

The Concentration and Isotopic Abundances of Carbon Dioxide in the Atmosphere

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Abstract

A systematic variation with season and latitude in the concentration and isotopic abundance of atmospheric carbon dioxide has been found in the northern hemisphere. In Antarctica, however, a small but persistent increase in concentration has been found. Possible causes for these variations are discussed.

The content of carbon dioxide in the atmosphere, in contrast to oxygen, nitrogen, and the rare gases, has been found to be significantly variable (GLUECKAUF, 1951). New data indicate, however, that the degree of variability is smaller and the variations are more systematic than previously believed (STEPANOVA, 1952, SLOCUM, 1955, FONSELIUS ET AL., 1956, CALLENDAR, 1958, BRAY, 1959).

Three gas analysers, as described by SMITH (1953), equipped with strip chart recorders, have been employed to measure the concentration of carbon dioxide continuously at stations in Antarctica, Hawaii, and California. A fourth analyser has been used in the laboratory to analyse samples of air collected in glass flasks at various places. These analysers provide direct comparisons of the partial pressure of carbon dioxide in air relative to that in prepared mixtures of carbon dioxide in nitrogen gas. The concentration of carbon dioxide in these reference mixtures is determined manometrically (KEELING, 1958).

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The relative accuracy of the data presented here is approximately ± 0.3 p.p.m. (parts per million by volume). The uncertainty in the absolute values is considerably larger, however, since only a preliminary calibration of the reference mixtures has been made. When an accurate manometric calibration is completed, the absolute accuracy is expected to approach ± 0.1 p.p.m.

Monthly averages of the data from the continuously recording stations and from collections in flasks are presented numerically in Table 1 and plotted in figures 1 and 2. The locations of the sampling stations and tracks are shown in figure 3.

Local contamination has been found to occur at all three continuous recording stations. At

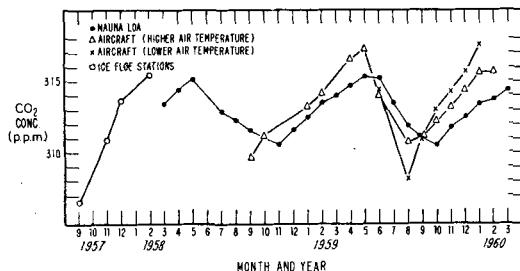


Fig. 1. Variation in concentration of atmospheric carbon dioxide in the Northern Hemisphere.

CONCENTRATION AND ISOTOPIC ABUNDANCES OF ATMOSPHERIC CO₂ 201

Table 1. Monthly Average Concentrations of Atmospheric Carbon Dioxide at Various Stations in Parts per Million of Dry Air by Volume.

Month	Year	Continuous Recording Stations			Surface Flask Samples			Flask Samples from Aircraft ²			
		Little America	Mauna Loa	La Jolla ¹	South Pole	Arctic Ice Floes	Downwind Cruise	Data at Lower Air temp.	Data at Higher Air temp.	Limiting Air temp. (°C.)	
Sept.	1957				311.1	306.5					
Oct.							310.9 ¹				
Nov.						310.8	311.9				
Dec.					312.0	313.6	311.6				
Jan.	1958	310.8									
Feb.		311.0	313.4			311.9	315.5		314.9 ¹	-27	
Mar.		311.4	314.4	314.3							
Apr.		311.7	315.1	315.3							
May		311.9	314.0	313.2		312.5			314.9 ¹	-21	
Jun.		312.0	312.9	311.1							
Jul.		312.3	312.9	308.4							
Aug.		312.9	312.6	308.7		313.3		308.3 ¹	309.6	-18	
Sept.		312.9	312.6	308.7				312.8 ¹	311.2	-27	
Oct.		313.0	311.1	310.8							
Nov.		310.6	313.2								
Dec.		311.6	314.3								
Jan.	1959	312.5	314.9	312.8					313.2	-36	
Feb.		313.5	314.4	313.4					314.1	-36	
Mar.		314.0	315.4	312.7							
Apr.		314.7	315.0	314.3				316.6 ¹	316.6	-27	
May		315.3	315.0	314.3					317.3	-24	
Jun.		315.2	315.2	314.4				314.3	314.1	-21	
Jul.		313.5	311.5	314.2							
Aug.		311.9	308.1	314.2				308.1	310.7	-18	
Sept.		311.1	308.7	314.0				311.0	311.1	-27	
Oct.		310.5	312.1					313.0	312.1	-27	
Nov.		311.8	313.7			313.9			314.2	313.2	-36
Dec.		312.5	313.5						315.6	314.3	-36
Jan.	1960	313.4	314.7						317.6	315.6	-36
Feb.		313.7	315.4							315.6	-36
Mar.		314.4	314.7								

¹ Data not shown in Figures 1 or 2.² Data have been separated into two groups based upon the temperature of the air at the point of sampling. Limiting air temperature refers to the temperature separating lower air temperature from higher. It has been chosen so that, for each period of sampling, the boundary between warmer and colder air lies at approximately 50° North (see figure 3).

Little America, Antarctica, it was evidently due solely to combustion of fuel in the immediate vicinity of the station. It could be readily spotted from the significant fluctuations in the otherwise steady trace of the recorder pen and was eliminated from consideration in the initial reading of the charts. At Mauna Loa Observatory, Hawaii, a less prominent variability has been found in approximately half of the records. This is attributed to release of carbon dioxide by nearby volcanic vents; combustion on the island associated with agricultural, industrial, and domestic activities; and lower concentra-

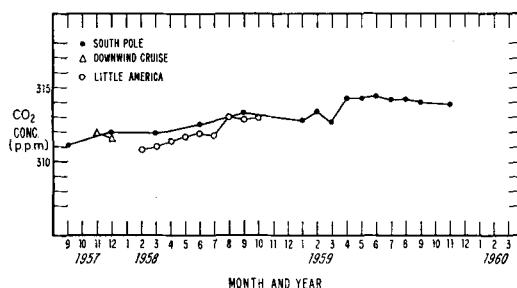


Fig. 2. Variation in concentration of atmospheric carbon dioxide in the Southern Hemisphere.

tion of carbon dioxide in the air transported to the station by upslope winds. The values reported here are averages of data for periods of downslope winds or strong lateral winds when the concentration remained nearly constant for several hours or more. At La Jolla, California, the concentration has been found to be highly variable. Highest concentrations occur during light winds from the north, from the direction of Los Angeles; lowest concentrations when the wind is from the west or southwest and of moderate force or greater. Lowest weekly values usually do not differ by more than ± 1 p.p.m. during any month, and, within a range of 2 p.p.m., agree with other data for the northern Pacific ocean. Monthly averages of these data, which presumably indicate nearly uncontaminated air, are cited here.

Data for air collected in flasks from aircraft flying at 5 to 6 kilometers above the Pacific and Arctic oceans and from surface stations at the South Pole and on Arctic ice floes show a high degree of regularity.

A clearly defined seasonal trend in concen-

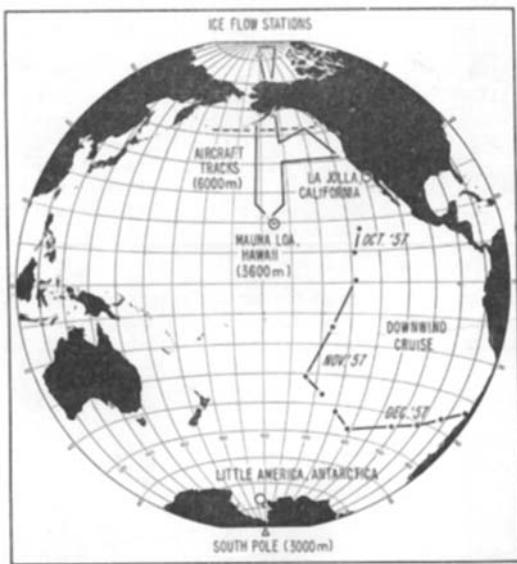


Fig. 3. Location of stations and tracks for sampling of atmospheric carbon dioxide. Circles denote continuous recording stations. Triangles denote flask sampling stations. Elevations in meters are given for locations more than 100 meters above sea level. The approximate mean position of the limiting temperature isotherm, used to separate the aircraft data into groups associated with higher and lower air temperature, is shown by a dotted line.

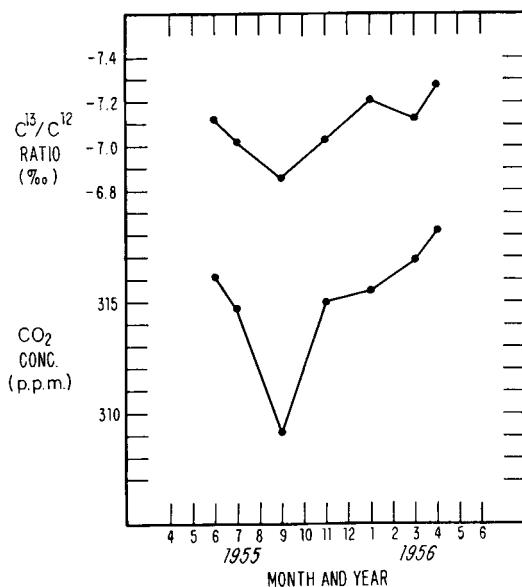


Fig. 4. Variation in concentration and C^{13}/C^{12} ratio of atmospheric carbon dioxide, based on Keeling (1961) for various locations near the Pacific coast of the United States.

tration is found at all locations in the northern hemisphere. Going from south to north, the annual range of concentration becomes greater and the month of minimum concentration occurs earlier. Separating the samples from aircraft into two groups based upon the temperature of the air at the point of sampling (see table 1), the values for the high latitude, or polar, air are seen to have a greater seasonal range than the comparable values for air of the temperate zone. In contrast, data for the southern hemisphere do not indicate any seasonal variation. Data from Downwind Cruise in November and December, 1957, suggest that the concentrations observed over Antarctica prevail at all southern latitudes of the Pacific ocean.

A seasonal variation in the isotopic abundance of carbon 13 in atmospheric carbon dioxide may also exist (KEELING, 1961). In figure 4 are plotted the observed seasonal variations in isotopic abundance and concentration, based upon samples collected at various stations near the Pacific coast of the United States during 1955 and 1956. Changes in relative abundance of carbon 13 with concentration obey a relationship found for air near plants (KEELING, 1958). The isotopic composition of

the carbon dioxide associated with the change in concentration, according to this relationship, is approximately —22 per mil, in good agreement with the value found for air of forests (KEELING, 1958) and for the carbon of plants growing on land (CRAIG, 1954, WICKMAN, 1952). These data, therefore, indicate that the seasonal trend in concentration observed in the northern hemisphere is the result of the activity of land plants. This interpretation receives further support from the fact that maximum concentrations have been found to occur in spring at the outset of the summer growing season for plants in the temperate zone; that minimum concentrations occur in the fall, approximately at the end of the growing season. The observed absence of a seasonal trend in the southern hemisphere is then to be explained by the smaller area of growing plants found in the southern hemisphere at temperate and polar latitudes. These conclusions should be considered tentative, however, since they are based on relatively few isotopic measurements.

Where data extend beyond one year, averages for the second year are higher than for the first year. At the South Pole, where the longest record exists, the concentration has increased at the rate of about 1.3 p.p.m. per year. Over the northern Pacific ocean the increase appears to be between 0.5 and 1.2 p.p.m. per year. Since measurements are still in progress, more reliable estimates of annual increase should be available in the future. At the South Pole the observed rate of increase is nearly that to be expected from the combustion of fossil fuel

(1.4 p.p.m.), if no removal from the atmosphere takes place (REVELLE and SUESS, 1957). From this agreement, one might be led to conclude that the oceans have been without effect in reducing the annual increase in concentration resulting from the combustion of fossil fuel. Since the seasonal variation in concentration observed in the northern hemisphere is several times larger than the annual increase, it is as reasonable to suppose, however, that a small change in the factors producing this seasonal variation may also have produced an annual change counteracting an oceanic effect.

Acknowledgements

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REFERENCES

- BRAY, J. R., 1959: An analysis of the possible recent change in atmospheric carbon dioxide concentration. *Tellus* **II**, pp. 220—230.
- CALLEDAR, G. S., 1958: On the amount of carbon dioxide in the atmosphere. *Tellus* **10**, pp. 243—248.
- CRAIG, H., 1954: Carbon-13 in plants and the relationship between carbon-13 and carbon-14 variations in nature. *J. Geol.* **62**, pp. 115—149.
- FONSELIUS, S., KOROLEFF, F., WÄRME, K. E., 1956: Carbon dioxide variations in the atmosphere. *Tellus* **8**, pp. 176—183.
- GLUECKAU, E., 1951: The composition of atmospheric air. *Compendium of Meteorology*, Amer. Meteorol. Soc., Boston, pp. 3—10.
- KEELING, C. D., 1958: The concentration and isotopic abundances of atmospheric carbon dioxide in rural areas. *Geochim. et Cosmochim. Acta* **13**, pp. 322—334.
- KEELING, C. D., 1961: The concentration and isotopic abundances of carbon dioxide in rural and marine air. *Geochim. et Cosmochim. Acta*, in press.
- REVELLE, R., SUESS, H. E., 1957: Carbon dioxide exchange between atmosphere and ocean and the question of an increase of atmospheric CO₂ during the past decades. *Tellus* **9**, pp. 18—27.
- SLOCUM, G., 1955: Has the amount of carbon dioxide in the atmosphere changed significantly since the beginning of the twentieth century? *Month. Weath. Rev.* **83**, pp. 225—231.
- SMITH, V. N., 1953: A recording infrared analyser. *Instruments* **26**, pp. 421—427.
- STEPANOVA, N. A., 1952: A selective annotated bibliography on carbon dioxide in the atmosphere. *Meteor. Abs. Bibl.* **3**, pp. 137—170.
- WICKMAN, F. E., 1952: Variations in the relative abundance of the carbon isotopes in plants, *Geochim. et Cosmochim. Acta* **2**, pp. 243—254.