

# The Carbon Dioxide Exchange Between the North Atlantic Ocean and the Atmosphere

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## *Abstract*

An approximate distribution of carbon dioxide exchange rates between the atmosphere and the North Atlantic Ocean is obtained for each month of the year on the basis of oceanographic data from Böhnecke's Atlas and the assumption that atmospheric carbon dioxide maintains uniformly the volume percentage of .03. The results indicate the direction in which such an even volume percentage must be changed to approach equilibrium.

Aside from other influences, the ocean-atmosphere exchange of carbon dioxide and the trajectories of tropospheric air masses combine to produce high carbon dioxide content in  $mT$  and  $cP$  air and low carbon dioxide content in  $mP$  air. Since water vapor is at a minimum in the continental polar anticyclones during the polar night, the carbon dioxide probably serves as an effective inhibitor of the outgoing infrared radiation. This inhibiting effect may well serve to limit the intensity of cooling during an ice age; it probably has much less significance during inter-glacial periods.

## **Introduction**

Carbon dioxide as a quantitatively minor constituent of the atmosphere is seldom treated in detail in the textbooks. Meteorologists generally learn that carbon dioxide uniformly makes up about 0.03 per cent by volume of the atmosphere. Brief consideration of biological and industrial processes, however, leads one to observe that carbon dioxide must be quite nonuniformly distributed near the ground. The rates of influx or efflux to or from the atmosphere vary with time in response to the diurnal cycle, the seasonal cycle, the work week, labor strikes, etc. These

effects produce such complexity in the carbon dioxide distribution near the earth's surface that it can be accurately drawn only upon the basis of numerous observations at well-distributed stations over extended periods of time. Such observations are not available.

There remains, however, the consideration of the carbon dioxide distribution in the air over the oceans. Since about seventy percent of the earth's surface is occupied by oceans, conceivably the oceans may yield significant information about the broad scale distribution of carbon dioxide in the atmosphere. It is clear from simple gas solubility considerations that warm water will not retain as great concentrations of carbon dioxide as cold water will. It is to be expected *a priori*, there-

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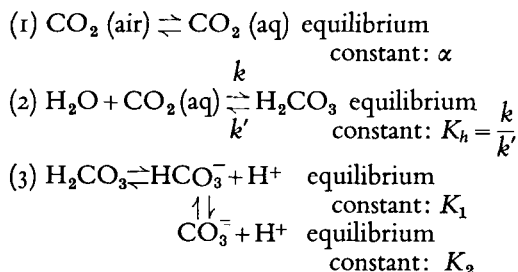
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fore, that the warm parts of the oceans will tend to release carbon dioxide to the air, and the cold parts to absorb it. This suggests that on the basis of exchange rates one should find certain air mass types enriched in carbon dioxide relative to certain others, and that the synoptic distribution of carbon dioxide in the atmosphere may prove interesting.

This synoptic distribution, in addition to its purely meteorological significance, is also pertinent to certain questions raised by at least three different writers during the last fifteen years. The first of these is G. S. CALLENDER (1940) whose findings have been reiterated by E. GLUECKAUF (1951), i.e., that the artificial burning of fossil fuels since 1900 could have produced an increase in atmospheric carbon dioxide equal to that which appears to have been observed up to 1935. The second is K. BUCH (1939, 1942, 1948) who has attempted to typify air masses of Northern Europe according to their carbon dioxide content. The third is M. DOLE (1949) who has hypothesized that the observed excess of the mass 18 isotope in atmospheric oxygen over that in the plants and waters of the earth with which the air should be in equilibrium, is maintained by the flow of carbon dioxide from the oceans to the air and subsequent release of  $O^{18}$  from the carbon dioxide to atmospheric oxygen in exchange for  $O^{16}$  under ultra-violet irradiation. In addition to these relatively recent works, the present study is certainly pertinent to the questions raised by T. C. Chamberlin and Svante Arrhenius almost sixty years ago, and perennially revived since, about the role of carbon dioxide in the radiational equilibrium of the earth.

### The Carbon Dioxide Exchange Rate

The exchange of carbon dioxide between an aqueous solution and the atmosphere above it involves the following equilibria:



Clearly the process is quite complex even in its simplest form, i.e., using pure water as solvent.

Generally speaking the reactions (1) and (3) are fast compared with (2). If one starts with this assumption, then at the water surface,

$$[\text{CO}_2(\text{aq})] = \alpha [\text{CO}_2(\text{air})], \text{ at equilibrium,}$$

and in the body of water  $[\text{CO}_2(\text{aq})]$  is determined by reaction (2). If finally one assumes that  $\text{H}_2\text{CO}_3$  is uniformly concentrated throughout the volume of water communicating directly with the surface, then  $[\text{CO}_2(\text{aq})] (=c)$  varies with  $x$  (depth measured from the surface) in a manner determined by the diffusion and hydration rates.

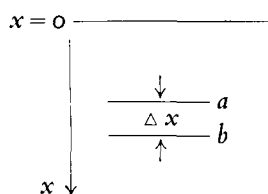


Figure 1.

If  $N$  is the number of moles of  $\text{CO}_2(\text{aq})$ , passing the level  $x$  within an area  $A$ , then

$$\frac{dN_a}{dt} - \frac{dN_b}{dt} = A (kc - k' \text{H}_2\text{CO}_3) \Delta x$$

$$\therefore \frac{d}{dx} \left( \frac{dN}{dt} \right) = A (kc - k' \text{H}_2\text{CO}_3).$$

Also  $\frac{dN}{dt} = D A \frac{dc}{dx}$ , assuming that the transfer

is entirely due to diffusion. Thus

$$D \frac{d^2c}{dx^2} = kc - k' \text{H}_2\text{CO}_3$$

the solution of which is

$$c = (c_0 - c_1) e^{-x \sqrt{\frac{k}{D}}} + c_1 \quad (I),$$

where  $c_1$  is the concentration of carbon dioxide in the water mass, below the region affected by the surface, i.e., at  $x_1 = \infty$ . Using equation (I), the curves of concentration,  $c$ , against depth,  $x$ , were computed for three typical situations (Figure 2). From these it is clear that the gradient of  $c$  with  $x$  has virtu-

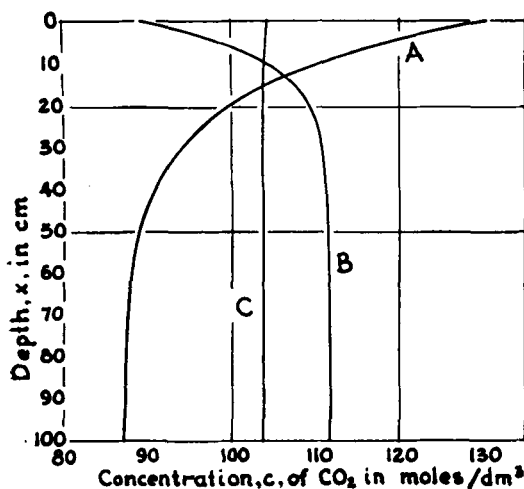


Figure 2. Carbon dioxide concentration,  $c$ , in ocean water as a function of depth,  $x$ , for three selected points, March.

- A.  $48.5^{\circ}\text{N}$ ,  $27.5^{\circ}\text{W}$ ;  $t = 1.3^{\circ}\text{C}$ ,  $S = 35.5\text{‰}$ , absorption rate  $= 40.2 \times 10^{-4} \text{ mol m}^{-2} \text{ sec}^{-1}$ .  
 B.  $24.5^{\circ}\text{N}$ ,  $70.5^{\circ}\text{W}$ ;  $t = 24.8^{\circ}\text{C}$ ,  $S = 36.8\text{‰}$ , emission rate  $= 50.6 \times 10^{-4} \text{ mol m}^{-2} \text{ sec}^{-1}$ .  
 C.  $30.5^{\circ}\text{N}$ ,  $63.5^{\circ}\text{W}$ ;  $t = 19.1^{\circ}\text{C}$ ,  $S = 36.7\text{‰}$ , absorption rate  $= 0.6 \times 10^{-4} \text{ mol m}^{-2} \text{ sec}^{-1}$ .

ally vanished at a depth of 1 m in the case of pure diffusion. The effect of mixing is clearly to depress this level to greater depth.

At the water-air interface,  $x = 0$ :

$$\frac{dN}{A dt} = \sqrt{kD} (c_1 - c_0) \quad (\text{II})$$

It is this equation which forms the basis for the calculation of the exchange rates.

By definition,  $c_0$  is the concentration of carbon dioxide (aqueous) at the surface in equilibrium with the overlying air, and hence it may be computed from the relation

$$c_0 = [\text{CO}_2(\text{aq})] = \alpha_s [\text{CO}_2(\text{air})].$$

The atmospheric concentration of carbon dioxide over the oceans is not known in detail. It must vary widely with location from the tropical to the polar oceans. As a starting point, an assumed atmosphere may be used, and subsequent developments should reveal how such an atmosphere must be modified to approach an equilibrium condition. The initial assumption is made, therefore, that carbon dioxide is uniformly present in the atmosphere in the amount of 0.03 % by volume. The

concentration,  $[\text{CO}_2(\text{air})]$ , is thus directly proportional to the barometric pressure at the surface of the water. The solution coefficient  $\alpha_s$  is a function of the temperature and the salinity of the surface waters. The values derived by HARVEY (1945) from the experimental data of BOHR (1899) have been used in this work.

The concentration  $c_1$  of carbon dioxide in the ocean "mass" (that part of the ocean water in communication with the surface by diffusion and mixing) has been computed by means of the oceanographic technique as described by HARVEY (1945). The result of Harvey's derivation is:

$$c_1 = \frac{\text{carbonate alkalinity} \cdot [\text{H}^+] \cdot \alpha_s}{K'_1 \cdot \left(1 + \frac{2K'_2}{[\text{H}^+]}\right) \cdot a_{\text{H}_2\text{O}} \alpha_0}$$

In oceanographic practice, the various characteristics of sea water such as "carbonate alkalinity", "chlorinity" and "total boron" are all related empirically to the "salinity" which is observed. The above equation thus may be written:

$$\text{Cl } \%_0 \left( 12.09 \cdot 10^{-5} - \frac{K'_B \cdot 2.2 \cdot 10^{-5}}{[\text{H}^+] + K'_B} \right) \cdot [\text{H}^+] \cdot \frac{\alpha_s}{\alpha_0} \\ K'_1 \cdot \left( 1 + \frac{2K'_2}{[\text{H}^+]}\right) \cdot a_{\text{H}_2\text{O}}$$

In this equation:

$$\text{Cl } \%_0 = \frac{S \%_0 - 0.030}{1.8050} \quad (\approx 15 \text{ to } 20)$$

$K'_B$  is the apparent dissociation constant of boric acid in sea water ( $\approx 10^{-9}$  to  $2.5 \cdot 10^{-9}$ )

$[\text{H}^+]$  is the hydrogen ion concentration ( $\approx 0.5 \cdot 10^{-8}$  to  $0.9 \cdot 10^{-8}$ )

$K'_1$  is the first apparent dissociation constant of  $\text{H}_2\text{CO}_3$  ( $\approx 0.6 \cdot 10^{-7}$  to  $1.1 \cdot 10^{-7}$ )

$K'_2$  is the second apparent dissociation constant of  $\text{H}_2\text{CO}_3$  ( $\approx 0.5 \cdot 10^{-9}$  to  $1.3 \cdot 10^{-9}$ )

$a_{\text{H}_2\text{O}}$  is the activity of water in sea water ( $\approx 0.98$  to  $1.00$  hence taken to equal 1)

$\alpha_s/\alpha_0$  is the ratio of the solubility of carbon dioxide in sea water to that in pure water ( $\approx 0.8$  to  $0.9$ )

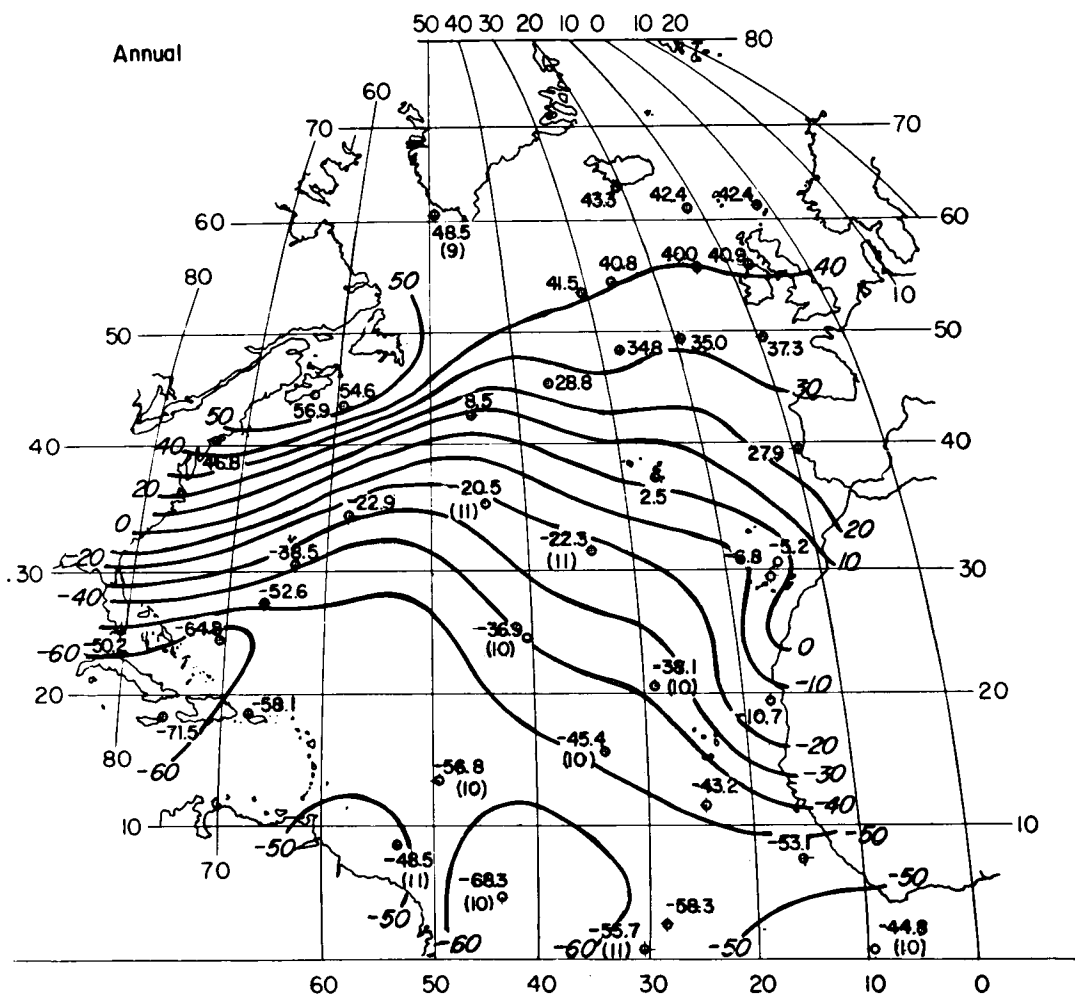


Figure 3. Distributions of annual average carbon dioxide exchange rates,  $10^{-4}$  mol  $m^{-2}$  sec $^{-1}$ .

Each of these quantities has been related experimentally to temperature and salinity (BUCH, 1939). For computational purposes one therefore constructs curves and reads the appropriate values therefrom.

Representative monthly mean temperature and salinity distributions in the surface waters of the North Atlantic have been tabulated by months and published in BÖHNECKE's Atlas (1936). Monthly mean distributions of sea level pressure were procured from the United States Weather Bureau.

After computing  $c_0$  and  $c$  as outlined above, the rates of exchange may be computed pointwise by means of equation (II).

$$\frac{dN}{Adt} = \sqrt{kD} (c_1 - c_0) \quad (II)$$

The diffusion coefficient  $D$  is evaluated by means of a curve derived from data given in the INTERNATIONAL CRITICAL TABLES (1928). The hydration rate  $k$  depends upon temperature and pH, but its variation with pH is relatively small. The pH of the surface waters varies between the limits 8.0 to 8.3 (HARVEY, 1945) hence for this purpose it is assumed constant at 8.15.  $k$  is then evaluated for each point by means of the thermodynamic relation

$$\log_{10} k = \log_{10} k_0 - m \left( \frac{1}{T} - \frac{1}{T_0} \right)$$

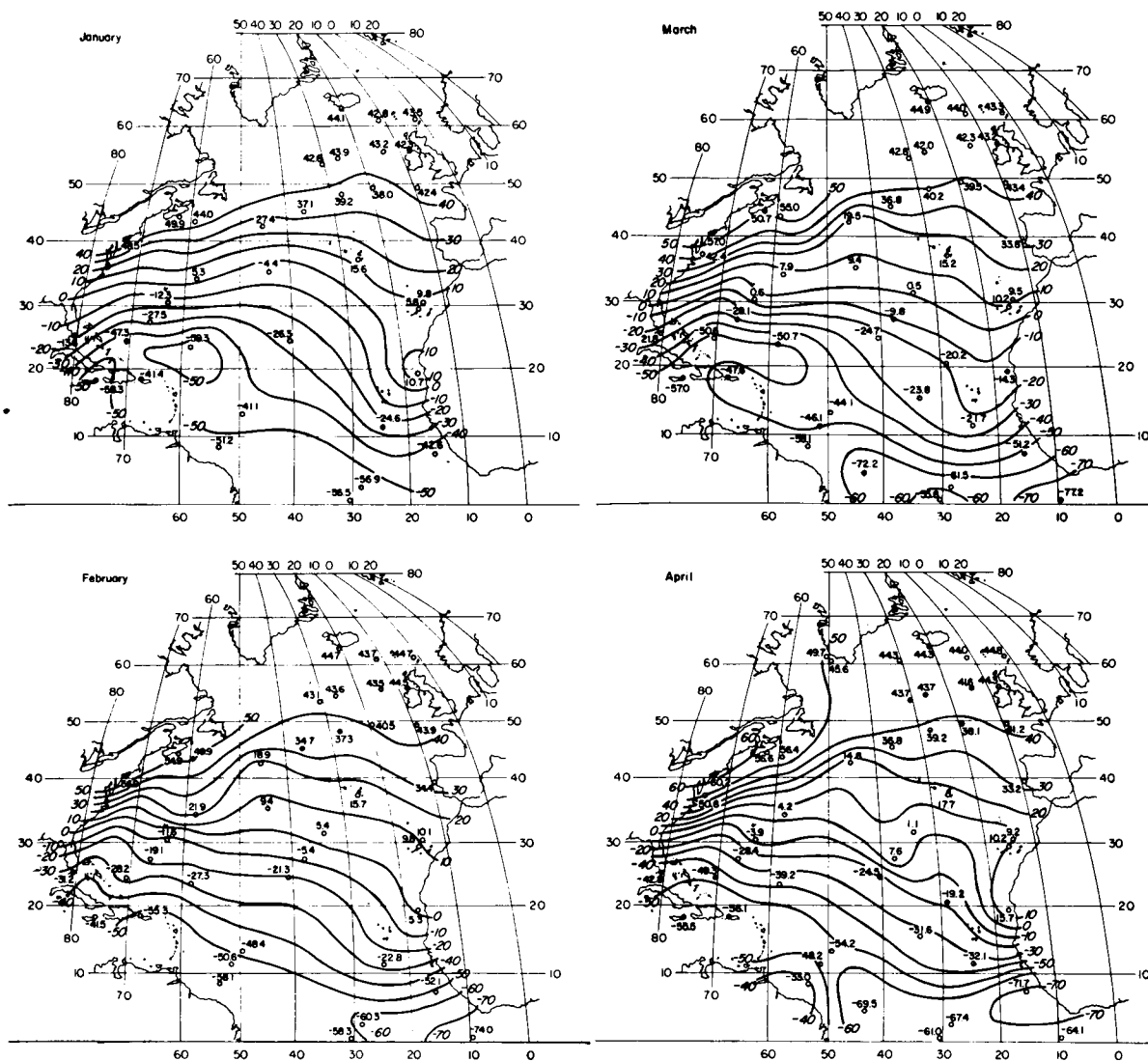


Figure 4. Distribution of monthly mean carbon dioxide exchange rates,  $10^{-4} \text{ mol m}^{-2} \text{ sec}^{-1}$ .

in which  $m$  was found from FAURHOLT'S (1924) determinations to be equal to 4220.

### The Results

The present work is necessarily somewhat crude, and hence to be regarded as a preliminary study. The network of points for which the computation has been made is limited to a minimum for the purpose, i.e., 48 points were chosen well distributed over the area. Data for some of these were missing for some

months, so that the map for January is based upon only 38 points, and those for February and December upon 40 points each.

The results are presented graphically in Figure 4. The map used is the equal-area projection of Mollweide, so that areal integration might be accomplished by use of a planimeter. The exchange rates are given in units of  $10^{-4} \text{ mole m}^{-2} \text{ sec}^{-1}$ . Application of an areal summation to the annual mean exchange chart (Figure 3) shows that a .03 % carbon dioxide atmosphere would have to gain a net

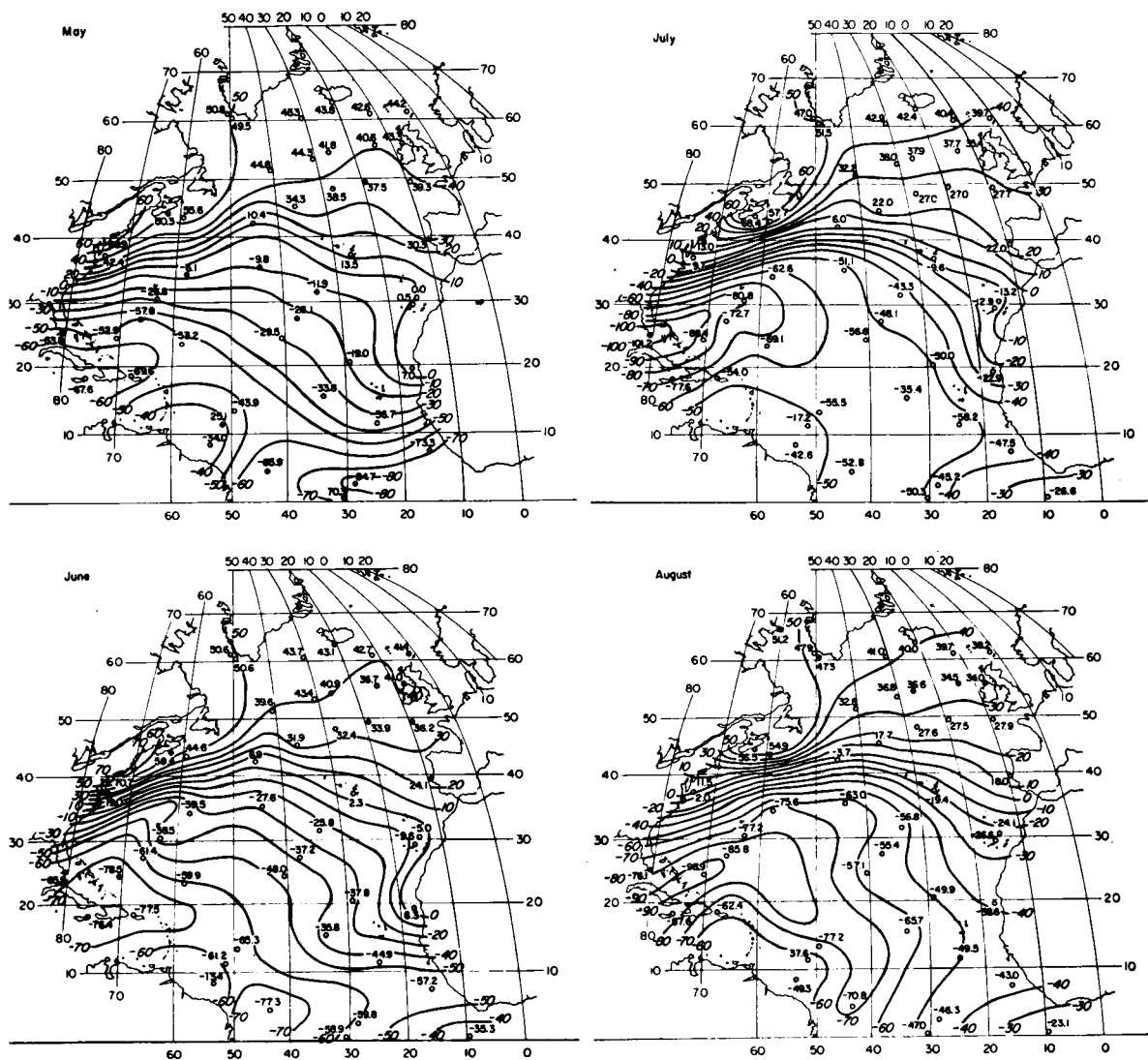


Figure 4. Distribution of monthly mean carbon dioxide exchange rates,  $10^{-4}$  mol  $m^{-2}$  sec $^{-1}$ .

amount of carbon dioxide in order to arrive at a dynamic equilibrium with the North Atlantic Ocean. A qualitative inspection of temperature and salinity relations in the other oceans of the world suggests that the worldwide ocean-atmosphere carbon dioxide equilibrium requires still greater increase of atmospheric carbon dioxide than that over the North Atlantic, thus it is evident that the actual average carbon dioxide content of the atmosphere must exceed 0.03 % somewhat. It is noteworthy that no great adjustment is needed, however.

Tellus VI (1954), 4

The charts of Figures 3 and 4 show numerous interesting features. Parallelism with the isotherm pattern is as anticipated. The reduced rate of emission of carbon dioxide in the area affected by fresh water drainage from the Amazon is quite marked, as is the similar reduction near the Gold Coast of Africa. This latter effect is produced mainly by cold water from the Benguela Current and from upwelling. Other points may be made, however it is not intended that detailed interpretations should be constructed upon the basis of these

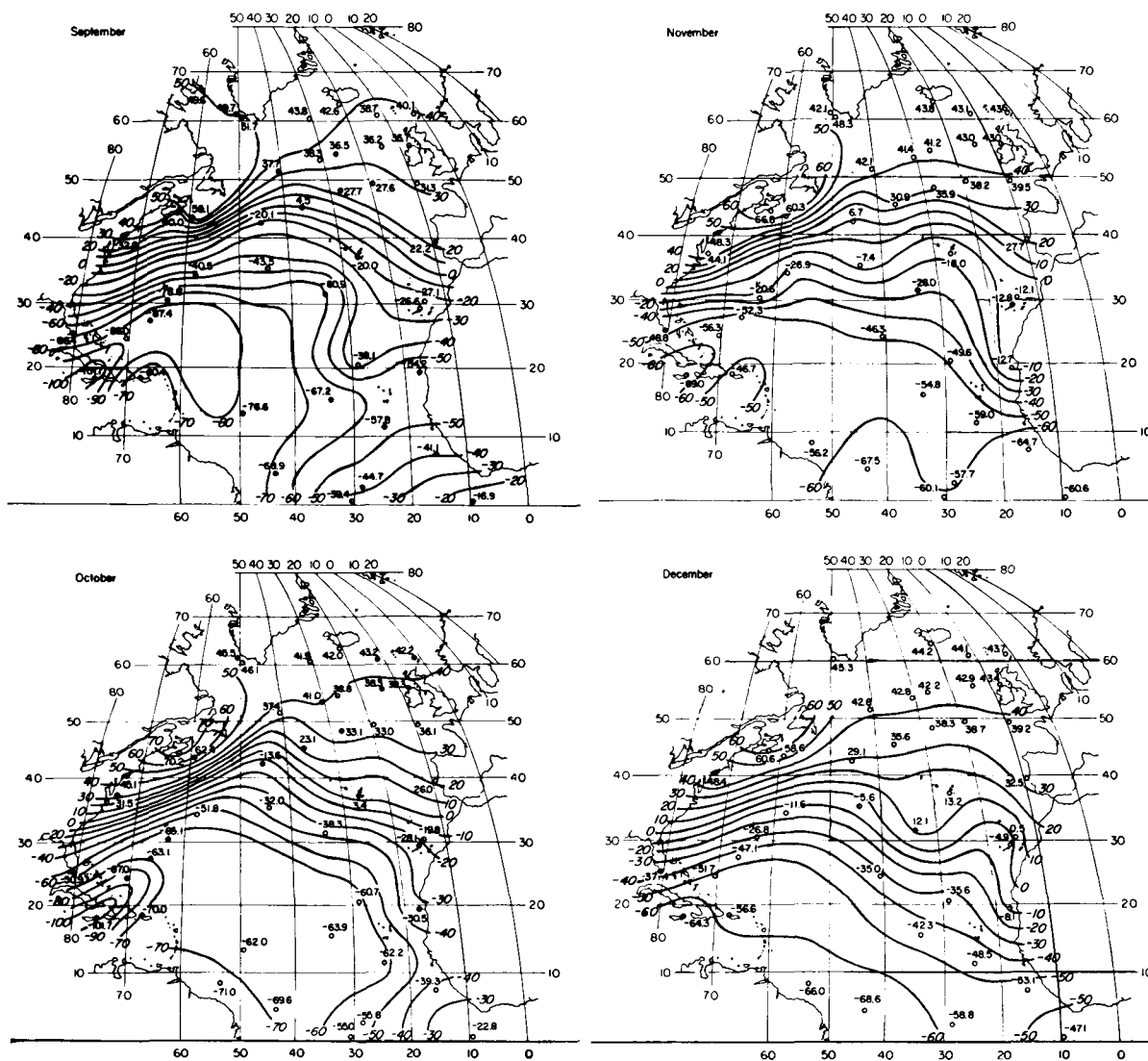


Figure 4. Distribution of monthly mean carbon dioxide exchange rates,  $10^{-4}$  mol  $m^{-2}$  sec $^{-1}$ .

charts which are not themselves based upon detailed data, but that a general picture may be presented.

### General Conclusions

Reference was made earlier to the work of BUCH (1939, 1942 and 1948) relating atmospheric carbon dioxide content to recent air mass history. Buch reports a minimum of carbon dioxide in air found near Spitzbergen which appeared to have a cool maritime

history, and relatively large amounts in continental air from the East and in maritime tropical air. It is clear from Figures 3 and 4 that maritime polar air in order to approach equilibrium with the surface waters must become relatively depleted in carbon dioxide as compared to average conditions, and that the reverse is true for maritime tropical air. If one envisions a meridional interchange of air following the convective model of the general circulation (HADLEY, 1735—6; ROSSBY, 1941) it is reasonable to hypothesize that the

air subsiding in the polar anticyclones must be relatively heavily laden with carbon dioxide. With respect to atmospheric carbon dioxide therefore, the tropical oceans are the principal source regions and they serve to maintain higher than average levels of carbon dioxide concentration in both continental polar and maritime tropical air. It is obvious that all gradations of carbon dioxide content must be present depending upon the respective trajectories, path lengths, speeds of motion, and low level stability of particular air masses. Thus in order to classify air masses by means of their carbon dioxide content one must trace their histories rather carefully. For this reason the attempt of CALLENDAR (1940) to perform such a classification is only moderately successful.

Implicit in these observations are the following tests for the general hypothesis set forward,

1. In relatively stable conditions a vertical gradient of carbon dioxide content (volume percentage) should be observed directed upward over the tropical oceans and downward over the polar oceans.
2. A nearly uniform content should be found upon sounding the subsiding air of the polar anticyclones.
3. Precipitation formed in maritime tropical air should contain higher concentrations of dissolved carbon dioxide than that formed in maritime polar and transitional air masses.

A carbon dioxide sounding device has been developed by WILLIAMS et al. (1953). Preliminary results obtained over New Mexico in summer show a rather sharp drop in carbon dioxide content upon ascending through the tropopause. Here evidently (over New Mexico in summer) the tropospheric stirring is sufficiently strong that no appreciable inhomogeneity occurs below the tropopause. That a definite decrease occurs upon passing through the tropopause suggests that mixing between the troposphere and the stratosphere is not as rapid as most meteorologists have believed. Unfortunately, the Williams instrument is not capable of giving quantitative information at this stage of development.

CALLENDAR'S (1940) hypothesis that an increase of atmospheric carbon dioxide has caused a rise of temperature over much of the earth, is peculiarly challenging. In the

first place, cause and effect in meteorology are seldom that clearly discernible; and secondly there are numerous other possibilities, reasonably plausible, which he appears not to have considered. It is clear, for example, that a warming of the ocean, from whatever cause, would require a shift toward higher carbon dioxide content of the air in order to preserve the dynamic equilibrium of the ocean-atmosphere exchange.

The possibility that long term shifts of the general circulation such as those implicit in secular trends of temperature and other weather elements might have altered the mean trajectories of air (and sea water) needs also to be considered. If the frequency of maritime tropical air invasions of Europe were to increase somewhat at the same time as the frequency of maritime polar air invasions decreased, one would expect an increase of carbon dioxide in the air of this region. If the trajectories were so modified that the maritime tropical air maintained a longer contact with warm, saline ocean water, and the maritime polar air was exposed more briefly to the cool and less saline waters, again an increase of the observed carbon dioxide should appear.

In light of the knowledge that the North Atlantic Ocean has become warmer during the period to which Callendar refers, it appears that the carbon dioxide concentrations in the air of Western Europe would be directly affected because of its trajectory. It is not known why the North Atlantic has become warmer. A sustained circulation shift might well account for this and contribute additional effects such as those discussed above. Thus the view that the observed changes are accountable to secular changes of the general circulation as the basic phenomena in this chain of events seems most attractive.

As regards the role of carbon dioxide in the radiation balance of the earth, two points are worthy of mention. The first is that preliminary results (HOWARD, 1954) of high dispersion infrared absorption studies of carbon dioxide and water vapor reveal that the absorption of these two gases is essentially additive. This would tend to refute HUMPHREYS' (1940) well-known conclusion that carbon dioxide isn't important because water vapor does a better job of absorbing the same wave lengths. The second point is that, according



to the model envisioned above, the polar anticyclones should be laden with carbon dioxide. This would place a relatively large amount of carbon dioxide into a region where water vapor is seriously depleted, and it would seem that this is an especially opportune distribution for controlling the flux of infrared radiation from the earth during the polar night. It appears conceivable therefore, that atmospheric carbon dioxide may serve the very important role of limiting the outward flux of heat during periods of maximum glaciation, since in such periods very little water vapor is available over the ice caps.

### Acknowledgments

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