Tellus (1986), *38B*, 87–105

Reassessment of late 19th century atmospheric carbon dioxide variations in the air of western Europe and the British Isles based on an unpublished analysis of contemporary air masses by G. S. Callendar

By ERIC FROM and CHARLES D. KEELING, *Scripps Institution of Oceanography, 2314 Ritter Hall, A-020, La Jolla, California 92093, USA*

(Manuscript received July 9, 1985; in final form January 20, 1986)

ABSTRACT

We have reassessed measurements of the concentration of atmospheric carbon dioxide made during the 19th century by examining original data published between 1880 and 1905 and an interpretation of these data carried out during the 1930's by C. S. Callendar, a British engineer. We have perused an unpublished notebook of Callendar which contains a detailed analysis of air masses and wind velocities attending some of these 19th century analyses. We find new evidence to support Callendar's contention that the concentration of CO_2 in the late nineteenth century was close to 290 ppm. Of particular interest are the observations of J. A. Reiset made on the coast of France from 1871 to 1880 which we show to be consistent with the seasonal cycle of CO_2 as known from modern measurements. From Reiset's data, we deduce that the mean annual concentration of atmospheric CO_2 circa 1880 in uncontaminated air at 50° N latitude was 292 ppm.

1. Introduction

Carbon dioxide was the first constituent of the earth's atmosphere to be isolated and identified. The discovery has been credited to Joseph Black who published a dissertation on "fixed air" in 1754 (Black, 1754). Quantitative methods of determining the concentration of CO_2 were slow to develop, however. Only after 1870 were data gathered which appear today to be precise enough to justify comparison with modern measurements. Even these data are of questionable value, but, the importance in establishing the concentration of CO_2 during the early stages of the industrial revolution has several times prompted their reappraisal in the 20th century.

Callendar (1938), over 40 years ago, investigated whether atmospheric CO_2 had increased as a result of burning of fossil fuels. Comparing data of the late 19th century of Brown and Escombe (1905b) with more recent data, he estimated that the CO_2 concentration had risen since 1900 from about 290 parts per million by volume of dry air (ppm) to 310 ppm. Evidently, roughly three-fourth's of the CO_2 from fuel combustion had remained in the atmosphere.

A short-time later Callendar (1940a) re-examined the literature on atmospheric CO_2 measurements. For the 19th century, he now focused on five sets of observations from Europe and England which he regarded to be the most reliable. Of particular interest to us, and the basis of this article, he made use of contemporary weather observations to screen these data on the basis of wind direction and air mass character. He established that the lowest measured, and presumably most reliable, CO_2 concentrations were found for air transported by southwesterly to northerly winds from off the Atlantic ocean. The weighted average concentration for this air, which he characterized as "marine" or "polar marine", was 290.4 ppm, essentially his best estimate of the northern hemisphere CO_2 concentration in air between 1872 and 1900. From 20th century observations, he now estimated an increase in atmospheric CO_2 concentration to approximately 320 ppm in the late 1930's.

Towards the end of his career, Callendar (1958) again revised his 1938 study, this time to take advantage of a new set of about 1000 CO_2 readings made over Scandinavia during 1955 and 1956. He still held to a figure of approximately 290 ppm for the late 19th century, whereas the Scandinavian data averaged near 325 ppm. From the implied increase in CO_2 it followed that essentially all of CO_2 from fuel combustion had remained in the atmosphere as his study in 1940 had suggested.

We know today that the Scandinavian data examined by Callendar were too high. The correct value for 1955 to 1956 is approximately 314 ppm (Keeling, 1978). Other 20th century data examined by Callendar can now be seen also to have been, in most cases, too high. That Callendar was evidently misled by the 20th century data does not prove, however, that his evaluation of the 19th century data is wrong, since the original literature shows evidence of great care taken in making some of the earlier measurements.

During the 1950's, two additional attempts were made to establish the reliability of the late 19th century data using mainly statistical criteria (Slocum, 1955; Bray, 1959). Neither study looked as closely at individual data sets as Callendar had done, and it is evident from the large range in values accepted in these studies that many contaminated or poorly analyzed samples of air were included in the means. Thus neither study adds significantly to the findings of Callendar, although Bray's analysis is clearly superior to Slocum's.

After a pause of more than 20 years, renewed interest in the nineteenth century CO_2 data has been reflected in several new studies. Stanhill (1982) made a detailed study of an extensive data set passed over by Callendar: a 33 year record from the Montsouris Observatory near Paris, obtained between 1877 and 1910. Stanhill found support for CO_2 concentrations somewhat higher than those accepted by Callendar, but Waterman (1983) showed persuasively that the Montsouris data are too variable to be trusted, and that Callendar was justified in rejecting them in his search for reliable measurements (Callendar, 1940a). Indeed, a nineteenth century researcher already had expressed serious misgivings about these data in a scathing review (Reiset, 1880b). Also, two contemporaries of Reiset disputed the conclusions of the observers of Montsouris (Petermann and Graftiau, 1892, p. 23).

Wigley (1983) reexamined data gathered from 1880 to 1883 by Müntz and Aubin, investigators whom Callendar *had* regarded as reliable. Wigley was especially impressed by low values for southern hemisphere air and was disposed to conclude that Callendar's estimate of a mean CO_2 concentration of 288 ppm for the 1880's was too high. The true value might be as low as 261 ppm.

In June, 1983 a conference of scientists reviewed the 19th century CO_2 measurements with special attention to the data of Müntz and Aubin (WMO, 1983). A not very startling consensus was reached that the concentration of atmospheric CO_2 around 1880 was probably not less than 250 ppm or greater than 290 ppm. The conference expressed skepticism regarding the low data reported by Müntz and Aubin for the southern hemisphere because the variations were much greater than the 3 ppm annual range in concentration existing there today. The conference concluded that a value "somewhat lower" than 290 ppm was more plausible than values near 250 ppm.

Siegenthaler (1984) also disputed the conclusions of Wigley, and suggested that the cause of the low concentrations of Müntz and Aubin may have been their failure to recover all of the CO_2 from their stored samples, owing to a reaction between the potassium hydroxide absorbant used to fix the CO_2 and the glass storage tubes. Since the southern hemisphere samples of Müntz and Aubin were stored for many months, these data could have been especially biased towards low values.

Pearman (1984) and Elliott (1984) summarized the results of the 1983 WMO conference on preindustrial atmospheric CO_2. They proposed that further study in the light of our modern understanding of CO_2 variability might help determine the reliability of the early data.

Further study, of course, cannot overcome major shortcomings in the early CO_2 data. Consistent long-term time series at suitable locations are lacking, and convincing calibrating data are very scarce, as can be seen by scanning the thorough literature search of Stepanova (1952) carried out over 30 years ago. We are induced to contribute to further study here, because we have recently examined an unpublished notebook of Callendar (1940b) in which he recorded the air mass classifications reported in his 1940 article and his estimates of wind speed and direction. With the aid of this notebook, we have reinterpreted Callendar's 1940 study in the light of modern CO_2 data.

To a large extent, we are disappointed in our findings. We are inclined to reject all but one of the data sets deemed reliable by Callendar. Our conclusions are not entirely negative, however. One set of data, obtained by Reiset (1880a), showed evidence of being without serious errors. Moreover, Reiset collected his air samples near the Atlantic ocean where air could arrive on site without having passed recently over land, a shortcoming with all of the other data sets examined by Callendar. Reiset's data are extensive enough to permit samples collected during unfavorable winds to be rejected and still retain data over all seasons. In our reexamination of Reiset's data we find a mean annual concentration near 290 ppm, in agreement with Callendar's mean from all five data sets. In two of the other sets we also find some evidence that tends to confirm Reiset's observations.

We furthermore have reexamined some data of Müntz and Aubin which were not included in Callendar's air mass study. Clearly of interest are high altitude mountain data from the Pic du Midi in south France (Müntz and Aubin, 1881b, 1886), collected at a well ventilated site far removed from major industrial CO_2 sources. We also comment on southern hemisphere data (Müntz and Aubin, 1883, 1884, 1886) not screened by Callendar. These have been several times questioned as being suspiciously low. We compare these data with the northern hemisphere data of Müntz and Aubin (1881a, 1881b, 1882) in an attempt to explain why they may be too low.

In our appraisal of the CO_2 data sets considered by Callendar (1940b), we particularly test whether individual sets exhibit a seasonal variation in agreement with modern observations. We also consider the magnitude of the scatter within each month of measurements, and where justified we compare monthly means of different investigators.

Since there are likely to remain doubts about the estimates of CO_2 concentration obtained by indirect means such as isotopic analyses of tree rings, air from ice cores, and inferences from deep ocean water (see Elliott, 1984), these 19th century data may help us establish the atmospheric CO_2 concentration before the industrial revolution produced a significant increase.

2. Expected seasonal variations

A similarity of Callendar's deduced seasonal variation to that of contemporary CO_2 data was noted by Keeling (1979, p. 283). A modern station, called Ocean Weather Station "P", located at 50° N from 145° W, is close in latitude to the northern European and British stations from which Callendar selected his data. At Station "P" the maximum CO_2, as observed from 1969 to 1981, occurs in late spring; the minimum in late summer. The magnitude of the difference is about 14 ppm (Keeling et al., 1985). Since this

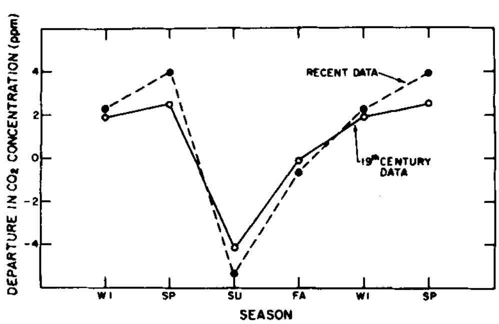

Fig. 1. Seasonal variation in atmospheric CO_2 for northern Europe and Great Britain in the late nineteenth century (departure from annual mean in ppm) as deduced by Callendar (1940a) together with similar data from Ocean Weather Station "P" at 50° N, 145° W from 1969–1981 (Keeling et al., 1985). Solid line: Callendar's values, dashed line: Station "P" values. WI = winter (January through March), SP = spring (April through June), SU = summer (July through September), FA = fall (October through December). Winter and spring are plotted twice to reveal the seasonal pattern more fully.

seasonal variation results mainly from plant activity in the northern hemisphere, the timing of maximum and minimum CO_2 values and the amplitude should not have changed greatly in 100 years. The Station "P" cycle corresponds, in most details with recent data at nearly the same latitude from a central European mountain station in the Swiss alps (Zumbrunn et al., 1983), and for an Atlantic weather ship at 54°N (Komhyr et al., 1985, p. 5576).

Fig. 1 shows how closely Callendar's CO_2 results agree with the cycle at Station "P". The peaks and troughs are positioned at the same seasons, and ranges from maximum and minimum are approximately the same. It is tempting to conclude from these similarities that Callendar's data are valid. However, as we will now show, the individual data sets, except Reiset's, do not substantiate this conclusion.

Table 1. *Callendar's scheme for air mass classification*

Callendar's abbreviation	Definition	General air flow	Quality
M	marine	west	good
MP or PM	polar-marine	north to northwest	good
T	tropical	southwest to southeast	poor
C	continental	northeast to southeast	poor
X	indefinite	difficult to trace trajectory	variable

3. Data sets examined

Five independent sets of data, gathered between 1872 and 1901, were the basis of Callendar's work: Reiset (1880a, 1882) (data gathered from 1872 to 1880), Müntz and Aubin (1881a, 1881b, 1882, 1884, 1886) (data from 1881 to 1883), Petermann and Graftiau (1892) (data in 1889 and 1890), Letts and Blake (1900) (data in 1897), and Brown and Escombe (1905b) (data from 1897 to 1901). Measurement repeatability better than 3 ppm of CO_2 was claimed by all investigators. Callendar summed the data to derive annual means of CO_2 for each investigator, and he summed three-monthly values from all five data sets to yield an average seasonal variation. He realized that his data might be affected by human activities and vegetation in Europe. To reduce such influences, he reviewed weather maps for each station and each day of measurements, and then he classified the measurements of CO_2 according to air mass type. His classification scheme is shown in Table 1. Details of his analysis were not published, but are to be found in a manuscript notebook, dated A.D. 1940 (Callendar 1940b), which was kindly provided for us by Dr. Justin Shove, St. David's College, Beckenham (Kent), England.

Callendar derived separate mean annual CO_2 concentrations for each air mass type, excluding indefinite cases. To derive seasonal variations, however, he aggregated all of the data, in spite of his finding that the annual means based on marine and polar marine air were lower than those based on tropical and continental air. Intuitively, it would seem reasonable to consider marine air separately from non-marine air in a seasonal analysis. Perhaps Callendar felt a need to employ larger data sets to derive statistically valid monthly means. To clear up this point, we have taken advantage of our having access to the complete compilation in Callendar's notebook to carry out a new seasonal analysis.

We find, in reviewing each original set of data, that no monthly means obtained by any investigator clearly show the expected seasonal variation, whether we use only marine and polar marine or more extensive data. Moreover, in several of the data sets large deviations of individual values from monthly averages suggest poor experimental or sampling techniques which circumstance renders questionable the combining of the data of several investigators to form means.

3.1. *Brown and Escombe at Kew, England*

Kew (51°29′N, 18′E) is located just west of metropolitan London as it existed in 1900. By separating out marine and polar marine air measurements from the full data set of Brown and Escombe (1905b) (expressed in ppm with respect to dry air), Callendar obtained means for air derived from the southwest, west, and northwest. The other air types: continental, tropical, and indefinite, were especially susceptible to

Table 2. *CO_2 data for Kew, England during 1898–1901*

Air type	No. of measurements	Average concentration (PPM)
M + MP	48	285.3
C	11	309.9
T	6	314.0
X	22	302.6

influence from London, and as expected, the latter data generally exhibit higher values, as shown in Table 2.

Some of the measurements made by Brown and Escombe are clearly questionable. On August 9, 1898, for example, they obtained an anomalously low value of 243 ppm which suggests that they did not recover all the CO_2 from the sample. The existence of this low value raises the suspicion that they may not have recovered all of the CO_2 in other measurements. During January 1901, the air mass averages obtained were 265 ppm for marine air and 303 ppm for polar marine air. Such a wide disparity in marine air cannot be valid in light of modern data showing much smaller CO_2 variations for air from over the oceans. Since, samples of continental air taken during the same month measured 305 and 308 ppm, close to the value for polar marine air, it is likely that the latter air was not free from contamination.

Though Brown and Escombe made measurements over several years, most of their observations occurred during the summer months. In some winter months only one or two measurements were made. With the data so unevenly distributed, we cannot make a meaningful comparison with the seasonal variation at Ocean Station "P". However, sufficient data were collected during some months to establish monthly means and standard deviations. Measurements were made during July during four successive years (1898 to 1901). Of 27 measurements, 16 marine and polar marine measurements have a mean of 287 ppm. The standard deviation of an individual measurement, so selected, is 8.2 ppm, and thus the standard error of the mean is 1.6 ppm. We compare this result to data for two December months during which considerable measurements were made (1898, 1900). Of 11 measurements, 7 similarly selected measurements have a mean of 283 ppm. The standard deviation of an individual measurement from the mean is 14.3 ppm, and the standard error of the mean is 5.4 ppm. The computed change of 4 ppm from July to December (287 to 283 ppm) is in the wrong direction (see Fig. 1) and is not significant, since the standard deviation in the difference is 6 ppm. Thus we cannot use these data to infer a seasonal relationship. The data for other months are still less satisfactory. We conclude that Brown and Escombe's data do not display a valid seasonal variation.

3.2. *Letts and Blake, Belfast, Ireland*

Due to especially large scatter, poor geographic locality, and monthly averages which range from 265 to 314 ppm, the data set of Letts and Blake (1900), obtained for the period from 8 February to 7 July, 1877, will be left out of our discussion. (We note in passing that Letts and Blake wrote a scholarly and interesting review of the nineteenth century data obtained by a large number of investigators.)

3.3. *Müntz and Aubin at Vincennes, France and elsewhere*

Müntz and Aubin rivaled Reiset at professing to be among the most careful of the 19th century investigators of CO_2. They extensively tested their apparatus with CO_2-free air, and they ran one experiment with a known CO_2 sample, in which they recovered almost all of the CO_2. Regrettably, they never again reported any calibrations of their apparatus. At Vincennes (48°51′N, 2°27′E), a park near the southeastern border of the city of Paris as it existed at that time, they made measurements from May to October 1881. A summary of the daytime data classified by air mass is given in Table 3. We exclude eight values for winds from the direction of Paris (W and NW).

The average of the tropical and continental values (280 ppm) is not significantly higher than that for marine and polar marine air (277 ppm). A review of all their data shows no strikingly low values; 270 ppm in May is the lowest. The highest value for marine and polar marine air (again excluding winds from the direction of

Table 3. *CO_2 data at Plaine de Vincennes during 1881*

Month	No. of measurements	Average CO_2 concentration (PPM)	Standard deviation (PPM)
	Marine and polar marine air		
May	2	272.0	1.4
June	3	282.3	3.1
July	2	277.5	0.7
August	3	273.6	1.5
	Tropical and continental air		
May	3	285.0	13.5
June	1	274.0	—
October	5	278.6	5.7

Paris) is 285 ppm, for tropical and continental air, 299 ppm. For air from the direction of Paris, (in all cases classified as marine air) the highest concentration is 310 ppm. These relations suggest that both distant and nearby sources contaminated some of the samples. Three measurements were made at night. These are too few to establish a statistically valid day-night difference.

Müntz and Aubin made measurements at several other sites both in France and overseas. The data which they collected within the city of Paris (December 1880–June 1881) and at l'Institut Agronomique near Paris (February 1881–December 1881) have mean values much higher than the mean of the data from Vincennes, irrespective of air mass. Evidently, for the urban environment of Paris it is impossible to find evidence of uncontaminated air by applying Callendar's selection system. Two other stations, though not included in Callendar's analysis, should have provided uncontaminated data: one at Cape Horn and the other at Pic du Midi in the Pyrenees, near the border between France and Spain. First, we will consider the data from Pic du Midi.

At an altitude of 2877 meters, Pic du Midi is far from any major urban center. Müntz and Aubin (1881b, p. 798) felt that prevailing winds would provide unusually suitable air for sampling ("courants superieurs"). The remoteness of the station indicates that the measurements should be free from local man-made CO_2. Therefore we examine these data even though Callendar did not include them in his classification scheme. The first series of data, taken in August, 1881, are reproduced in Table 4.

The range of values from 269 ppm to 301 ppm is larger than we would expect for an area free from contamination. Considering the strong winds, at least one of the two widely varying values obtained on 13 August probably involves analytical error. If we exclude these values, the range is reduced between 275 and 301 ppm. If we further exclude the two high values on the first day of the experiment on the excuse that their equipment was perhaps not yet working quite

Table 4. *CO_2 data for Pic du Midi during 1881*

Date	Time of sampling	Wind	CO_2 concentration (PPM)
9 August	12:36 p.m.– 4:00 p.m.	southwest very strong	301
9 August	4:00 p.m.– 7:35 p.m.	southwest	295
10 August	8:33 a.m.– 2:07 p.m.	northwest weak	291
10 August	2:07 p.m.– 6:58 p.m.	northwest	275
11 August	7:34 a.m.–11:18 a.m.	southeast variable	293
11 August	11:19 a.m.– 3:01 p.m.	southeast variable	280
11 August	3:02 p.m.– 6:45 p.m.	southeast variable	276
12 August	7:19 a.m.–10:50 a.m.	southeast very weak	287
12 August	10:51 a.m.– 2:24 p.m.	southeast very weak	285
12 August	2:25 p.m.– 6:07 p.m.	southeast very weak	279
13 August	11:10 a.m.– 2:40 p.m.	southeast very strong	287
13 August	2:43 p.m.– 6:28 p.m.	southwest very strong	269
14 August	9:31 a.m.– 1:17 p.m.	southwest	293
14 August	1:17 p.m.– 4:55 p.m.	southwest	289

correctly, the range is further reduced between 275 and 293 ppm. This range is not totally unreasonable when we take a close look at the daily trends.

Müntz and Aubin made repeated measurements each day, one in the morning and one or two in the subsequent afternoon or early evening. Thus, a check can be made for influence by local affects, especially photosynthesis and respiration of plants. On each day, without exception, the concentration of CO_2 decreases during the day. This is the trend expected from plant activity, which tends to increase the concentration of CO_2 during the night and decrease it as the day progresses. The average daily range of 12 ppm of CO_2 (no data excluded) may be acceptable for the month of August when we expect a maximum influence of plant activity from not-too-distant vegetation at lower elevations. The median of the data, which removes the high and low values most likely to be associated with photosynthesis and respiration, is 288 ppm. This is close to the mean value of 285 ppm for all of the data excluding the 9th and 13th of August. These non-excluded data are typically not skewed positively as one would expect from contamination. They have a standard deviation of individual measurements of 6.9 ppm. We propose that these data may be valid.

The following year, Müntz and Aubin (1886) carried out 5 additional measurements at Pic du Midi, shown in Table 5. The two results on 22 August show a greater diurnal difference than ever found in 1881. The first sample is lower than the second in contrast to the 1881 data and seems likely to be affected by analytic error. A single value on 23 August appears to be unreasonably high. This leaves for consideration only a single pair of values on 21 August. These are consistent with the results for 1881. The data set is clearly too small to be of much value in confirming the 1881 data.

In 1883 Müntz and Aubin (1886) report a more extensive revisit to Pic du Midi in which 19 samples were taken between 7 and 19 August. The data show a striking change to lower values. The range is from 252 ppm to 294 ppm; the mean is 267 ppm. We postpone further comment on these data until we discuss the southern hemisphere data of Müntz and coworkers.

In 1882 Müntz and Aubin, assisted by a Dr. Hyades, established a remote CO_2 monitoring station at Cape Horn, at the extreme southern point of South America. Between 31 October 1882 and 1 July 1883, Dr. Hyades made 17 measurements at night and 22 during the day and found almost identical means (Müntz and Aubin, 1884). Furthermore, on occasions when consecutive day and night measurements were made, the values agreed within a few ppm. Evidently neither local plant activity nor combustion influenced this data set. Nevertheless, the scatter of the data from Cape Horn is greater than that at Pic du Midi.

The mean of the 39 Cape Horn measurements is 256 ppm, astonishingly low compared to the 1881 data at Pic du Midi. The range of values is from 231 to 285 ppm. Three measurements lie between 230 and 240 ppm, and 5 more between 240 and 250 ppm. All but four of the remaining measurements lie between 250 and 270 ppm. In the sole instance that measurements were made on two consecutive days, June 16 and June 17, 1881, the values of 232 and 259 ppm respectively. Since the annual range in southern hemispheric CO_2 concentration south of 20°, according to modern data, is less than 3 ppm (Fraser et al., 1983), these measurements almost surely involves

Table 5. *CO_2 data for Pic du Midi during 1882*

Date	Time of sampling	Wind	CO_2 concentration (PPM)
21 August	11:13 a.m.– 1:27 p.m.	northeast weak	286
21 August	8:30 p.m.–11:50 p.m.	violent	283
22 August	11:50 a.m.– 2:15 p.m.	northeast and southeast	263
22 August	8:30 p.m.–11:10 p.m.	west	285
23 August	12:05 p.m.– 2:15 p.m.	west southwest	307

Table 6. *CO_2 data from the Romanche during 1883*

Date	Time of day	Latitude	CO_2 concentration (PPM)
Sept 20	2:35 to 5:15 p.m.	42°37′S	274
Sept 28	2:40 to 4:30 p.m.	25°45′S	277
Oct 1	9:30 to 11:35 a.m.	23°36′S	272
Oct 4	2:34 to 5:40 p.m.	16°44′S	270
Oct 16	12:36 to 2:48 p.m.	7°10′N	249
Oct 21	12:27 to 2:46 p.m.	14°40′N	270

large analytical errors. The same explanation seems likely for the anomalously low measurement made on board a ship, the *Romanche* by Dr. Hyades on his return voyage from Cape Horn. These measurements are listed in Table 6. The low measurement of 16 October is clearly at odds with the remaining data.

Müntz and Aubin do not report that Dr. Hyades tested the CO_2 apparatus, for example with samples of known concentration, while at Cape Horn or at sea. Considering that these authors typically provided such details in their articles, we presume that he did not. The anomalous measurements reported from the station at Cape Horn and aboard the *Romanche* make both sets of data suspect. Additional data collected in the western hemisphere during an expedition to observe the planet Venus (Müntz and Aubin, 1883) show a similar tendency toward low concentrations. We conclude that these southern hemisphere data cannot be relied upon.

Nearly 30 years later, Müntz and Lainé (1911) reported 11 additional measurements made in high southern latitudes between 64°S and 70°S. The reported range in concentration is from 145 ppm to 255 ppm. These data are so variable as to be of little intrinsic value, and furthermore were obtained by an inferior method in which 3 l evacuated flasks were exposed at the site, sealed there, and then analyzed later in France by absorption in potassium hydroxide. They show, however, that Müntz, if not his former partner Aubin, was willing to accept very low data as valid. In the authors' words, the low concentrations not only "verify" the earlier Cape Horn studies. but "singularly accentuate" them! Even Callendar (1958, p. 247) was intrigued by these data.

We are struck by the fact that the means of all of the data reported by Müntz and Aubin after 1881 are lower than their earlier data. Most of their later air samples were from the southern hemisphere and thus imply a large hemispheric gradient. The August 1883 data for Pic du Midi dispute this inference, however, since they agree with contemporary southern hemisphere data within the statistical uncertainty of the means. During August 1883 the atmospheric CO_2 concentrations at Pic du Midi, on the other hand, really could not have differed so greatly from those of 1881 and 1882. Müntz and Aubin's CO_2 data, as they became progressively lower with time, showed increased scatter. Thus, it is likely that their later data are more in error than their earlier data. Incomplete recover of the CO_2 absorbed in their sample tubes, as suggested by Siegenthaler (1984), seems to us to be a likely cause of their low values, but Siegenthaler's further suggestion that incomplete recovery was a result of long storage times does not appear to account very well for the low values at Pic du Midi. Presumably these samples were stored for approximately the same length of time as the samples from 1881 and 1882. Very cold air, proposed by Wigley as another possible cause of incomplete absorption, also cannot apply to the Pic du Midi data. The 1881 values of 269 ppm on 13 August, 1881 and 263 ppm on 22 August, 1882, suggest that the tendency to produce low values existed at Pic du Midi from the outset of the study, and simply became worse as the experiments progressed.

Most of the 1882 and 1883 data of Müntz and Aubin were obtained outside France by assistants. It is not uncommon for field apparatus operated at remote sites for long times to degrade in performance, especially when operated by assistants. It seems to us that CO_2 may have been incompletely recovered in some of the sample tubes at the time of collection, perhaps owing to too rapid flow rates or a leak in the connecting lines. In any case, we feel justified in rejecting all of the data of Müntz and Aubin taken after 1881. During 1881 only the set from Pic du Midi are likely to indicate uncontaminated air, because the other data were obtained too near to the city of Paris. These 10 mountain air data (excluding data for the 9th and 13th of August) yield, on average, a CO_2 concentration for August of 285 ppm relative to moist air, with a standard deviation in the mean of 2.2 ppm.

3.4. *Petermann and Graftiau at Gembloux, Belgium*

Petermann and Graftiau (1892) made 525 measurements at Gembloux, a village some 40 km south-east of Brussels, (at 50°34′N, 4°42′E) between May 1890 and November 1891 presumably during day light hours. Their data were reported with respect to dry air. Callendar found that marine or polar marine air had been sampled during 265 of the measurements. Considering the large number of data it should be possible to determine monthly trends and compare them with the Station "P" data. Unfortunately, these data appear, after those of Letts and Blake (1900), to be the least reliable of the five sets which Callendar compiled.

The standard deviations of individual measurements of selected marine and polar marine air from the monthly means of 19 different monthly sets of data range from 5.9 ppm to 18.9 ppm. For 13 of the 19 months the standard deviation is over 10 ppm. Although the selection of only marine and polar marine air eliminates some suspicious data, many values above 315 ppm still remain. For example, in August, 1890, individual values of 319, 321, and 339 ppm of CO_2 for

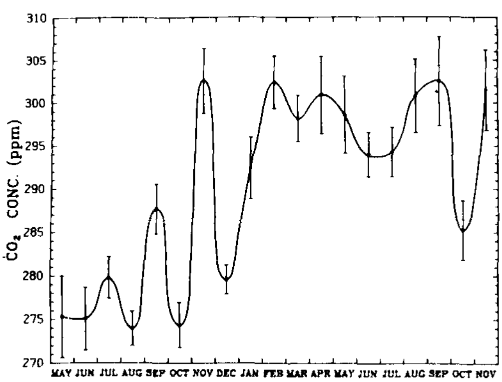

Fig. 2. Monthly average concentration of CO_2 in ppm for marine and polar marine air as measured by Petermann and Graftiau (1892) at Gembloux, Belgium (50°N, 5°E). Vertical bars indicate the range of uncertainty expressed as the standard deviation of the monthly means.

marine and polar marine air were reported. These were listed by Callendar without any suspicion, expressed in his notebook, that these data were contaminated.

Although Gembloux is not close to a metropolitan area, it is far enough inland that air sampled there may well have been influenced locally by combustion and plant activity. A graph of the monthly averages, given in Fig. 2, further emphasizes that the measurements of Petermann and Graftiau do not reflect the expected annual cycle found at Ocean Station "P". Thus, this data set is of unexpectedly poor quality even after applying Callendar's selection scheme. Unfortunately the data set's large size strongly influences Callendar's means for the seasonal variation, since he averaged with the same weight all of the individual measurements of the 5 investigators.

3.5. *Reiset at Ecorchebouef, France*

The data of Reiset (1880a, 1882), for several reasons, show the most promise for reliability. Reiset made measurements at Ecorcheboeuf (45°57′N, 1°08′E) along the Atlantic coastline of northwestern France about 8 km southwest of Dieppe. This station was the only one studied by Callendar that was both far from a major city and near a coast. Reiset's measurements were made over an extended period, from September 1872 to August 1873, from June 1879 to November 1879, and from June 1880 to August 1880. They are second only to Petermann and Graftiau in number, and are sufficient to allow some checking for seasonal variations. Reiset made a substantial number of measurements during the night, so that we may assess diurnal variability. He removed the influence of water vapor on the CO_2 concentration by reporting CO_2 data relative to dry air, a refinement not mentioned by Müntz and Aubin. His articles indicate that he had a sound grasp of his subject. For example, he declared (Reiset 1880b), as did Müntz and Aubin (1881b; 1882), *that the* CO_2 *concentration should* not show significant variations with altitude at a time when this idea was still controversial. His set of measurements commence the earliest of the five sets considered by Callendar (1940b). He was thus the first investigator to obtain measurements to a precision approaching that attained in recent times.

The data set of Reiset is large enough that measured differences between day and night values of selected marine and polar marine air should be significant. For samples collected during sea breezes, no diurnal variation should have existed, since plant activity in sea water does not appreciably affect CO_2 in the overlying air owing to the slow rate of air-sea exchange for CO_2. The night time data of Reiset are, nevertheless, typically higher than the daytime data. For 14 of the 17 months in which measurements were made both during the day and the night, the monthly means for night measurements are higher by 5 ppm or more than the day time data. On numerous occasions the nighttime sampling occurred with the wind coming from the ocean. These results suggest some local influence of vegetation or combustion at the site even during sea breezes. The increase in turbulence during the day makes daytime measurements less susceptible to local influence. Thus, except for periods of exceptionally strong winds, we prefer to consider only the daytime values.

For marine and polar marine measurements, the standard deviations from monthly means are considerably lower than those for all other investigators except Müntz and Aubin. Night time standard deviations are larger than daytime values. Overall, the nighttime monthly standard deviation of individual measurements is 5.1 ppm, the daytime deviation is 3.7 ppm. There are no conspicuously low values; the lowest individual value is 276 ppm. There is only one conspicuously high daytime value of 315 ppm. This overall consistency of Reiset's data, and the small standard deviations suggest good sampling and analysis techniques. The daytime monthly means are plotted in Fig. 3.

Even for Reiset's marine and polar marine daytime data, there is no well defined seasonal variation in the monthly means. Unfortunately, after removing nighttime values and continental, tropical, and indefinite data, only a few, typically 2 or 3 data per month, remain. (These low numbers cause the standard deviations of the monthly means to be nearly as large as those of Petermann and Graftiau (1892) although the individual errors are considerably smaller.) Without regard to season, the 74 selected marine and polar marine daytime values have an overall

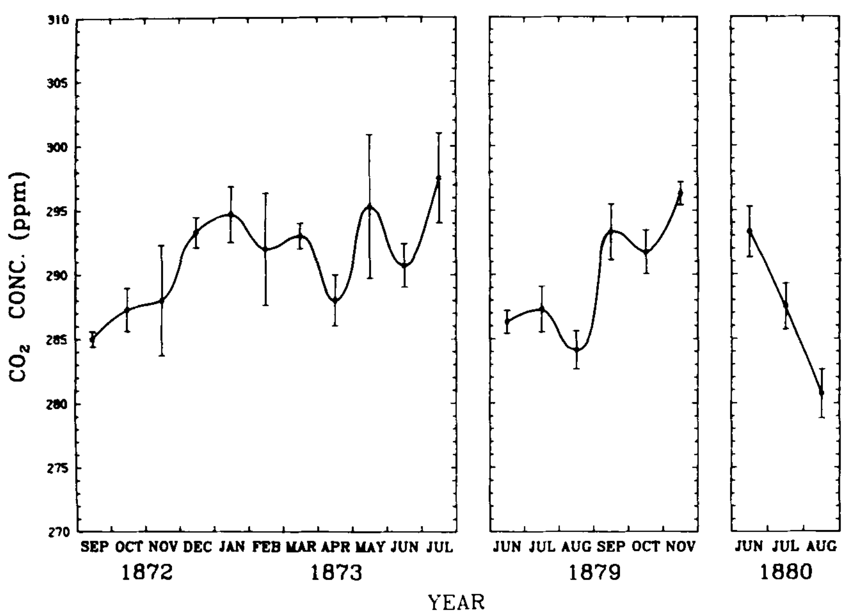

Fig. 3. Similar plot to Fig. 2 showing daytime data of Reiset at Ecorcheboeuf, France (46° N, 1° E). For November, 1872, which has only one concentration value, the error is assumed to be equal to the average error of individual measurements for the other months.

Table 7. *Data of Reiset according to time of day and wind vector*

Symbol in Figs. 5, 6	Time	Wind force	Wind directions
Accepted data:			
	□ day	6–9	SW, WSW, W, WNW, NW, NNW, N
	□ day	4–5	WSW, W, WNW, NW, NNW, N
	□ day	2–3	WSW, W, WNW, NW, NNW, N
	○ day and night	4–9	WSW, W, WNW, NW, NNW
	○ day and night	2–3	WSW, W, WNW, NW, NNW
	△ night	6–9	W, WNW, NW, NNW
Rejected data:			
	+ day	6–9	NNE to SSW
	+ day	2–5	NNE to SW
	• day and night	2–9	N to SW
	× night	6–9	N to WSW
	× night	2–5	all directions
	× all times	0–1	all directions, calm, variable

mean of 289 ppm, and a standard deviation of individual measurements of 5.9 ppm.

Reiset (1882) furnished many details regarding his measurements, including, in most cases, wind direction (16 point compass) and in many cases wind strength. Weather conditions were reported for most dates of sampling. The terminology is not always consistent, but enough information is available further to screen his data beyond merely assigning air mass characteristics. Accordingly, we have organized his entire data set with respect to the scheme shown in Table 7. The definition of wind force is discussed below. As shown in Fig. 4, the coast line near the site runs approximately east-northeast and west-southwest. Thus the air there is likely to be without influence of nearby land, if the winds are between W and N. Directions of marginal land influence are SW to W, and N to NE. Winds from NE clockwise to SW probably bring in air which has passed extensively over nearby land. Because Great Britain, at closest approach, is only about 120 km away, CO_2 concentrations may also be influenced by this land mass, especially owing to combustion from the urbanized region around London, which lies 200 km NNW of the site. Thus the most favorable sampling directions for Reiset were W or WNW, where winds from over the Atlantic Ocean could reach the site by blowing through the English Channel. Air from NNE might also miss the British Isles, but the oceanic sector is too narrow to expect reliable samples from this direction.

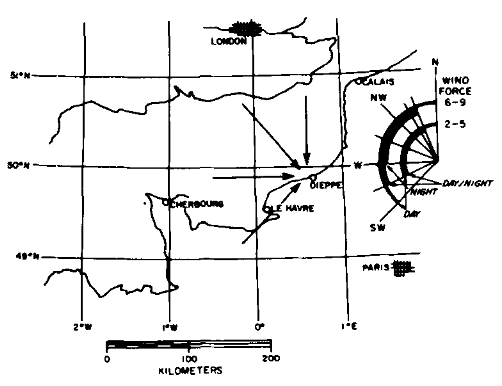

Fig. 4. Location of Reiset's sampling site at Ecorcheboeuf, France. Inset: wind directions and velocities of accepted data.

The strength of the wind is also important in judging air quality. Our experience sampling on a 300 meter long pier at the Scripps Institution of Oceanography indicates that strong on-shore winds from the Pacific ocean must persist for at least 12 h after a period of light off-shore winds before the CO_2 concentration becomes typical of marine air. Thus, those data of Reiset during sustained strong winds from off the ocean are most likely to be valid.

We were aided in our analysis of wind by information supplied in Callendar's notebook. We checked Callendar's wind data against

Table 8. *Scale of wind speed used by Callendar (1940b, p. 41)*

Wind	Force
calm and variable	—
light	1
moderate breeze	2 and 3
fresh and strong	4 to 9

Table 9. *Monthly departures in the concentration of atmospheric CO_2 in ppm from the long-term trend at ocean weather station "P" (50° N, 145° W)*

Month	Departure (ppm)	Month	Departure (ppm)
Jan	1.47	Jul	−2.44
Feb	2.24	Aug	−7.11
Mar	3.15	Sep	−6.76
Apr	4.49	Oct	−2.82
May	4.80	Nov	−0.01
Jun	2.50	Dec	0.78

Reiset's. We find that in most cases the wind directions are the same or nearly the same. Reiset, however, indicated wind strength only by descriptive terms such as "fort" and "tres fort" (for strong and very strong), whereas Callendar indicated strength on a scale of 1 to 9 from light to strong (see Table 8). Callendar supplied no information on how he determined the wind. He indicated winds for all of the data sets of his study, some of which (Brown and Escombe for example) furnished no wind data at all. For Müntz and Aubin's data at Pic du Midi he reported winds stated to be for Biarritz, a nearby coastal community. These appear to be direct observations. Perhaps with respect to the Reiset data he found wind data for the nearby town of Dieppe. We have not proved this, however, and we therefore have accepted Callendar's wind data on the basis that they correspond closely with Reiset's descriptive wind data. Reiset reported "very strong" winds on 23 occasions. Callendar classified 19 of these as "6" two as "7" and one each as "2" and "9". Thus only in one instance is there a discrepancy. Reiset reported "strong" winds on 15 occasions. Callendar classified 14 of these as "5" and one as "2", again a single discrepancy. Thus with few exceptions Callendar classified Reiset's "strong" winds as "5", and "very strong" winds as "6" to "9".

There are 12 additional occasions when Callendar classified the wind as "5" or greater. Of these, 7 were reported by Reiset as some kind of violent or stormy weather, 4 were not noted, and one was called only "rather strong", again no important discrepancy. In one case Callendar wrote a "10" for a wind strength. The concentration appears to be too high (310 ppm), and since Reiset's information does not substantiate a strong wind and Callendar defined strength only to "9", we presume that this is a copy error. In this instance, we have assumed that the wind was light. Finally, Reiset indicated stormy or violent weather on 8 occasions when Callendar reported wind strengths below "5".

We adopted Callendar's wind force designations in our scheme to classify Reiset's data, as shown in Table 8. To appraise Reiset's data we have compared various selected portions with the average seasonal cycle for Ocean Station "P" (see Table 9) using for the latter a four harmonic fit of observations from 1969 to 1981 with coefficients taken from the analysis of Keeling et al. (1985). The mean concentration of the curve is adjusted to produce the best least squares fit to the selected data of Reiset.

As a first step we fitted Reiset's data without regard for wind vector, but with a separate analysis of daytime data. We found, as previously, that the daytime data are lower and less scattered. On this basis we established different criteria of wind selection depending on the time of sampling. For winds from W to NNW and strengths from "6" to "9" we accepted data for all times of sampling, because the data for these strong winds show no correlation with day or night sampling. For daytime data we included data for all winds from SW to N if the strength was from "6" to "9", all winds from "WSW" to "N" for strengths "2" to "5". Data collected during both day and night were treated in the same way as daytime data except that we rejected winds from "N".

In Figs. 5 and 6, we compare the Reiset data with the CO_2 trend for Ocean Station "P" for 1872–1873 and 1879–1880 respectively. We distinguish by separate symbols selected and rejected data; day, day-night, and night data; and, for accepted data, we plot smaller symbols

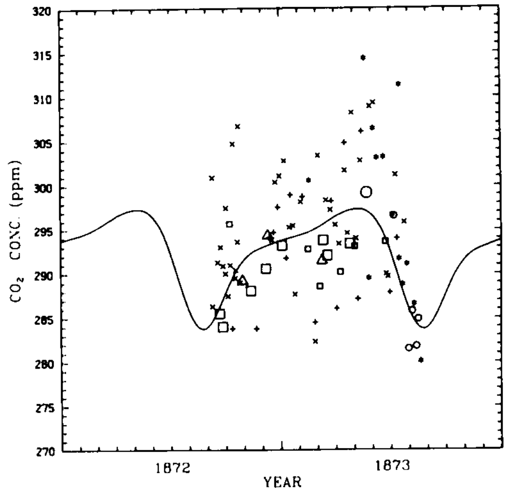

Fig. 5. Atmospheric CO_2 data of Reiset, in ppm, during 1872–1873 compared with the average seasonal trend in atmospheric CO_2 at Ocean Weather Station "P", during 1969–1981. The individual data points are distinguished with respect to time of day, and wind vector, as shown in Table 7. Open squares, circles, and triangles denote accepted data. The symbols +, *, and × denote rejected data. The smooth curve is a four-harmonic representation of the seasonal cycle for Station "P". The mean value of this curve is chosen to give the best fit to the accepted data of Reiset, including data for 1889–1890 as well as 1872–1873.

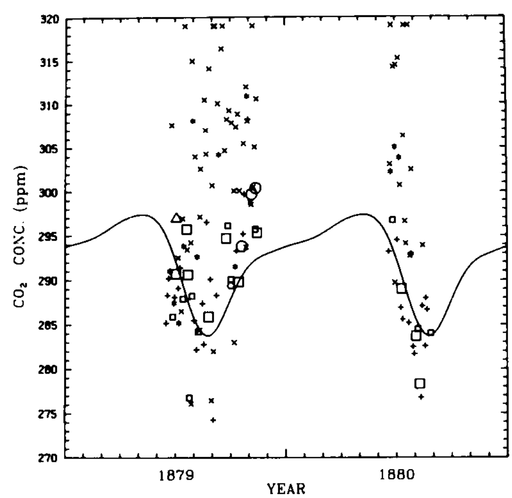

Fig. 6. Same as preceding figure except for 1889–1890. Concentrations above 314 ppm are plotted at the top of the figures.

for weak winds (of strength "2" and "3") than for stronger winds. The mean concentration for the Station "P" curve is adjusted to minimize the standard error in the fit to the accepted concentration values over the full record, 1872–1880. In Figs. 7 and 8 are similar plots with only the accepted data shown.

For the 1872–1873 period, which covers a full year, the accepted Reiset data appear to reflect the seasonal cycle of Station "P". This cycle

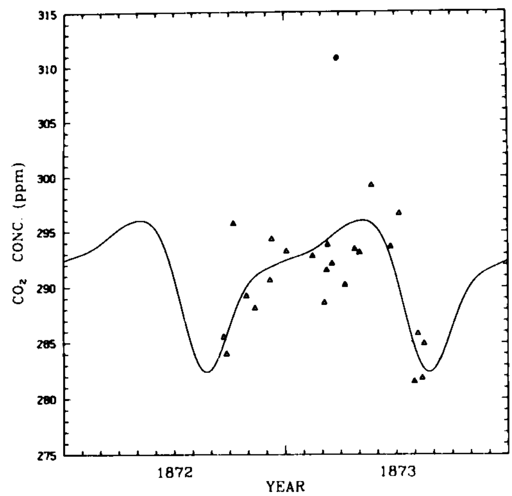

Fig. 7. Same as Fig. 5 except that only the accepted data of Reiset are plotted (as triangles).

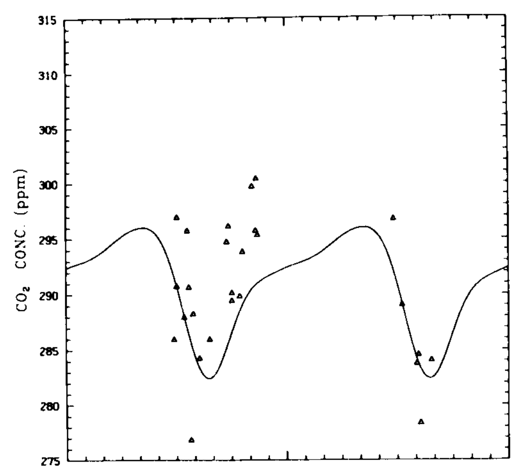

Fig. 8. Same as preceding figure except for 1889–1890.

demands an amplitude from peak to trough of 14 ppm. For a separate fit of the 1872–1873 data, this amplitude is realized with a standard error per point of only 3.4 ppm. The 1879 and 1880 data are for shorter periods, mainly during the summer. For 1879 a separate fit is clearly less good, having a standard error of 5.0 ppm, but the 1880 data fit, with a standard error of 3.2 ppm, is as good as for the 1872–1873 data. The mean annual concentration determined by a separate fit is also higher for 1879 than at other times: 294.6 ppm compared to 290.7 ppm for 1872–1873 and 291.2 ppm for 1880. The differences are not statistically significant, however. The mean of all of the selected data is 292.4 ppm, the mean, rejecting 1879 data, is 290.8 ppm.

The standard error of the mean owing to scatter of the data is clearly not a major cause of uncertainty. For all 49 selected data we arrive at 292.4 ± 1.2 ppm where the uncertainty is given now as *twice* the standard error of the mean. The average scatter is approximately three times that of the daily averages for Station "P" (1.20 ppm), shown in Fig. 9, not strikingly greater considering that Station "P" is situated over 900 km distant from the nearest land. In an extreme case the accepted data at Station "P" during the summer of 1980 are scattered over a range of 6 ppm, comparable to the scatter in Reiset's data.

In the autumn of 1879 higher values are found both in accepted and rejected data, suggesting a real difference in concentration compared to the autumn of 1872. It would be of interest to determine whether the average weather patterns of the 2 years show any basis for this difference. We did not, however, attempt this study.

Reiset reported some quite low daytime concentrations. Almost all of these occurred during light winds from the south or east. Several of these in the 1872–1873 period occurred during the winter. It would be interesting to determine whether that particular winter was mild enough to permit some photosynthesis.

Although further study of the Reiset data might uncover additional information, we are struck by the extent that variations in his data seem to reflect possibly real variations correlating with wind speed and direction. Our greater success in obtaining low scatter using wind criteria rather than the air mass classification of Callendar suggests that local sources and sinks rather than large scale processes produce most of the variations seen.

Early investigators, as well as Callendar, and

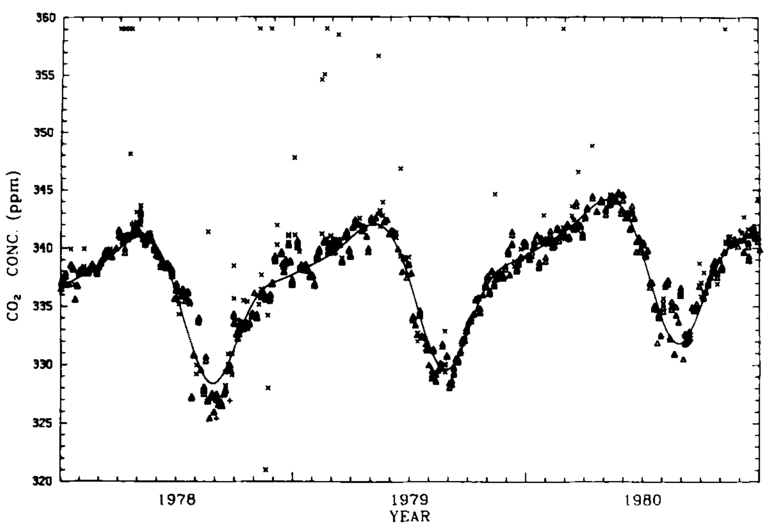

Fig. 9. Atmospheric CO_2 data, in ppm, for Ocean Weather Station "P" during 1978–1980. Triangles: data accepted as valid by Keeling et al. (1985); crosses: data rejected because replicate samples did not agree to within 0.40 ppm. The smooth curve is a least squares fit to the data as described by Keeling et al. (1985) in which the seasonal component is represented by the same four harmonic function shown in the curves of Figs. 5 to 10.

even more recently Fonselius et al. (1956), were impressed by the apparent correlation of atmospheric CO_2 concentrations with air mass history. Modern data demonstrate, however, that large spatial differences in the CO_2 above the friction layer do not exist (Bischoff, 1965, 1966, Keeling et al. 1968), and that clear cut variations from one air mass to another should not be seen in data that scatter to the order of 3 ppm or more. It is therefore reassuring that the Reiset data can as well be interpreted on the basis of more local characteristics of the air sampled.

With respect to Reiset's daytime data, we obtain nearly the same mean concentration whether or not we exclude the more questionable data during light winds from over land. This suggests that the data of Brown and Escombe, and the early measurements of Müntz and Aubin may be nearly correct in their means in spite of showing considerable scatter in the individual values. We reexamine these data, below.

4. Discussion

Our original goal was to find, if possible, a seasonal cycle in the nineteenth century atmospheric CO_2 data in agreement with modern observations by applying the air mass criteria of Callendar (1940a) to screen out contaminated data. This goal we have demonstrated to be unachievable.

We find, after screening out suspicious data on the basis of air mass, that none of the five data sets of Callendar show the seasonal cycle which Callendar found in combination. Only two of his data sets were extensive enough to establish seasonality separately. When these were pooled by Callendar with equal weight to each measurement, the more numerous set of Petermann and Graftiau considerably outweighed the data set of Reiset. With or without screening by air mass, the Petermann and Graftiau data are unsatisfactory. Adding to this data set, and Reiset's, the three short records of predominantly summer data cannot produce a more reliable estimate of the seasonal cycle. Thus, it is probably accidental that the seasonal means reported by Callendar are in agreement with the seasonal cycle of Ocean Station "P" as shown in Fig. 1.

Taking a different approach, we have shown that the data of Reiset (1882), individually screened by time of day and by wind speed and direction rather than by air mass, are largely consistent with the expected seasonal cycle in CO_2. Thus, if Reiset's data could be shown to be without analytical bias, they would be nearly as reliable as modern data. It is of considerable value, therefore, to consider what evidence there is that other 19th century data obtained by different techniques yield the same results under similar conditions. In this more limited quest we may obtain useful information even for short records, provided that they show no internal evidence of seriously faulty sampling or analysis. The data of Müntz and Aubin for the summer of 1881 are thus worth another look.

At Vincennes and Pic du Midi, Müntz and Aubin passed 200 to 250 liters of air through pumice stone impregnated with potassium hydroxide contained in a metal tube, whereas Reiset at Ecorcheboeuf passed 500 to 600 liters of air through 9 successive absorption chambers of barium hydroxide solution. The Reiset method allowed for a visual check against incomplete absorption, since the down stream chambers should remain clear of precipitated $BaCO_3$ if all of the CO_2 was absorbed in the first two bottles. Müntz and Aubin, on the other hand, confirmed their method near the beginning of their study with one sample of known concentration.

Since the Vincennes CO_2 measurements show no systematic differences for different air masses, let us consider them as a single set. These data, omitting winds from the direction of Paris (see Table 3), have a mean of 278 ppm. Corrected for water vapor (average recorded temperature 22.0°C, air pressure 757 mm/Hg, 70% humidity assumed) raises the value to about 283 ppm. If the Vincennes air exhibited the seasonal cycle of Ocean Station "P" (see Table 9) these data, on average, would have been 0.33 ppm lower than the annual mean. Thus they imply an annual mean of 283 ppm, somewhat lower than the 292 ppm which we deduce from the data of Reiset.

Because the Vincennes measurements were made during the daytime in May through October, they may have been depleted in CO_2 owing to photosynthesis. But even if photosynthesis was not an important factor, or was offset by contamination from combustion sources, comparison with Reiset's data suggests that analytical errors should not have been greater than about 10 ppm between the two methods used.

The 14 analyses for Pic du Midi in August 1881 are a second source of possibly valid data. The average of all 14 analyses is 286 ppm. If we exclude the analyses of the 9th and 13th of August, the average is 285 ppm. Corrected for water vapor (average recorded temperature 13.3°C, air pressure 537 mm/Hg, 70% humidity assumed) the August mean would probably have been near 289 ppm. If we apply as a seasonal adjustment, the monthly departure for Ocean Station "P" of −7.11 ppm (Table 9) we arrive at 296 ppm as an estimate of the annual mean, in closer agreement to Reiset's data than the Vincennes data.

The efforts of Brown and Escombe (1905b) may also furnish a useful test of Reiset's analytical techniques. These botanists reported making their measurements with a "Reiset's absorption apparatus". Thus instead of an independent method, they provide us with an independent application of the same method. They evidently regarded the Reiset apparatus as being so well known to the readers of the Royal Society Proceedings that they did not need to describe it or even cite a reference to Reiset's articles. This lack of specificity is in contrast to the careful expositions on methodology of Müntz and Aubin and of Reiset. On the other hand, in a preceding article, Brown and Escombe (1905a) compared a "Reiset's apparatus" with a "new method" for the determination of atmospheric carbon dioxide based on the rate of its absorption by a free surface of a solution of caustic alkali. They found agreement between individual samples to within 2% with no systematic difference between the methods. Thus we may regard their measurements at Kew gardens as equivalent to having been carried out by a method independent of Reiset's.

Brown and Escombe's data (see Table 2) show systematic variations with air mass. Marine and polar marine air, having been sampled during south westerly to northerly winds, was probably only slightly, if at all, affected by contamination from London, as Callendar (1940a) believed. The most numerous data of Brown and Escombe are for the month of July. The 16 observations during 1898 through 1901 for marine and polar marine air average 287 ppm relative to dry air. When seasonally adjusted by the Ocean Station "P" monthly departure of −2.44 ppm, this value converts to an annual mean of approximately 289 ppm. The average of all marine and polar marine data (see Table 2) is 287 ppm, so that the July data are consistent with the rest of their data set, so selected. Thus Brown and Escombe closely duplicated Reiset's observations using a similar apparatus checked by an independent method.

5. Comparison with data from ice core samples

Measurements of the CO_2 concentration in air occluded in ice cores, recently reported by Neftel et al. (1985) provide a time series of atmospheric CO_2 concentrations from 1750 to recent times. For each data point they estimated a standard deviation of CO_2 concentrations of about 1.5 ppm, and an uncertainty in the time of occlusion of about ±11 years. In Fig. 10 we compare their results with the mean concentration which we derive from the direct observations of Reiset (1882). The Reiset data point agrees within statistics with the ice core data.

6. Conclusions

The investigation of Reiset (1882) stands out as the most authoritative of 5 studies singled out by

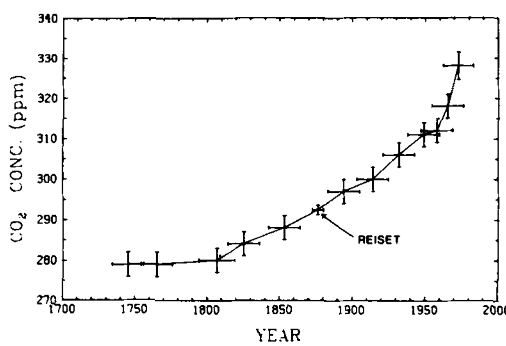

Fig. 10. Comparison of our estimate of the CO_2 concentration in 1872–1880 from direct observations of Reiset (1882) with recent measurements of air extracted from ice cores by Neftel et al. (1985). Vertical bars indicate the range in uncertainty in concentration expressed as twice the standard deviation of the mean. Horizontal bars indicate the range in time of the air sampled. Straight lines connect the ice core data points to show their trend with time.

Callendar (1940a) as providing reliable observations of atmospheric carbon dioxide during the late nineteenth century. Reiset used an absorption apparatus which could be visually checked for completeness of the removal of CO_2 from an air stream, and his results show no abnormally low concentrations suggestive of incomplete absorption. He chose as a sampling site a coastal location not near any major city. He carried out measurements over all months of the year. He included a correction for water vapor, thus indicating that he was concerned about systematic errors of the order of 1 or 2 ppm. He was keenly interested in the significance of his data and entered into discussions of the controversies of his day with regard to the natural variability of atmospheric CO_2. From his data we estimate that the annual mean concentration of atmospheric CO_2 between 1872 and 1880 near 50° N and the Greenwich meridian was about 292 ppm.

Müntz and Aubin (1886) carried out an even more extensive investigation than Reiset and showed an equally keen interest in their results. Their data are not as convincing, however. From the onset some of their results seem to be too low, and after the first year of their study, the number and disparity of low values increases. They probably did not correct for water vapor. Their principal site, at Vincennes, inland and near Paris, was not as well chosen as Reiset's. On the other hand, they took the great trouble to sample on a high mountain in the Pyrennes. The Vincennes data imply an annual mean 9 ppm lower than we deduce from Reiset's data, the mountain data of Pic du Midi for 1881, imply a value 4 ppm higher. Thus their data, obtained by a different technique than Reiset's, although not entirely consistent, suggest that Reiset's data are without serious analytical bias.

Brown and Escombe (1905b) investigated atmospheric carbon dioxide only as a side line to botanical studies. They provide minimal information on methodology and weather conditions. A few of their data seem abnormally low. Their sampling was sporadic over a four year period at a site poorly chosen to study CO_2, albeit convenient to their botanical laboratory. Their results are of interest mainly because they used an apparatus similar to Reiset's which had been carefully tested by an independent method. We find their relatively abundant data for July of 1897 to 1901 to be in close agreement with Reiset's (3 ppm lower).

The other 2 investigators considered by Callendar (1940a) produced data too unsatisfactory to encourage comparison with Reiset's. We did not attempt to search further for data not considered by Callendar, although this might be worthwhile.

In conclusion, the measurements of atmospheric carbon dioxide carried out by Reiset (1882) from 1872 to 1880 on the coast of northern France appear to be valid. They indicate a mean annual concentration, with respect to dry air, of 292.4 ± 1.2 ppm. Comparisons with other possibly valid contemporary data suggest that these data are not biased by more than 10 ppm. It is thus unlikely that the CO_2 concentration was less than 282 ppm in the late nineteenth century, and was probably close to 292 ppm.

7. Epilogue

Since the writing of this article it has been brought to our attention that Fraser et al. (1986) have a report in press reappraising the nineteenth century data in the manner proposed by the June, 1983 conference of WMO (1983). Using selection criteria designed to accept data collected during periods of maximum atmospheric mixing, and based on six independent sets of observations (the five preferred by Callendar, 1940a, supplemented with data of Schultze (1871), they arrive at 285 ± 7 ppm for the northern hemisphere mean concentration near 1880, if they give equal weight to each investigator, or 280 ± 12 ppm, if they give equal weight to each location sampled. They have used modern data from continental Europe and from weather ships and the Azores islands to adjust the 19th century data seasonally. The article does not furnish all the details of their analysis. However, they find nearly the same means and standard errors for each observer as we do, in spite of using different selection and detrending criteria. Their combined means of 6 sets of observations are lower than the mean which we find from Reiset's data principally owing to their inclusion of data of Müntz and Aubin, which, as we have discussed, give typically lower values than other nineteenth century investigators. They agree with us that the data of Reiset appear to be the most likely to benefit from detailed analysis, and indeed they recommend, as a further study, the construction of a Reiset apparatus calibrated against modern standards, a recommendation in which we concur.

8. Acknowledegments

We are most grateful to Mr. Justin Schove for the loan of Callendar's notebook on atmospheric CO_2 observations and for his sharing with us his understanding of Callendar's work. We thank Dr. William Elliott for supplying us with copies of several old articles and for his comments on them, and Mr. Timothy Whorf who carried out the calculations leading to Figs. 5 and 6, and Mr. Justin Lancaster for comments on our text.

This work was supported under contract RP2333 with the Electric Power Research Institute, Palo Alto, California, and the Climate Dynamics Program of the U.S. National Science Foundation, grant ATM83-10667.

REFERENCES

Bischof, W. 1965. Carbon dioxide concentrations in the upper troposphere and lower stratosphere. I. *Tellus* *17*, 398–402.

Bischof, W. 1966. Space and time variations of the CO_2 content of the troposphere and lower stratosphere. *Tellus 18*, 155–159.

Black, J. 1754. De humore acido a cibis orto, et magnesia alba. Ph.D. thesis. Univ. of Edinburgh.

Bray, J. R. 1959. An analysis of the possible recent change in atmospheric carbon dioxide concentration. *Tellus 11*, 220–230.

Brown, H. T. and Escombe, F. 1905a. On a new method for determination of atmospheric carbon dioxide, based on the rate of its absorption by a free surface of a solution of caustic alkali. *Proc. R. Soc. B.* *76*, 112–117.

Brown, H. T. and Escombe, F. 1905b. On the variations in the amount of carbon dioxide in the air of Kew during the years 1898–1901. *Proc. R. Soc. B.* *76*, 118–121.

Callendar, G. S. 1938. The artificial production of carbon dioxide and its influence on temperature. *Q. J. R. Meteorol. Soc. 64*, 223–240.

Callendar, G. S. 1940a. Variations of the amount of carbon dioxide in different air currents. *Q. J. R. Meteorol. Soc. 66*, 395–400.

Callendar, G. S. 1940b. Observations on the amount of carbon dioxide in the air. Manuscript Notebook, dated "1939–1940", 136 p.

Callendar, G. S. 1958. On the amount of carbon dioxide in the atmosphere. *Tellus 10*, 243–248.

Elliott, W. P. 1984. The pre-1958 atmospheric concentration of carbon dioxide. *EOS 65*, 416–417.

Fonselius, S., Koroleff, F. and Wärme, K.-E. 1956. Carbon dioxide variations in the atmosphere. *Tellus* *8*, 176–183.

Fraser, P. J., Pearman, G. I. and Hyson, P. 1983. The global distribution of atmospheric carbon dioxide. 2. A review of provisional background observations, 1978–1980. *J. Geophys. Res. 88*, 3591–3598.

Fraser, P. J., Elliott, W. P. and Waterman, L. S. 1986. Atmospheric CO_2 record from direct chemical measurements during the industrial era. In *Proceedings of the Sixth ORNL Life Sciences Symposium, 'The global carbon cycle'*. Springer-Verlag, New York, in press.

Keeling, C. D. 1978. The influence of Mauna Loa Observatory on the development of atmospheric CO_2 research. In *Mauna Loa Observatory 20th Anniversary Report*. Ed. by J. Miller, National Oceanographic and Atmospheric Administration, Special Report, pp. 36–54.

Keeling, C. D. 1979. The Suess effect: ^{13}Carbon-^{14}Carbon interrelations. *Environ. Int. 2*, 229–300.

Keeling, C. D., Harris, T. B. and Wilkins, E. M. 1968. Concentration of atmospheric carbon dioxide at 500 and 700 millibars. *J. Geophys. Res. 73*, 4511–4528.

Keeling, C. D., Whorf, T. P., Wong, C. S. and Bellagay, R. D. 1985. The concentration of atmospheric carbon dioxide at Ocean Weather Station 'P' from 1969 to 1981. *J. Geophys. Res. 90*, 10511–10528.

Komhyr, W. D., Gammon, R. H., Harris, T. B., Waterman, L. S., Conway, T. J., Taylor, W. R. and Thoning, K. W. 1985. Global atmospheric CO_2 distribution and variations from 1968–1982 NOAA/GMCC CO_2 flask sample data. *J. Geophys. Res. 90*, 5567–5596.

Letts, E. A. and Blake, R. F. 1900. The carbonic anhydride of the atmosphere. *Sci. Proc. R. Dublin soc.* *9*, New Series, 107–270.

Müntz, A. and Aubin, E. 1881a. Sur le dosage de l'acide carbonique das l'air. *Acad. Sci., Paris, Comptes Rendus 92*, 247–250.

Müntz, A. and Aubin, E. 1881b. Sur les proportions l'acide carbonique dans les hautes regions de l'atmosphére. *Acad. Sci., Paris, Comptes Rendus 93*, 797–799.

Müntz, A. and Aubin, E. 1882. Recherches sur les proportions d'acide carbonique contenues dans l'air. *Ann. Chim. Phys., 26, ser. 5*, 222–254.

Müntz, A. and Aubin, E. 1883. Dètermination de l'acide carbonique de l'air dans les stations d'observation du passage de Vénus. *Acad. Sci., Paris, Comptes Rendus 96*, 1793–1799.

Müntz, A. and Aubin, E. 1884. Détermination de l'acide carbonique de l'air effectuée par la mission du Cap Horn. *Acad. Sci., Paris, Comptes Rendus 98*, 487–494.

Müntz, A. and Aubin, E. 1886. Recherches sur la constitution chemique de l'atmosphere, d'aprés les expériences de M. le Dr. Hyades. *Mission Scientifique de Cap Horn 1882–1883, Tome III*, Gauthier-Villars, Paris, A1–A90.

Müntz, A. and Lainé, E. 1911. La proportion d'acide carbonique dans l'air des regions antarctiques. *Académie des Sciences*, 1116–1118.

Neftel, A., Moor, E., Oeschger, H. and Stauffer, B. 1985. Evidence from polar ice cores for the increase in atmospheric CO_2 in the past two centuries. *Nature 315*, 45–47.

Pearman, G. I. 1984. Pre-industrial atmospheric carbon dioxide levels: A recent assessment. *Search 15*, 42–45.

Petermann, A. and Graftiau, A. 1892. Recherches sur la composition de l'atmosphère. Première partie-Acide carbonique contenu dans l'air atmosphérique. Academic Royale des Sciences des lettres, et des beaux-arts de Belgique. *Couronnes et autres Memoires 47*, 3–77.

Reiset, J. 1880a. Recherches sur la proportion de l'acide carbonique dans l'air. *Acad. Sci., Paris, Comptes Rendus 90*, 1144–1148.

Reiset, J. 1880b. Proportion de l'acide carbonique dans l'air; réponse á M. Marié-Davy. *Acad. Sci., Paris, Comptes Rendus 90*, 1457–1459.

Reiset, J. 1882. Recherches sur la proportion de l'acide carbonique dans l'air. *Ann. Chim. et Phys. ser. 5, 26*, 145–221.

Schneider, S. H. 1983. The problem of pre-industrial CO_2 concentration—an editorial. *Climatic Change 5*, 311–313.

Schulze, F. 1871. Tägliche Beobachtungen über den Kohlensäuregehalt der Atmosphäre zu Rostok vom 18 October 1868 bis 31 Juli 1871. *Landw. Vers. Stat. 14*, 366–388.

Siegenthaler, U. 1984. 19th Century Measurements of Atmospheric CO_2—a comment. *Clim. Change 6*, 409–411.

Slocum, G. 1955. Has the amount of carbon dioxide in the atmosphere changed significantly since the beginning of the 20th century? *Mon. Wea. Rev. 83*, 225–231.

Stanhill, G. 1982. The Montsouris series of carbon dioxide concentration measurements, 1877–1910. *Clim. Change 4*, 221–237.

Stepanova, N. A. 1952. A selective annotated bibliography on carbon dioxide in the atmosphere. *Meterol. Abstr. Bibliogr. 3*, 137–171.

Waterman, L. S. 1983. Comments on "The Montsouris series of carbon dioxide concentration measurements, 1877–1910", by G. Stanhill. *Clim. change 5*, 413–415.

Wigley, T. M. L. 1983. The pre-industrial carbon dioxide level. *Clim. Change 5*, 315–319.

WMO, 1983. Report of the WMO (CAS) meeting of experts on the CO_2 concentration from pre-industrial times to I.G.Y. World Meteorological Organization World Climate Research Program, Publication WCP-53. Geneva, Switzerland, 34 p. plus appendices.

Zumbrunn, R., Friedli, H. J., Neftel, A. and Rauber, D. 1983. CO_2 measurements with an infrared laser spectrometer on flask samples collected at Jungfraujoch high-altitude research station (3500 m asl) and with light aircraft up to 8000 m over Switzerland. *J. Geophys. Res. 88*, 6853–6857.