exposed by opening a greased stopcock so that air expanded into the flask. In the earlier years of the program, two flasks were routinely exposed on the same day; after 1964 this number was increased to three.

Although this procedure is simple to execute, special precautions must be consistently observed to avoid contaminating a high proportion of the samples. The sample taker, to minimize contamination from his own breath, was instructed to sample only when the wind was at least 5 knots (2.6 m sec^{-1}). After first breathing normally near the site for some moments, he exhales, then inhales slightly, and finally without exhaling again, walks 10 steps into the wind, where he takes the sample. He should have a clear idea of the wind direction and be certain that no local source of CO_2, even another human being, is upwind.

According to our current instructions, in force since 1962, the flask, after exposure to air, is brought indoors and the stopcock is slowly warmed and turned back and forth to work out any streaks in the grease. The flask is then repacked immediately to avoid prolonged exposure to light. Except for the flasks collected from Feb. 1969 to Jan. 1970, which were analyzed twice each at the Institute of Nuclear Sciences in New Zealand, flasks have always been returned to the Scripps laboratory where each is analyzed twice at ambient pressure using successive 500 cc aliquots according to the procedure described by Keeling et al. (1968). All analyses at Scripps laboratory were performed with an Applied Physics Corporation dual detector infrared analyzer, as described by Smith (1953); the analyses in New Zealand were obtained using a Hartmann-Braun URAS I.

Only one member of the South Pole field party was designated each year to take samples. Prior to arrival in Antarctica, he received two days of instruction from Scripps personnel. The results of his practice sampling were determined by gas analysis while he was still undergoing training.

Procedures for continuous monitoring with an analyzer at the station have been described by Brown & Keeling (1965).

Reference gas calibration

The laboratory analysis of flask samples and continuous monitoring of air at field stations were accomplished by repeatedly comparing the

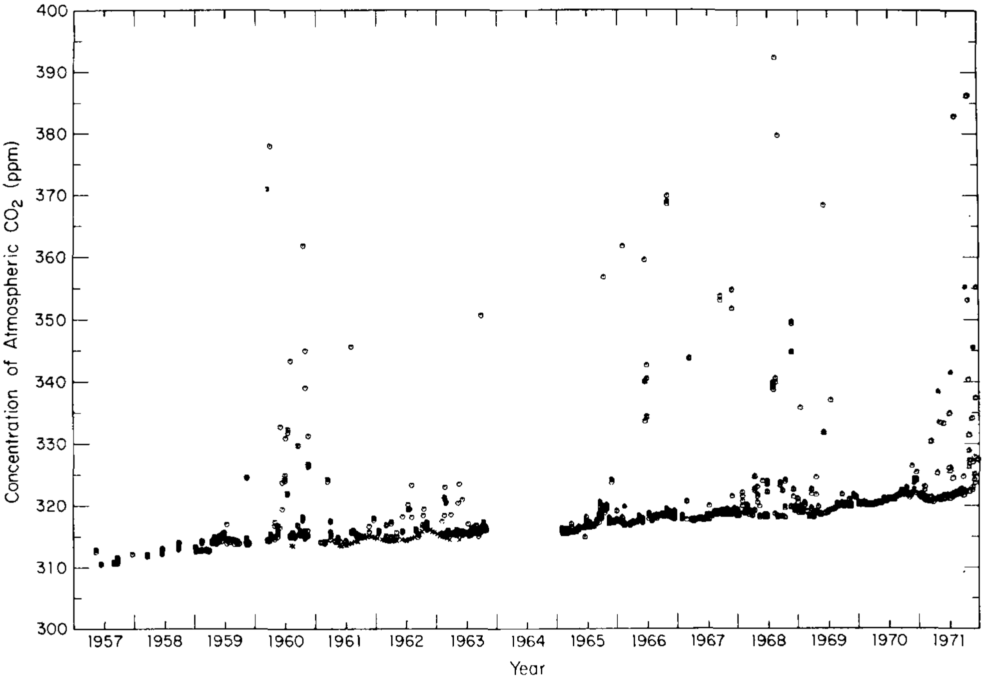

Fig. 1. Time plot of the CO_2 concentration in flask samples of air collected at the South Pole (shown as circles), and twice monthly averages of analyses of the CO_2 concentration obtained with a continuous analyzer during 1960 through 1963 (shown as crosses). Concentrations are plotted on the adjusted CO_2 index scale.

responses of the infrared analyzer to air and to specially prepared calibrating or "reference' gases consisting of CO_2 in nitrogen. The analyses of flask samples involved transferring air from a glass flask and reference gas from a high pressure steel cylinder alternately into the previously evacuated cell of the analyzer installed at the Scripps laboratory. The continuous measurements for 1960 through 1963 involved flowing air and reference gas alternately through the cell of the infrared analyzer installed at the station. In both cases, the actual measurements consisted in observing the displacement of a pen trace on a strip chart recorder as one gas mixture was replaced by another.

The sensitivity of the analyzer was determined periodically by mutually comparing two or more additional reference gases of differing CO_2 concentration. All gases used in the field and at the laboratory were in turn compared repeatedly with semipermanent standard reference gases kept at the Scripps laboratory. The latter gases were also compared repeatedly with a set of special standard gases for which the CO_2 mole fraction had been determined manometrically to a precision of approximately 0.1 ppm.

To provide a common basis for tabulating all gas comparisons, the original data in recorder scale divisions were converted to an approximate concentration scale by assigning magnitudes to two reference gases such that the converted data very nearly expressed the true CO_2 concentration in the range of atmospheric CO_2, i.e. from 310 to 330 ppm (parts per million of dry air). All other reference gas analyses were then expressed on this scale, even if their concentration was outside the range of atmospheric CO_2. The numerous individual infrared data have thus been tabulated consistently without the necessity of updating should the manometric calibration of the reference gases later be readjusted. This instrumental scale, which we refer to below as an "adjusted CO_2 index scale", has been the basis for all data published so far as part of our atmospheric CO_2 program.

Table 1. *Standard deviations of parent distributions associated with flask analysis and sampling technique*

	No. of analyses N_a	No. of flasks N_f	No. of sample dates N_d	Standard deviation of adjusted CO_2 index	
				σ (analysing) (ppm)	σ (sampling) (ppm)
South Pole (all flasks exposed at South Pole)	1 453	749	291	0.20	9.20
Control Group 1 (flasks exposed at Scripps Pier in 1971)	152	76	12	0.22	0.32
Control Group 2 (flasks exposed at South Pole during November, 1959)	43	21	10	0.16	0.20
Control Group 3 (flasks exposed at South Pole during Observer Year 1970)	147	74	25	0.12	0.23

We relate this instrumental scale to the CO_2 mole fraction, valid in the range 200 to 450 ppm, by the general expression:

$$X = \sum_{n=0}^{3} a_n (J + a_4 + a_5 t)^n (a_6 + a_7 P + a_8 P^2)^n a_9^n \qquad (1)$$

where X denotes the CO_2 mole fraction, in parts per million (ppm); J, the adjusted CO_2 index of air (proportional to infrared instrument response); t, the time of air analysis in years since January 1, 1957; P, the total gas pressure in the infrared sample chamber in mmHg.

On the basis of manometric studies, most of which were carried out in 1974:

$a_0 = 76.582$ $\qquad a_5 = 0.060$
$a_1 = 0.584910$ $\qquad a_6 = 1.003157$
$a_2 = 3.1151 \times 10^{-4}$ $\qquad a_7 = -2.237 \times 10^{-6}$
$a_3 = 7.3225 \times 10^{-7}$ $\qquad a_8 = -2.522 \times 10^{-9}$
$a_4 = -1.050$ $\qquad a_9 = 1.01201$

This expression is described in greater detail in the article which follows (Keeling et al., 1976 b). For data collected *in situ*, we substitute for P 512.1 mmHg based on the mean station pressure during 1957 (Anon, 1961). For flask samples we substitute for P the pressure of the samples as measured in the laboratory (usually 1 atmosphere, but approximately 400 mm Hg for the samples collected in 1957). The manometrically determined CO_2 mole fractions are approximately 3 ppm higher than the corresponding index values (Keeling et al., 1976, Table 2).

To provide continuity with previously reported data, we have expressed tabular results and have plotted Figs. 1 through 8 in terms of adjusted CO_2 index values. For data obtained at low pressure, we have, however, corrected the index values to one atmosphere pressure by a method equivalent to multiplying the index value, J, by the factor $(a_6 + a_2 P + a_8 P^2)$.

Description of data

Original data. Individual infrared analyses of the CO_2 concentration of flask samples, expressed as adjusted index values, are plotted in Figure 1 versus the date of exposure. Also shown are twice monthly averages of all available continuous analyzer data. Concentration values which lie noticeably above the general trend of the data we attribute to contamination. From the grouping of these abnormal data, it is evident that this contamination varies with the technique of the sample takers, who are replaced in November of each year.

Precision of the data. To derive criteria for rejecting contaminated data, including less obvious examples, we have first estimated the inherent precision in the procedures for flask sampling and laboratory analysis. Since, with rare exceptions, each flask was analyzed twice at Scripps, and more than one flask was exposed on any sampling date, it is possible to obtain estimates of the standard deviations for the parent distributions of random errors associated with both procedures. With respect to laboratory errors in analyzing the samples we evaluated:

$$\sigma\,(\text{analyzing}) = \left[\frac{\sum_{i=1}^{N_a} d_i^2}{N_a - N_f}\right]^{1/2} \qquad (2)$$

where d_i is the deviation of the ith analysis from the flask mean (expressed in terms of the adjusted CO_2 index scale), and N_a and N_f are the total number of analyses and flasks, respectively. With respect to errors in sampling technique we evaluated:

$$\sigma\,(\text{sampling}) = \left[\frac{\sum_{i=1}^{N_f} \sigma_i^2}{N_f - N_d}\right]^{1/2} \qquad (3)$$

where σ_i is the deviation of the flask mean for a given date from the daily average of these means, and the total numbers of flasks and sampling dates are given by N_f and N_d respectively.

The results of these calculations are given in Table 1. Also included for comparison are the results of CO_2 analyses of three control groups. The first control consists of flasks routinely exposed near the Scripps laboratory at the end of a 300 m ocean pier in 1971 by experienced observers. The second and third controls were obtained from two portions of the South Pole record which show especially low scatter. One portion is all data for the month of November, 1959, a period during which an exceptionally large number of flasks were exposed within a short time. One of these was obviously contaminated and rejected for this study. The second portion of record consisted of data from all flasks exposed by the observer in residence from November, 1969 to November, 1970. These data show the lowest scatter of any complete year's set obtained by a single observer.

Exclusion of contaminated data. The exceptionally large σ (sampling) listed in Table 1 for all the South Pole data primarily reflects the inclusion of data resulting from sampling blunders. In the absence of such blunders the standard deviation, σ (control), of the combined sampling and analyzing distribution (obtained by adding the variances σ^2 (analyzing) and σ^2 (sampling) for the average of the two South Pole control groups to obtain σ^2 (control)) is evidently about 0.30 ppm.

As noted above, flask values obtained during the years 1960 through 1962 were subject to a systematic error attributed to photo-oxidation of stopcock grease. For this period and for 1963, only data obtained from the continuous analyzer have been used in the subsequent analysis. This procedure reduces the original set of 1453 individual analyses of 749 flask samples to 1164 analyses of 590 samples.

In order to achieve statistical weighting of the continuous analyzer data compatible with the flask data, the continuous data were compressed into twice monthly averages to correspond to the twice monthly flask sampling. These averages were plotted, taking into account the actual days with data control. In three instances when a half month contained fewer than 5 days of data, that time interval was augmented by borrowing adjacent days with data control from the other half of the month. In all cases two sets of at least 5 days with data control were thus obtained. These twice monthly averages were assigned a weight of 4 so that they corresponded to the normal number of analyses obtained on a sampling date with flasks. The precision of these averages is comparable to (actually somewhat higher than) that of four typical flask samples.

As a basis for rejecting data influenced by contamination, a statistical procedure was developed for reducing the skewness of the data distribution. An estimate of the population mean was first obtained as discussed below, and the standard deviation, σ, of each analysis from this mean was calculated. Then, data with deviations from the mean greater than $1.25\,\sigma$ were rejected, but only if their value was greater than the mean, since flask contamination can only lead to an error on the high side. After this rejection of probable blunders, the population mean and sample standard deviation were recalculated and again high data with deviations greater than $1.25\,\sigma$ were rejected. This procedure was reiterated until σ was equal to or less than the standard deviation estimated from the control groups (0.30).

This procedure was complicated by the time dependence of the CO_2 concentration at the South Pole and hence of the population mean for the distribution of samples. Statistical analysis of the long and nearly continuous record on the island of Hawaii [Keeling et al., 1976 b] suggests that the CO_2 monthly mean concentration as a function of time for the order of 10 years at any atmospheric CO_2 station with small seasonal variations is represented to a good approximation by an oscillating power function of the form:

$$J(t) = Q_1 \sin 2\pi t + Q_2 \cos 2\pi t + Q_3 \sin 4\pi t + Q_4 \cos 4\pi t + Q_5 + Q_6 t + Q_7 t^2 + Q_8 t^3 \quad (4)$$

where J is the time dependent population mean CO_2 concentration (expressed as an adjusted index), t is the elapsed time in years from a reference date, and the eight parameters, Q_i, are obtained from the data using the method of least squares. The standard deviation, σ, of the individual analyses, J_i, from the calculated value of J at the time of sampling, t_i, is derived from the expression:

$$\sigma^2 = \sum_{i=1}^{N_a} [J_i - J(t_i)]^2 / N_a \quad (5)$$

In applying this method the record before 1971 was broken into two segments with the year of missing data, 1964, as the divider. (Very high scatter in the 133 analyses for 1971 posed a problem because these data occur near the end of the record. As a provisional measure we visually screened the individual data points for 1971.) The iterative procedure was carried out more times than required for reduction of σ to 0.30 ppm, while at the same time statistical parameters relating to the first three moments of the sample distribution were monitored. These were, besides σ, the coefficient of skewness,

$$sk = \sum_{i=1}^{N_a} [J_i - J(t_i)]^3 / N_a \sigma^3 \quad (6)$$

and the coefficient of kurtosis,

$$ku = \sum_{i=1}^{N_a} [J_i - J(t_i)]^4 / N_a \sigma^4 \quad (7)$$

These parameters are graphed versus the number of iterations in Figs. 2, 3, and 4. The fraction of analyses rejected per iteration is graphed in Fig. 5. The iteration at which σ attains a value below the 0.30 ppm level is circled on each plot. These graphs demonstrate that carrying the iteration beyond this point gives no significant change in the dispersion of the data, as characterized by σ and the coefficient of kurtosis. Excessive iteration, however, introduces asymmetry opposite in sense to the original skewness.

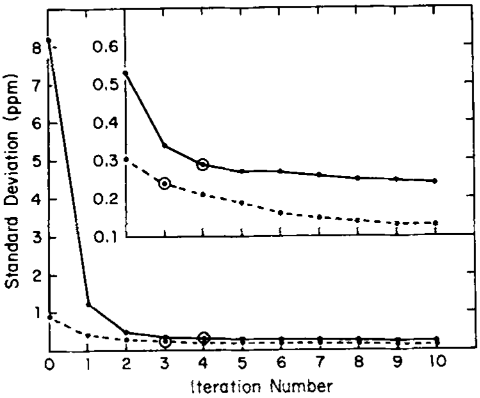

Fig. 2. Standard deviation of individual flask sample analyses versus number of rejections of high values. Broken line: data prior to 1964; solid line: data after 1964. Inset shows ordinate expanded by a factor of ten. Circled points indicate the iteration at which the $\sigma < 0.30$ ppm criterion is first satisfied.

The information we wish to extract from the South Pole record is embodied in the time varying mean CO_2 concentration $J(t)$, and its first derivative, the secular trend. Ideally, after sufficient iteration, the estimates of these should attain almost the correct values relative to the calibrated gases to which the flask air was compared. To investigate probable errors associated with our choice of number of iterations

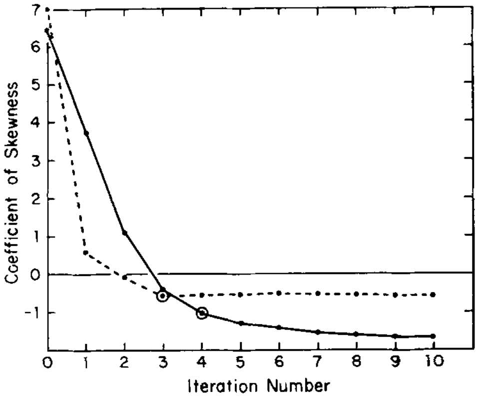

Fig. 3. Coefficient of skewness of individual flask analyses versus number of rejections of high values. Broken line: data prior to 1964; solid line: data after 1964. Circled points indicate iteration at which the $\sigma < 0.30$ ppm criterion is first satisfied.

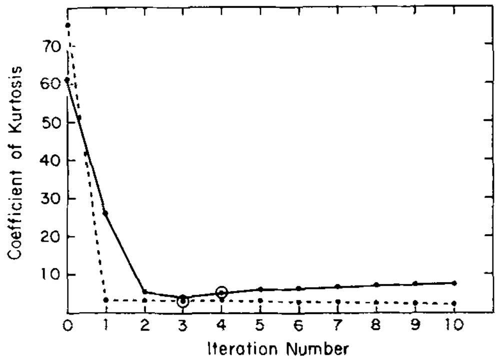

Fig. 4. Coefficient of kurtosis of individual flask analyses versus number of rejections of high values. Broken line: data prior to 1964; solid line: data after 1964. Circled points indicate iteration at which the $\sigma < 0.30$ ppm criterion is first satisfied.

the time average of the mean and its time derivative were calculated for an integral number of years from

$$\bar{J} = \frac{1}{t-t_0}\int_{t_0}^{t} \bar{J}(u)\,du \tag{8}$$

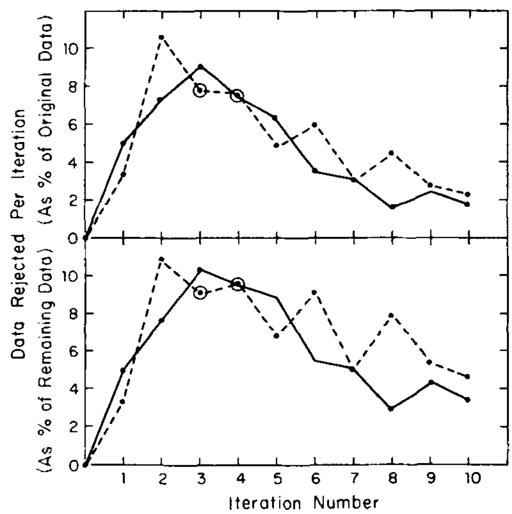

Fig. 5. Flask analyses rejected per iteration versus number of iterations. The fraction rejected is shown both relative to original number of data (upper plot) and relative to remaining number of data (lower plot). Broken line: data prior to 1964 (397 original analyses, including averages of 60 twice monthly continuous analyzer data each with a statistical weight of 4;) solid line: data after 1964 (874 original analyses). Circled points indicate iteration at which the $\sigma < 0.30$ ppm criterion is first satisfied.

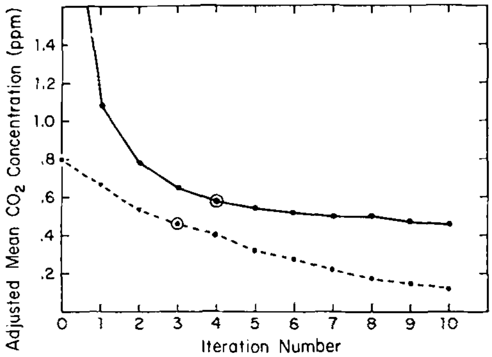

Fig. 6. Estimated mean CO_2 concentration versus number of rejections of high flask analyses. Broken line: data prior to 1964 (for plotting purposes adjusted by subtracting 313 ppm); solid line: data after 1964 (adjusted by subtracting 318 ppm). Circled points indicate iteration at which the $\sigma <$ 0.30 ppm criterion is first satisfied.

for the average of the mean, and

$$\langle \bar{J}' \rangle = \frac{1}{t-t_0}\int_{t_0}^{t} \frac{d\bar{J}(u)}{du}\,du \tag{9}$$

for the time average of its first derivative.

As is seen from Fig. 6, after the cutoff criterion of $\sigma = 0.30$ ppm is passed, the change in $\langle \bar{J} \rangle$ per iteration is less than 0.08 ppm for the pre-1964 data, and less than 0.03 ppm for the post-1964 data. Since the correct mean is probably to be found between the values obtained on the third and fifth iterations, the uncertainty in the mean owing to iteration is probably less than ±0.15 ppm. The average

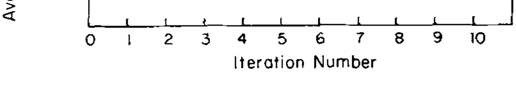

Fig. 7. Estimate of the average secular increase in CO_2 concentration plotted versus number of rejections of high flask analyses. Broken line: data prior to 1964; solid line: data after 1964. Circled points indicate iteration at which the $\sigma < 0.30$ ppm criterion is first satisfied.

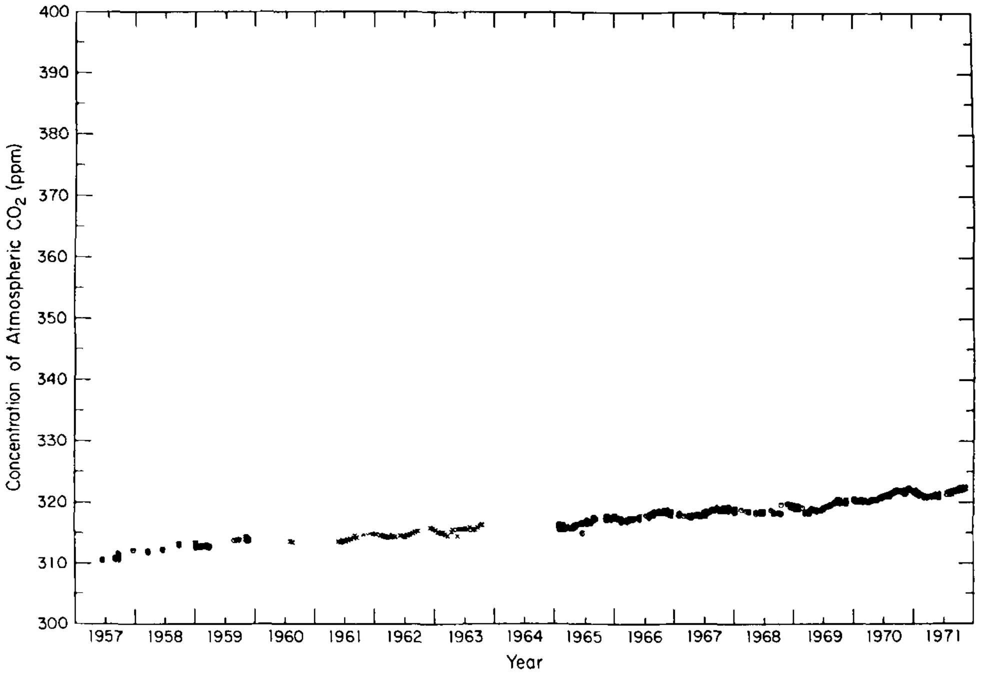

Fig. 8. Time plot similar to Fig. 1 except for deletion of data rejected as contaminated.

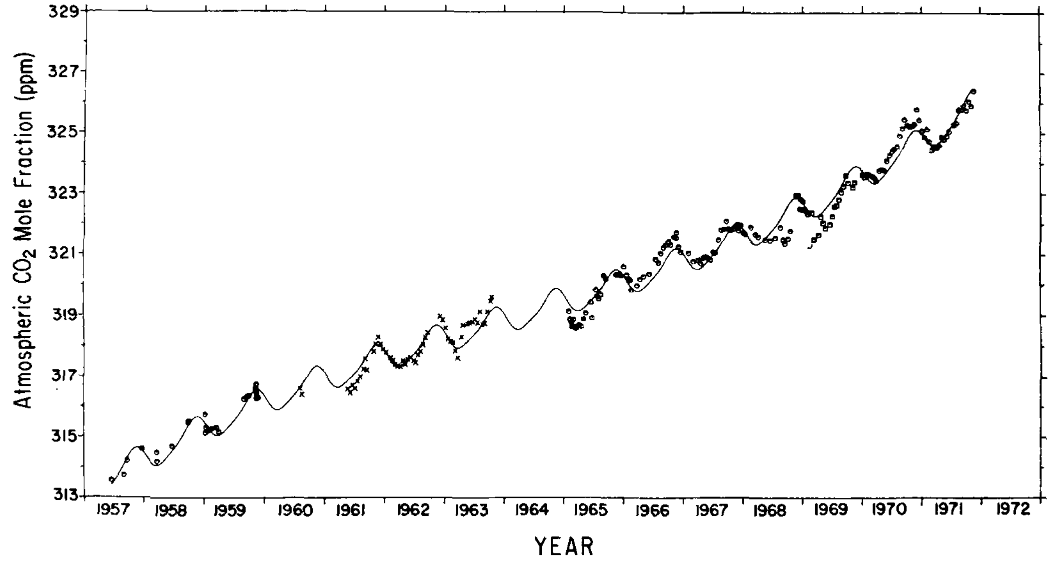

Fig. 9. Long term variation in the atmospheric CO_2 concentration at the South Pole according to best fit of daily averages to the oscillating power function given by equation (4). Circles and squares indicate daily averages based on flask analyses, circles for Applied Physics Analyzer data and squares for URAS Analyzer data. Crosses indicate twice monthly continuous analyzer averages. Concentrations are plotted as the CO_2 mole fraction of dry air in ppm.

rate of increase of CO_2, $\langle J' \rangle$, converges to a value steady within 0.02 ppm yr^{-1} after the second iteration, as seen in Fig. 7. Clearly, in this case no risk exists that the iterative procedure was carried too far. (The estimated annual rate of increase for 1957 to 1963 as shown in Fig. 7 is higher than Brown & Keeling (1965) found for 1958 through 1963 because of values lower than the mean trend in 1957.)

Analysis of retained data. The result of terminating the iteration with the $\sigma < 0.30$ ppm criterion is illustrated in Fig. 8. To obtain this plot, 314 analyses, comprising 30% of the flask data record for 1957–1959, 1965–1971, were rejected. Six of the 30 twice monthly averages from the continuous analyzer were also rejected.

All data retained for each sampling date were next averaged and these daily average adjusted index values converted to CO_2 mole fractions in dry air by use of eq. (1). These averages were then fit by the method of least squares (with X replacing J) to an expression of the form of (4) for the entire period of record through 1971. The parameters of best fit were found to have the values:

$$\left.\begin{aligned} Q_1 &= -0.408 \text{ ppm} & Q_5 &= 313.089 \text{ ppm} \\ Q_2 &= 0.206 \text{ ppm} & Q_6 &= 1.266 \text{ ppm/yr} \\ Q_3 &= -0.086 \text{ ppm} & Q_7 &= -0.097 \text{ ppm/yr}^2 \\ Q_4 &= 0.032 \text{ ppm} & Q_8 &= 0.00469 \text{ ppm/yr}^2 \end{aligned}\right\} \quad (10)$$

The elapsed time in years, t, is taken relative to the first of January, 1957. The standard deviation of the daily averages with respect to this expression is σ (daily) = 0.33 ppm. The daily averages and curve based on eq. (10) are shown in Fig. 9.

Monthly average adjusted CO_2 index values derived from the individual flask analyses are listed in Table 2. These averages were obtained from daily averages, expressed as CO_2 mole fractions, by adjusting the latter to the fifteenth of the month using eqs. (4) and (10). Averages for each month were then computed with each retained flask value assigned a weight of unity and each continuous analyzer daily average a weight of four. These monthly averages were then converted to adjusted CO_2 index values consistent with eq. (1).

Supplementary data. The individual flask analyses, 1957 through 1971, are too numerous to reproduce here. They have been summarized

Table 2. *Monthly average concentration of atmospheric carbon dioxide (ppm) at the South Pole*

	Adjusted CO_2 index														
	1957	1958	1959	1960	1961	1962	1963	1964	1965	1966	1967	1968	1969	1970	1971
January			312.90			315.08	315.66			317.47		318.50	319.29	320.27	321.57
February			312.82			314.90	315.39		315.97	317.05	317.92	318.78	319.24	320.32	321.45
March		311.93	312.79			314.69	314.99		315.80	317.04	317.70	318.55	318.32	320.23	321.11
April						314.73	315.71		315.79	317.24	317.75	318.50	318.64	320.46	321.23
May					313.93	314.79	315.92		316.14	317.38	317.89	318.37	318.73	320.53	321.47
June	311.23	312.27			313.97	314.86	316.01		316.13	317.44	317.84	318.34	318.90	320.91	321.65
July					314.10	314.88	316.04		316.75	317.85	318.06	318.42	319.34	321.16	321.87
August			313.63	313.95	314.46	315.21	316.13		316.76	317.93	318.56	318.75	319.66	321.44	322.17
September	311.71	312.96	313.80		314.80	315.63	316.16		317.44	318.32	318.91	318.40	320.16	321.96	322.50
October			313.98		315.10		316.74			318.41	318.77	318.58	320.19	321.95	322.51
November			313.96		315.52				317.40	318.57	318.84	319.77	320.07	321.93	322.66
December	312.27				315.32	316.16			317.36	318.13	318.70	319.44		322.16	

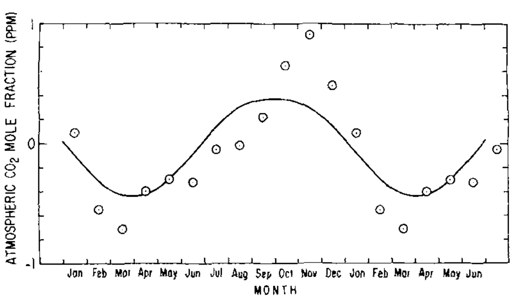

Fig. 10. Average seasonal variation of the atmospheric CO_2 concentration at the South Pole, 1957 to 1971, based on the data shown in Fig. 9. Circles indicate monthly means of continuous analyzer data, 1958–1963. January through June are plotted twice to reveal the seasonal pattern more fully. Concentrations are expressed as the CO_2 mole fraction of dry air in ppm.

in a data report (Keeling et al. 1976a) and deposited with the National Auxiliary Publications Service of the American Society for Information Sciences.[1]

Discussion of results

The seasonal variation of the CO_2 concentration based on the values of Q_1 to Q_4 of eq. (10) (Fig. 10) is similar to, but somewhat smaller than, the seasonal variation deduced from continuous analyzer data (including 11 months of data from Little America for 1958) by Brown & Keeling (1965, Fig. 6). The annual variation of all retained data has an amplitude of 0.46 ppm, and the first harmonic 0.09 ppm. The combined annual and semiannual variation, peak to peak, is 0.82 ppm.

The secular trend based on the values of Q_5 to Q_8 of eq. (10) is shown in Fig. 11, where we have also plotted daily flask averages and twice monthly analyzer averages of the CO_2 mole fraction after subtracting the seasonal variation given by the first four terms of equation (10). The values of the secular trend for 1 July of each year are listed in Table 3. The increase in concentration from 1957 to 1971 is 3.7%. From 1959 to 1971 it is 3.1%. The latter increase compares with 3.4% over the same time period for Mauna Loa Observatory in Hawaii (Keeling et al., 1976). Indeed, the entire secular trend in CO_2 for the South Pole is similar to that obtained from the record of atmospheric CO_2 at Mauna Loa Observatory using the same third order trend function (Keeling et al., 1976), (Fig. 12).

Table 3. *Seasonally adjusted concentration of atmospheric CO_2 (in ppm) at the South Pole*[a]

Year	Adjusted CO_2 index	CO_2 mole fraction
1957	311.36	313.70
1958	312.39	314.79
1959	313.24	315.72
1960	313.99	316.54
1961	314.64	317.26
1962	315.22	317.91
1963	315.76	318.52
1964	316.30	319.13
1965	316.84	319.75
1966	317.44	320.42
1967	318.11	321.16
1968	318.87	322.00
1969	319.75	322.98
1970	320.79	324.11
1971	322.02	325.43

[a] Values are for 1 July of each year. Those expressed as mole fractions were derived from the last four terms of eq. (10). The adjusted index values were obtained from the corresponding mole fractions by inverting eq. (1) with P set equal to 1 atmosphere.

The significance of the seasonal and longer term variations revealed in the South Pole and Mauna Loa records, and the relationship between the two stations, have been dealt with by Bolin & Keeling (1963) and Ekdahl & Keeling (1973). Nevertheless, a few comments are in place here.

1. The increase in CO_2 concentration observed at the South Pole is approximately one half of what would have occurred if all of the CO_2 released by the burning of fossil fuel and limestone (to make cement) had remained airborne. For a precise estimate of the air-borne fraction we have selected ten consecutive years of data beginning on January 1, 1959. The data for the first and most recent years of record were omitted because of the large un-

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[1] This information has been deposited with ASIS as NAPS document 02889. 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 $23.50 Microfiches are $ 3.00. Outside the United States and Canada, postage is $ 2.50 for a photocopy or $ 1.00 for a fiche.

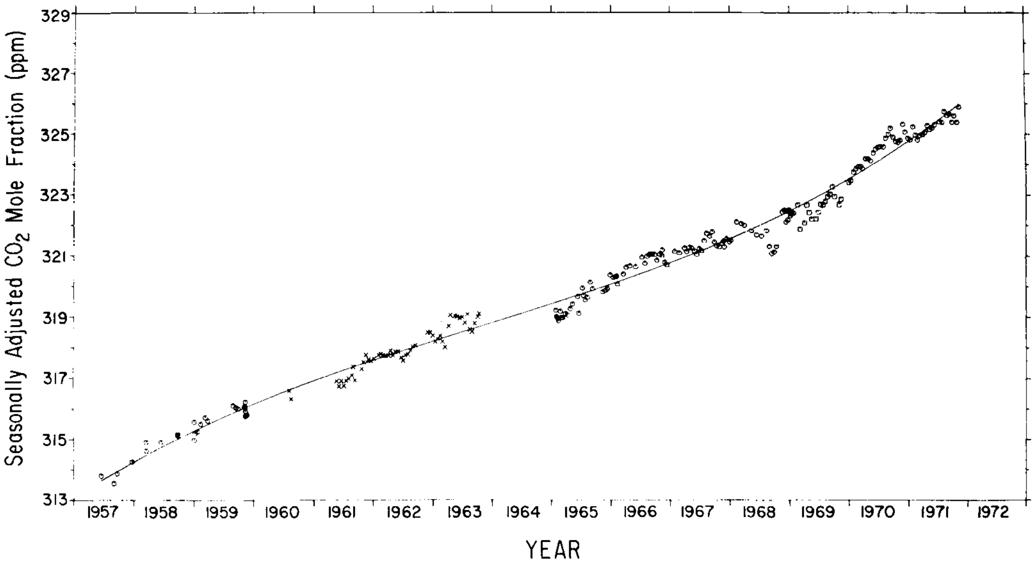

Fig. 11. Secular trend of the atmospheric CO_2 concentration at the South Pole, based on cubic trend function. Symbols have same significance as in Fig. 9. Concentrations are expressed as the CO_2 mole fraction of dry air in ppm.

certainties in the least square fit near the beginning and end of the record. According to an estimate of Keeling (1973) based on a reassessment of commercial data for production of fossil fuels and cement, burning introduced enough CO_2 into the air during the decade under consideration to raise the concentration globally by 13.90 ppm. The South Pole cubic trend function indicates an actual rise of 7.20 ppm, and hence an air-borne fraction of 52%. In comparison, a cubic trend representation of the data of Mauna Loa Observatory, Hawaii for the same time interval indicates a rise of 7.57 ppm, and an air-borne fraction of 54%. (These fractions are some 5% higher than values based on the adjusted index values, principally because of correction for drift in the system of calibrating gases as indicated by the manometric calibrations as described by Keeling et al. (1976)). A higher fraction for Mauna Loa Observatory is to be expected because most industrial CO_2 is introduced into the northern hemisphere and spreads into the southern hemisphere only after a delay of the order of six months (Bolin & Keeling, 1963 and Junge & Czeplak, 1968).

2. For the same reason that the airborne fraction is higher in the northern than in the southern hemisphere, the average concentration of CO_2 observed in the northern hemisphere exceeds that in the southern. When the data reported by Bolin & Keeling (1963, Fig. 2) (fit of five polynomials) are adjusted to the CO_2 mole fraction scale, the concentration decline from 20° N to 90° S in 1960 is estimated to be about 1.8 ppm. Ten years later, in 1970, the fossil fuel production had increased by 55%. The concentration difference should therefore have increased to about 2.8 ppm. In contrast the trends shown in Fig. 12, from which the airborne fractions were estimated, indicate that the trend difference increased from 0.52 to 1.66 ppm, between 1960 and 1971. Since the annual means for both the South Pole and Mauna Loa stations are imprecise to about 0.30 ppm, the estimates of the difference are too uncertain to expect the observed increase to agree closely with prediction. The disagreement with the earlier estimates exceeds expected errors, however. Also, the earlier estimates seem too high in comparison to the difference in observed airborne fractions. The data used by Bolin and Keeling for the northern hemisphere were obtained by several different kinds of sampling efforts, and probably are too high because of contamination of some of the samples.

3. The decline in rate of CO_2 increase in the mid-1960's during a period of rising industrial

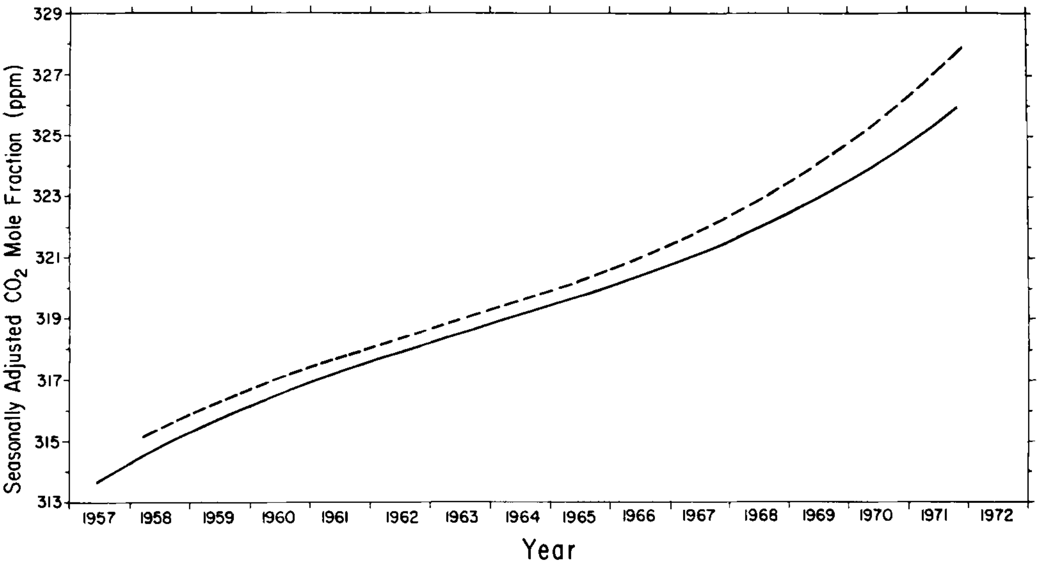

Fig. 12. Comparisons of secular trends of atmospheric CO_2 concentration at Mauna Loa Observatory, Hawaii, and the South Pole. The dashed curve is for Mauna Loa; the full curve for the South Pole. Concentrations are expressed as the CO_2 mole fraction of dry air in ppm.

CO_2 production, if real, suggests a temporary increased uptake by either the oceans or land plants. The former possibility was suggested by Bainbridge (1971) as a consequence of cooling of surface ocean water by about 1°C. In 1964 such cooling occurred in the North Pacific (Namias, 1970) and since the cooling trend began almost immediately after the spread of an enormous stratospheric dust cloud from the eruption of the volcano Agung in Bali, and since more dust remained in the southern hemisphere than moved into the northern (Dyer & Hicks, 1968), a prolonged period of cooler water mainly in the southern oceans may account for the declining rate. Even in the northern hemisphere the dust cloud apparently reduced the transmission of solar radiation for over six years (Ellis & Pueschel, 1971). On the other hand, for the north Pacific Ocean, the only extensive region where water temperatures have been analyzed, the period of cooler water, about three years, is too short, and the cooling after the first year too slight, to account for the CO_2 trend.

Conclusions

From duplicate analyses of duplicate air samples collected twice monthly at the South Pole we have deduced the seasonal and secular variation in atmospheric CO_2 concentration over interior Antarctica. About one third of the samples were contaminated owing to sampling blunders, but, because of the large number of samples which were processed, these errors could be distinguished statistically. Agreement of flask data with continuous *in situ* measurements during 1963 indicates that the flask sample data are not systematically biased except for sampling mistakes. This agreement is scarcely grounds for recommending flask sampling as a generally reliable substitute for *in situ* continuous measurements, but at a station as utterly remote from vegatation and fuel combustion as is the South Pole, flask sampling can evidently yield useful data.

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many years. Sample takers are listed by Keeling et al. 1976a.

Mrs Blanche Christman, Messrs Thomas B. Harris, William H. Price, Eugene N. Wilkens, and authors J.A.A., P.R.G., and C.D.K. analyzed the flask samples.

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ВАРИАЦИИ ДВУОКИСИ УГЛЕРОДА В АТМОСФЕРЕ НА ЮЖНОМ ПОЛЮСЕ

Двойной анализ 749 дискретных проб воздуха, взятых на Южном полюсе показывает, что приспособленные к сезону концентрации двуокиси углерода в атмосфере росли на 3,7 % за период от 1957 до 1971 гг. Этот рост, приписываемый, главным образом, сжиганию ископаемых топлив, не был устойчивым. В середине 1960-х гг., возможно, в результате широко распространившегося охлаждения поверхности океанских вод он замедлился на несколько лет, а недавно ускорился.

Подобные изменения скорости роста наблюдались также на Обсерватории Мауна Лоа, Гавайи, в северном полушарии и являются, очевидно, глобальным явлением.