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VARIATIONS OF THE AMOUNT OF CARBON DIOXIDE IN DIFFERENT AIR CURRENTS

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SUMMARY

The first measurements to determine the composition of the atmosphere were made at least 180 years ago, but chemists worked more than a century before they obtained really accurate values for the amount of carbon dioxide in the air.

In the following a brief review is given of the present state of knowledge concerning the variations of atmospheric carbon dioxide, together with some observations which appear to show that the amount of this gas in the air has increased of late years.

CAUSES OF VARIATIONS OF CO_2 IN DIFFERENT AIR CURRENTS

The changes of the amount of CO_2 in the air which are often observed during quiet weather are generally of local origin, and are caused by organic or human activities; but the variations occurring in the great wind currents have a more fundamental basis which seems to be connected with the differences of CO_2 pressure in the surface waters of the oceans.

Theoretical considerations suggest that this gas should be more abundant in the air of equatorial regions than elsewhere, because:— (*a*) The CO_2 pressure in water varies directly with the temperature, so that warming water gives up the gas to the air, whilst cooling water withdraws it. (*b*) Owing to organic action CO_2 tends to accumulate in deep water; in equatorial regions, where this water rises to the surface, the excess gas is returned to the air. These considerations are supported both by observations in the water and in the air. For the water the extensive and well-spaced measurements taken by the "Meteor" expedition (Wattenberg, 1933) in the Atlantic Ocean, have been used to compute the average CO_2 pressure in the surface layers 0 to 50 metres depth; the following pressures were obtained:—

Equatorial region,	20N. to 20S. Lat.,	from 291	observations,	3·27 atmos./10,000
Temperate ,,	40S. to 60S. Lat.,	,, 192	,,	2·99 ,, ,,

The amount of CO_2 in the air of these southern latitudes was measured by Muntz and Aubin (1886), whose observations are known to be amongst the most reliable which have been made; they obtained the following mean values, in volumes of CO_2 per million volumes of air, from readings taken over a period of several months in each region:—

West Indies region,	20N. Lat.,	from 40	observations,	284 parts per million
S. American ,,	40S. Lat.,	,, 34	,,	272 ,, ,, ,,
At Cape Horn	56S. Lat.,	,, 39	,,	256 ,, ,, ,,

It will be seen that the amount of CO_2 in the air shows a marked falling off in high southern latitudes, the actual difference being approximately the same as that for the CO_2 pressure in the water of corresponding latitudes. The value obtained by Muntz and Aubin at Cape Horn appears to be the lowest reliable period mean ever recorded, and it confirms the exceptional " purity " of the air carried by the stormy and rain-washed winds of the great southern oceans. The lowest single readings obtained at Cape Horn were 231 and 232 p.p.m. of CO_2 on June 16, 1883, a day of moderate SW. gale and sleet.

As regards the upper air there is no reason to suppose that the proportion of CO_2 changes to an appreciable extent, at any rate until great heights in the stratosphere are reached; here the greater density of this gas and the small amount of vertical mixing might be expected to reduce the proportion. It is worth noting that Muntz and Aubin obtained exactly the same average amount of CO_2 in the air at the summit of the Pic du Midi (2·9 km.) as in the country air of France.

Observed variations of CO_2 in the air

It is difficult to say who was the first to obtain accurate values for the proportion of CO_2 in the air, although T. E. Thorpe (1867) has a good claim to this honour. In the latter part of the last century a considerable amount of interest was taken in the subject and a number of reliable measurements were made; some of the best of these have been compared with the daily weather maps of the period to find whether the amount of CO_2 varies in the different air currents, and the results obtained from three of the most reliable and extensive series of measurements are given in Table I.

The following is a brief review of the most reliable observations of this period.

(1) *Jean Reiset at Ecorchebœuf,* 1872-1880

This series is perhaps the foremost of all the CO_2 observations on account of the exceptional precautions taken by Reiset to ensure the highest accuracy; and it is difficult to believe that such precision, scarcely exceeded by any subsequent measurements, was attained nearly seventy years ago. These observations were made near the village of Ecorchebœuf, which is some five miles along the coast from Dieppe; they were mean values for periods of from 6 to 24 hours, during which about 600 litres of air was passed through the absorption apparatus. Probably because of this long period for each measurement, and also, no doubt, owing to the general accuracy of his work, Reiset's values show less variation from day to day than those of other observers.

(2) *Muntz and Aubin,* 1881

The values obtained by these observers in distant parts of the world have already been mentioned. They used a very elaborate observing method designed to secure the highest precision, but the number of readings they took in any one region was not large enough to give comparative figures for the different air currents. The mean of their measurements in France is given in Table II.

(3) *Petermann and Graftiau at Gembloux,* 1889-1891

This important series of measurements was made at a rural site near Gembloux, Belgium; more than 500 readings were taken on different days, and the mean of these, 294 parts per million of CO_2, shows that the basis was reliable, although the individual values do not appear to have quite the accuracy of some of the other sets.

(4) *Letts and Blake, near Belfast,* 1897

This series was taken in the grounds of Queen's College, Belfast, and, although the number of observing days was too small for comparison of the different air currents, the basis of their observations was exceptionally accurate, and the mean obtained is included in Table II.

(5) *Brown and Escombe at Kew Gardens,* 1898-1901

These observations share, with those by Reiset and by Muntz and Aubin, the distinction of precision measurements. Reiset's method was used with smaller volumes of air, but with greatly improved titration indicators.

As Kew lies to the west of the great city of London, it is not surprising to find that the easterly winds carried much more CO_2 than those from the west; the mean values obtained were as follows:—

All SE to NE winds, number of days = 20, mean CO_2 = 313 parts per million
All SW to NW ,, ,, ,, ,, = 54, ,, ,, = 286 ,, ,, ,,

Several other reliable series of CO_2 measurements were made in the latter part of the last century; but it is unlikely that any of them exceeded in accuracy those mentioned above, and in most cases the precision attempted was a good deal less; some of the best mean values are given in Table II.

To obtain the comparative figures in Table I about 900 weather maps were examined, and only those days are included, some 70 per cent of the whole number, in which the air movement over the region was definite.

TABLE I.—VARIATIONS OF CO_2 IN DIFFERENT AIR CURRENTS, WEST EUROPE, 1872-1900. OBSERVED BY : (1) J. REISET, (3) PETERMANN & GRAFTIAU, (5) BROWN & ESCOMBE.

Air Mass	Marine		Polar-Marine		Continental		Sub-Tropical	
General Winds	SW to W		W to N		NE to SE		SSE to SSW	
Location	No.	CO_2	No.	CO_2	No.	CO_2	No.	CO_2
(1) Near Dieppe .	93	291·7	45	292·9	24	297·9	17	299·0
(3) Gembloux .	199	290·8	73	290·3	98	298·6	45	301·9
(5) Kew . . .	35	284·6	15	287·0	13	308·7*	6	305·0
Mean . .	327	290·2	133	291·0	122	298·4	68	301·2

* Increased by London air, not included in the mean.

It will be seen from Table I that, although the observers obtained rather different average values for the same air mass, they all agree in finding a greater amount of CO_2 in tropical or continental air than in air which has come directly from the Atlantic Ocean. In general they all found the most consistently high values when the air supply came from far to the south, and the most consistently low values during periods of windy unsettled weather with numerous depressions moving in from the Atlantic. For long easterly winds the results were more variable, being generally high during winter and spring, but often below the average in summer and autumn. Long north-westerly and northerly winds present a difficulty owing to the restricted area of the early weather maps, and when these winds were associated with a large anticyclone to the west they often gave rather high CO_2 values. The relatively low value for marine air at Kew is partly caused by the consistently low readings obtained at this station during very strong winds, for neither of the other sets shows a marked deficiency of CO_2 during gales.

Seasonal variation of CO_2

All the observations mentioned under (1) to (5) above have been arranged on a monthly basis to see whether the average amount of CO_2 varies at different times of year. The seasonal means obtained from over 1,000 observing days, between 1872 and 1901, are as follows:—

Spring = 297·1, summer = 290·5, autumn = 294·4, winter = 296·5.

The fall in the amount of CO_2 between spring and summer is partly due to meteorological factors, prevailing winds, etc., and partly to the actual reduction of the amount in the air to supply the seasonal growth of plants.

Measurements in the twentieth century

The close agreement attained by the observers in the latter part of the nineteenth century was doubtless the cause of the scarcity of CO_2 measurements during the first thirty years of the present century. The only systematic observations in the free air during this period seem to have been those of the long series at the Nutrition Institution, Boston (Benedict, 1912). These readings were of the rapid type, made with a small volume of air, and were not accurate enough for correlation with wind direction, etc., but the basis seems to have been reliable and the mean value obtained is included in Table II.

K. Buch at Petsamo Fjord, 1934-35

The numerous observations by Professor Buch, of Abo, Finland, make a very welcome addition to the long series of CO_2 measurements, their accuracy appearing to equal that of the best nineteenth century observations.

Prof. Buch gives the following values for the amount of CO_2 in the air currents reaching Petsamo Fjord, North Finland, from a long series of measurements made in 1934 and 1935:—

Continental = 332, Marine = 329, Arctic = 310 p.p.m.

He attributes the deficiency of CO_2 in the arctic winds of this region to absorption of the gas by the cold waters between Greenland and Nova Zemla.

Buch also made a number of observations whilst crossing the north Atlantic Ocean in temperate latitudes; the mean of these

(Table II) was almost the same as at Petsamo, but, as would be expected, the variation for the different air masses was less.

A secular increase of carbon dioxide

It will have been noticed that the values obtained by Prof. Buch are somewhat larger than those recorded by the nineteenth century observers, the difference of the mean values being as much as 10 per cent. In order to see how far this increase is supported by other measurements a number of the most reliable mean values have been assembled in Table II to cover the whole period, of about seventy years, since accurate observations were first made.* Measurements which were not designed to give the highest precision have been omitted. In nearly all cases the mean values have been computed from the single readings given in the original papers.

TABLE II.—THE OBSERVED PROPORTION OF CARBON DIOXIDE IN THE AIR, 1866-1935. VOLUMES CO_2 PER MILLION VOLUMES OF AIR

Authority	Location	Date	No. obs.	Mean CO_2
T. Thorpe	North Atlantic	1866	51	295
F. Schulze	Rostock	1868–71	1034	292
J. Reiset	Near Dieppe	1872–73	80*b*	292*a*
A. Levy	Montsouris, Observatory	1876–87	(1000)	292
G. Armstrong	Grasmere, England	1879	53*b*	296
J. Reiset	Near Dieppe	1879–80	89*b*	291*a*
Muntz & Aubin	France (country)	1881	64	287*a*
Petermann & Graftiau	Near Gembloux	1889–91	525	294
Letts & Blake	Near Belfast	1897	64	289*a*
Brown & Escombe	Kew Gardens	1898–01	92	294*a*
F. Benedict	Near Boston, Mass.	1909–12	645	303
K. Buch	North Atlantic	1932	28	318
K. Buch	Petsamo, Finland	1934–35	95	321*a*
K. Buch	North Atlantic	1935	53	320
J. Haldane	Near Perth, Scotland	1935	152	324

a Thought to be the most accurate values; *b* excluding night values.

The modern measurements in Table II show an increase over those taken in the nineteenth century of approximately 30 p.p.m. of CO_2; if this increase is assumed to have occurred throughout the whole atmosphere, then the additional mass of CO_2 in the air would be 200,000 million tons. In the period between 1900 and 1935 the amount of coal and oil burnt has been very nearly 50,000 million tons, equal to the direct addition to the atmosphere of 150,000 million tons of CO_2. As by far the larger proportion of this has been produced in the North Temperate zone, where the observations were also made, the greater increase found in the air might be due to incomplete mixing of the whole atmosphere.

For the period from 1866 to 1900 the amount of CO_2 produced by the combustion of fossil carbon was relatively small, and the observations do not record a change in the air.

The importance of the sea water in regulating the amount of CO_2 in the air has already been mentioned, and one would expect to find that a considerable part of the gas produced from fuel had been absorbed by the sea; but the observations in Table II appear to

* In the early part of last century most of the values obtained were far too large, often by 200 or 300 per cent, because nearly all the common errors of the CO_2 measurement tend to increase the apparent value.

show that all this extra gas has remained in the air. The most probable reason for the failure of the sea to absorb the excess can be traced to the very slow vertical circulation in the oceans; for it is only the shallow contact surface, about 1·3 per cent of the whole volume, which quickly reaches equilibrium with the atmospheric gases, and the period required for the whole volume of water to pass through this surface zone has been estimated at several thousand years. Also the excess CO_2 pressure has only reached about 0·00002 atmos. at present, and this is not large enough to force much of the gas into the surface zone.

Thus, although the total capacity of the sea water to absorb CO_2 is immense, it is very slow in action, and will doubtless take many centuries to stabilise the great eruption of this gas, now about 300 million cubic metres per hour, which has resulted from human activities. There is, of course, no danger that the amount of CO_2 in the air will become uncomfortably large because as soon as the excess pressure in the air becomes appreciable, say about 0·0003 atmos., the sea will be able to absorb this gas as fast as it is likely to be produced.

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