On the Amount of Carbon Dioxide in the Atmosphere

By G. S. CALLENDAR

A. R. D. E. Ministry of Supply, London

(Manuscript recieived June 17, 1957)

Abstract

Of late years there has been much interest in the effect of human activities on the natural circulation of carbon. This demands a knowledge of the amount of CO_2 in atmosphere both now and in the immediate past. Here the average amount obtained by 30 of the most extensive series of observations between 1866 and 1956 is presented, and the reliability of the 19th century measurements discussed. A base value of 290 p.p.m. is proposed for the year 1900. Since then the observations show a rising trend which is similar in amount to the addition from fuel combustion. This result is not in accordance with recent radio carbon data, but the reasons for the discrepancy are obscure, and it is concluded that much further observational data is required to clarify this problem. Some old values, showing a remarkable fall of CO_2 in high southern latitudes, are assembled for comparison with the anticipated new measurements, to be taken in this zone during the Geophysical Year.

Introduction

During the last few years there has been much interest in problems associated with atmospheric carbon dioxide, and new methods have been brought to bear on some of them. Examples of the latter include the exchange of this gas between atmosphere, oceans and biosphere (CRAIG 1957, ARNOLD & ANDERSON 1957), its influence on climate (CALLENDAR 1949, PLASS, 1956), and the effect of human activities on the amount in circulation. The significance of man's activities for all these problems has been emphasised by Revelle and Suess (1957 P. 19) who say —"Thus human beings are now carrying out a large scale geophysical experiment of a kind which could not have happened in the past nor be reproduced in the future. Within a few centuries we are returning to the air and oceans the concentrated organic carbon stored over hundreds of millions of years."

In order to follow the course of this "experiment" it is important to know as accurately as possible how much CO_2 the atmosphere contained before the use of fossil fuel began to add a significant amount. Fortunately there was a lot of interest in the CO_2 problem towards the end of last centry, and a number of measurements of its amount in the atmosphere were made at a time when the contribution from fossil fuel was relatively small, certainly less than 2 % of the total already there.

These early measurements are scattered through the literature of many countries and the original papers are often difficult to find, or absent from central libraries. For this reason it has been thought worth while to include a summary, with references in appendix tables, of what appear to be the most representative average CO_2 values reported during the last 90 years. Others are rejected with the aid of simple criteria. From this summary a few 19th century averages have been selected as the most accurate, and, together with a brief discussion of the basis for selection, they should provide a reasonably accurate base line for the amount of CO_2 in the air of the north Atlantic region at the end of last century. The value proposed here for this quantity is 290 p.p.m. by volume.

Similar data for the present century is given in the Appendix, and compared with the amount of fuel CO_2 in Figure 1. Most of these recent averages appear to be quite reliable, and only a few scattered readings have had to be rejected because of the criteria mentioned above. They show a marked tendency for the amount of CO_2 to rise during the last few decades, roughly in proportion to the addition from fuel. However, the possibility of the latter causing such an increase of atmospheric CO_2 has been strongly questioned in the light of new radio-carbon measurements (REVELLE & SUESS l.c.) and the whole question is in a very interesting stage at the present time. Some further comments on it will be found below.

1. Rejection of inaccurate values

Because the measurement of CO_2 in the air may be, and often has been in the past, 100 % or more in error unless great care is taken in both air sampling and analysis, it is essential to use discrimination in deciding which of the old values are reliable. In some cases examination of the original papers will show that the samples used were not representative of the free air, but for others this is not so, and rejection criteria such as those given below must be used.

The following have been excluded from the tables as not representative of the free air:—

(a) Period mean values 10 % or more different from the general average of the time and region.

(b) Air samples taken in towns, because these often give 5 to 20 % more CO_2 than uncontaminated air.

(c)[1] Averages depending on only a few samples, or made within s short period, because real fluctuations may exceed 10 % in such cases.

(d) Measurements intended for special purposes, such as biological, soil air, atmospheric polution, etc.

As a result of these criteria practically all values reported before about 1870 had to be rejected. In those early days a relatively crude instrumentation seems to have been responsible for differences of 50—100 % between many of the reported averages. (See FONSELIUS et al. 1956. Fig. 1.) In addition to the sets which, quite obviously, do not represent free air conditions, there remain a few borderline cases where the reported value comes within 10 % of the genral average, but it has not been possible to estimate the quality of the air samples used. Either the original papers could not be found, or else the given data was insufficient for this purpose.—The latter being an all too common fault in reporting the old measurements. In some of these borderline cases the rather high average suggests that town air may have been included in the samples, these are marked + in the tables. On the other hand the rather low values reported from Dorpat suggest instrumental causes, and the overall average of the 18 sets in Appendix table A comes out only 1 % above the more certain measurements discussed in the next section.

2. The most reliable of the 19th Century observation

Although the weight of numbers in appendix table A gives what is probably a good average for the period and region, it will be appreciated that the sets used are a very mixed lot. Some of these averages are from an elaborate research, including flow rate—absorption studies, artificial sample checks, preferential surface absorption of CO_2 in sampling vessels, etc., whereas others are based on a large number of rapid determinations, or a few dozen free air samples taken in connection with some biological research.[1] In addition most of the averages include a significant proportion of local effects, such as:— Samples taken in stagnant surface air, at night, or over

[1] This criteria has been neglected in a few special cases, (Krogh, Spector, and certain of Muntz and Aubins obs.), where study of the original papers showed that it did not fully apply.

[1] Letts & Blake (Appx. A) in particular, made a study of the instrumental errors which arise in the CO_2 measurement.

water in which photosynthesis is active, in air which has recently traversed large urban areas, and so on. Hence some further selection is very desirable.

This has been attempted as far as the published data allow, with the asistance of the daily weater maps for west Europe, and the result is summarized in Table 1. It is, of course, a subjective estimate, but the writer is fairly confident that a completely independent assessment of the data for this period would find an average within about 1 % of that given. These sets are amongst several examined in relation to the weather maps of the period, and the results of this analysis have been discussed in an earlier paper (CALLENDAR 1940), which should be consulted for further details of the measurements.

Table 1. Preferred 19th century CO_2 averages. (All daytime obs.)

Authority [Ref. Appx. Table A]	Location	Observations			Average CO_2	
		Date	Period	No.	p.p.m.	Ref. Fig. 1
J. Reiset	N. Coast of France	1872—73	12 months	56	291.1	a
J. Reiset	» » nr. Dieppe	1879—80	9 »	67	288.7	a
Muntz & Aubin	France. Country	1881	9 »	64	287.0	b
Letts & Blake	Nr. Belfast	1897	5 »	67	289.4	c
Brown & Escombe	Kew. Nr. London	1898—1901	20 »	54	286.1	d
5 Sets average	W. Europe	1872—1901	55 »	305	288.5	

Apart from the probable accuracy of the measurements themselves, other reasons for selecting the particular averages assembled in Table 1, include the following:— (a) Reiset. The average of all air samples taken at night was 4 % higher than for the day samples as given here. On calm foggy nights it was 10 % higher. (b) Muntz and Aubin: The free air quality of their average is supported by the fact that they obtained the same value from 14 samples taken at the summit of the Pic du Midi, 2,900 m, on very windy days. The dispersion of single reading was only half as great for the latter series. (c) From time to time Letts and Blake standardized their analysis with artificial air samples of exactly known CO_2 content. (d) At Kew the easterly winds from London averaged 10 % more CO_2 than westerly winds from the country. Only the latter are included here. Apart from this set, all the reported day measurements are included in Table 1.

Neither the perferred values in Table 1, nor the many averages in Appendix table A, show a significant trend between 1870 and 1900. Together these two sets of averages give a mid-point of 290 p.p.m., hence it seems reasonable to choose this round figure as the amount of CO_2 in the free air of the north eastern Atlantic region at the turn of the century. Its probable accuracy is thought to be ± 1 %, and, without further hair splitting, it is difficult to see how a more precise base value could be obtained from the old data.

3. The 20th Century Observations

With the exception of a few measurements excluded by the criertia given in section (1) above, all the 20th century CO_2 averages known to the writer are assembled in Appendix table B. As in the case of the earlier values, very different methods were used by most of these observers. Some like Benedict, Carpenter, and Haldane, relying on large numbers of small air samples, whilst others, like Krogh and Spector, aimed at basic accuracy with a few very careful measurements.

The average values from Table B are plotted against the years of observation in Fig. 1. The full curve on this figure shows how the CO_2 from fossil fuel combustion would increase the amount in the whole atmosphere if there were no net losses to other CO_2 reservoirs. For this curve the base line is taken as 290 p.p.m. in the year 1900, and one part per million of CO_2 by volume as equal to 8.10^9 tons. By 1956 this "fuel line" is up to 325 p.p.m., or 12 %, owing to the addition of 280 thousand million tons of fuel CO_2 since 1900.

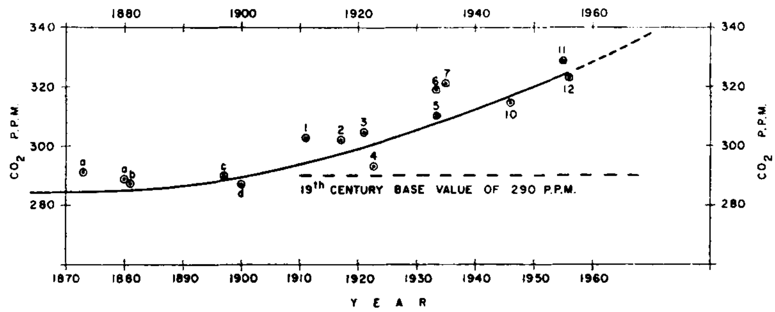

Fig. 1. Amount of CO_2 in the free air of the N. Atlantic region. 1870—1956. Full curve, amount from fossil fuel (See Appx. Table B. for numbered obs. points, and text Table 1 for the 19th century obs. points.)

4. Discussion of Figure 1

It will be seen that the observed points show a decided rising tendency in the later decades, but they appear rather scattered on the scale used for the figure. This scatter is, however, less disturbing when it is realized that both seasonal mean values, and those taken in different parts of Europe during the same season, may differ on occasion by over 5 %. This has been demonstrated by the valuable and extensive new series from Scandinavia, (FONSELIUS et al. 1956). Similar differences are also seen in the 19th century sets covering several seasons, and must result from the interaction of meteorological, biological, and oceanic factors. Certain of these factors have been suggested, (CALLENDAR 1957), to account for the relatively high CO_2 values in the 1930's reported by some observers.

Coming to the present time. It happens that the average of all the new Scandinavian measurements from Dec. 1954 to Dec. 1956, (326 p.p.m. from about 1,000 readings in 25 months at 15 stations. Lat. 56°—68°N. Long. 10°—28°E), lies almost on the fuel line, 12 % above the 1900 base value of 290 p.p.m. Although such very close agreement may be a coincidene, the general upward trend of the observations since the turn of the century, and especially the manner in which most of them keep near the fuel line, seems very significant. It is, however, most difficult to account for such a large increase of atmospheric CO_2 from the fuel addition only, because radio-carbon methods have recently shown it is in active exchange with very large CO_2 reservoirs in the oceans and biosphere. (CRAIG, l. c. & others). Thus, if the increase shown by the measurements discussed here is even approximately representative of the whole atmosphere, it means that the oceans have not been accepting additional CO_2 on anything like the expected scale. However, this important and interesting problem awaits further observational data, in particular from the Southern hemisphere.

5. CO_2 observations in the Tropics and South

It seems probable that new measurments of atmospheric CO_2 will be made in distant parts of the world during the Geophysical Year, and therefore it may be useful to give a summary of old values taken in the Tropics and south Atlantic. The averages known to the writer are assembled in Table 2, but there may be others reported in the literature of the southern countries. Even so the most valuable is likely to be the series reported by MUNTZ & AUBIN, (1886)[1], not only because of their wide extent, probable accuracy, etc., but also because they took many values in France, by the same elaborate technique, which are directly comparable, Table 2.

Although Thorp's values in Table 2 are possibly a few percent up for instrumental reasons, his high Belem average could well be accounted for by rapid decay of river debris from the Selvas, in the esturies and swamps

[1] Dr. C. H. Keeling, of the California Institute of Technology, who is directing the United States CO_2 program for the I. G. Y., considers that the measurements by Muntz & Aubin are probably amongst the most reliable of the 19th century CO_2 observations. (Private communication).

Table 2. CO_2 averages from the Tropics and south in the 19th Century

Authority	Region or place	Lat. Range	Observations				Diff. from Europe p.p.m.
			Date	period	No.	CO_2 p.p.m.	
Thorp	West Indies region	0—22 N	1866	2 mts	38	297	—
»	Para (Belem)	1. S.	1866	3 mts.	31	328	—
Muntz & Aubin	West Indies region	14—25 N	1882	4 »	23	282	— 5
» »	S. Atlantic & Chile	0—42 S	1882—3	4 »	13	273	— 14
» »	At Santa Cruz	50 S	1882	2 »	10	267	— 20
» »	Nr. Cape Horn	56 S	1882—3	10 »	39	256	— 31

of this hot region. Of more general significance is the regular fall of Muntz and Aubin's averages as higher latitudes were reached in the southern hemisphere. This fall is a good pointer to where the oceans withdraw atmospheric CO_2 on a large scale.

The latter phenomenon has since been confirmed, and more precisely located, by some very low readings from the Antarctic reported by MUNTZ and LANE (1911). These averaged as little as 205 p.p.m. over near freezing water in 65°—70° S. lat. Another "CO_2 sink" evidently exists near the Artic ice margin, for Prof. BUCH (1948), reports an average of only 225 p.p.m. from several samples of cold Arctic sea air. This nothern sink, however, must be relatively small compared with the southern, because the north temperature zone measurements do not show an appreciable change of CO_2 with latitude.

In conclusion, perhaps we may anticipate that the CO_2 measurements in distant parts, promised during the Geophysical Year, will resolve the discrepancy between the radio carbon data and that discussed here, although one suspects that the final answers to this problem lie in the chill darkness of the ocean abyss.

Table A. Appendix.
19th Century mean CO_2 values

Ref.	Authority	Location of observations	Date obtained	No. obs.	Mn. CO_2 p.p.m.
1.	T. E. Thorp	N. Atlantic 0—52° Lat.	1865—66	77	297
2.	F. Schulz	Nr. Rostock	1868—71	1 034	292
3.	J. A. Reiset	France N. W. Coast	1872—73	124	293
4.	— Risler	Cleves — Switzerland	1872—73	—	303 +
5.	J. Claesson	Nr. Lund	1875	31	279
6.	G. F. Armstrong	Grassmere, N. W. England	1879	53	296
7.	J. A. Reiset	Nr. Dieppe	1879—80	122	296
8.	A. Muntz & E. Aubin	France Country	1881	64	287
9.	A. Levy	Montsouris Obs. Nr. Paris	1876—87	Large	292
10.	— Blockmann	Koningsberg	1885	40	310 +
11.	— Dragendoff	Nr. Dorpat	1886	366	266
12.	T. Van Nuys & B. Adams	Nr. Bloomington U.S.A.	1887	18	282
13.	E. Von Frey	Nr. Dorpat	1887—88	932	264
14.	A. Petermann & J. Graftiau	Belgium Country	1889—91	525	293
15.	A. Palmquist	Nr. Stockholm	1891—92	395	312 +
16.	— Libedineff	Odessa	1896—97	—	303 +
17.	E. Letts & R. Blake	Nr. Belfast	1897	67	289
18.	H. Brown & F. Escombe	Nr. London	1898—1901	92	294
		Average of 18 Sets	1865—1901		291.5

+ See text Sec. (1).

REFERENCES — Appx. Table A.

1. THORP, T. E.: *J. Chem. Soc.* **5**, 189, 1867.
2. SCHULZ, F.: *Landu, Vers, Stationer* **14**, 366, 1871.
3. REISET, J. A.: *Ann. Chim.* **26**, 145, 1882.
4. No ref. found.
5. CLAESSON, J.: Berichte. *Deut. Chem. Ges.* **9**, 1876.
6. ARMSTRONG, G. F.: *Proc. Roy. Soc.* **30**, 343, 1880.
7. REISET, J. A.: loc. cit.
8. MUNTZ, A and AUBIN, F.: *Ann. Chim.* **26**, 1882.
9. LEVY, A.: *Annu. Montsouris*, 1877—87.
10. No ref. found.
11. DRAGENDOFF: *Chemi. Central Blatt* **3**, Fol. 18, 1367, 1887.
12. NUYS, T. and ADAMS B.: *Amer. Chem. J.* **9**, 1887.
13. FREY, E.: *Inarig. Diss.* Dorpat 49 p. 1889.
14. PETERMANN, A and GRAFTIAU, J.: *Mem. Cour. Akad. Roy. Belg.* **47**, 87, 1892.
15. PALMQUIST, A.: *Sevens. Vet. Hand.* **18**, 1, 1892—3.
16. No ref. found.
17. LETTS, E. and BLAKE, R.: *Sei. Proc. Roy. Dublin Soc.* **9**, N. S. Part 2. 107, 1900.
18. BROWN, H. and ESCOMBE, F.: *Proc. Roy. Soc. B.* **76**, 118, 1905.

Table B. Appendix

20th Century mean CO_2 values.

Ref. to Fig. 1	Authority	Location	Date obtained	No. obs or Period	CO_2 p.p.m.
1.	F. G. Benedict	Nr. Boston, Mass.	1909—12	645	303
2.	A. Krogh	Nr. Copenhagen	1917	4 mts.	302
3.	H. Lundegardh	Hallands Väderö, S. Sweden	1920—23	4 yrs.	305
4.	B. Schultz	N. Sea & Baltic	1922—23	2 yrs.	293
5.	T. M. Carpenter	New England	1930—35	1 156	310
6.	K. Buch	N. Atlantic 40—50° Lat.	1932 &35	81	319
7.	K. Buch	Petsamo — Finland	1934—35	95	321
8.	J. B. Haldane	Nr. Perth — Scotland	1935	152	324 +
9.	E. Pozzi Eskot	Lima, Peru	1937	—	323 +
10.	N. Spector & B. Dodge	Yale Uni. Conn.	1946	Few	315
11.	S. Fonselius & F. Koroleff	Scandinavia. 15 Stations. 500. Obs.	1955	12 mts	328
12.	S. Fonselius & F. Koroleff	Scandinavia. 15 Stations. 522. Obs.	1956	12 mts	322

+ See text Sec. (1)

Refs. Appx. Table B.

1. BENEDICT, F. G.: *Pub. Carnegie Inst.* No. 166, 1912.
2. KROGH, A.: *Dan. Videns. Sel. Math-fys. Medd.* 1. 1—19, 1919.
3. LUNDEGARDH, H.: "Der Krieslauf der Kohlensaure in der Nature". Jena 1924.
4. SCHULZ, B.: *Arch. Deut. Seewarte*, 41. 6, 1923.
5. CARPENTER, T. M.: *J. Amer. Chem. Soc.* 59. 232, 1937.
6. BUCH, K.: *Acta Akad. Aboensis. Math. Phys.* 11. No. 12 1939.
8. HALDANE, J. B.: *Nature.* 137. 573, 1936.
9. POZZI-ESCOT, E.: *Revista der Cieneias*, Lima. 40, 133, 1938.
10. SPECTOR, N. and DODGE, B.: *Anal. Chem.* 19. No. 1 55, 1947.
11—12. FONSELIUS, S. and KOROLEFF, F.: *Tellus*, **7**, **8**, and **9**, 1955 to 1957.

REFERENCES

ARNOLD, J. R. & ANDERSSON, E. C., 1957: *Tellus* **9**, No. 1. pp. 28—32.

BUCH, K., 1948: Geophysica (Helsinki) **3**, p. 63.

CALLENDAR, G. S., 1940: *Quart. J. R. Met. Soc.* **66**, p. 395.

— 1949: »Weather». (London). **4**, p. 310.

— 1957: *Tellus* **9**, p. 421.

CRAIG, H., 1957: *Tellus* **9**, pp. 1—17.

FONSELIUS, S., KOROLEFF, F., and WÄRME, K., 1956: *Tellus* **8**, pp. 176—183.

MUNTZ, A. and AUBIN, E., 1886: »Researches sur la constitution chimique de l'atmosphere». Tome 3. Les Ministeres de la marine et de l'Instruction Publique. Paris.

MUNTZ, A. and LANE, E., 1911: *Compt. Rend.* **153**, p. 1116.

PLASS, G. N., 1956: *Amer. J. Phys.* **24**, pp. 376—387.

REVELLE, E. and SUESS, H. E., 1957: *Tellus* **9**, pp. 18—27.