INCREASE OF EXCHANGEABLE CARBON IN THE EARTH'S RESERVOIRS FROM COMBUSTION OF FOSSIL FUELS

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ABSTRACT

The distribution of excess carbon dioxide produced during and after the consumption of all fossil fuel is determined with the aid of a four-reservoir model of carbon exchange as developed previously for carbon-14. From estimates of the total hydrocarbon fuel resources originally on earth, it is calculated that about 3000 billion tons of carbon ultimately may be released to the atmosphere from this source. At a moderate consumption rate, this fuel supply will be consumed within 200 years and, according to the model, the atmospheric carbon dioxide concentration will reach a maximum value of twice its normal (pre-1900) concentration before declining to a new equilibrium level about 8 percent above the normal. Carbon excess in the surface layers of the ocean reaches a peak a few years later than the atmosphere and retains somewhat less of the excess carbon at equilibrium, while the deep sea eventually absorbs over 90 percent of the excess carbon released by fossil fuel consumption. It was found that the results are highly sensitive to the assumptions as to future fossil fuel consumption rates, but that the atmospheric carbon concentration is not critically affected by the amount of direct exchange between the atmosphere and deep sea.

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INTRODUCTION

Carbon dioxide is the only one of the many air pollutants that has been identified as increasing on a global scale. Measurements in recent years have shown that the carbon dioxide concentration in the atmosphere has been slowly increasing since the late 19th century [Callendar, 1958] and the current annual rate of increase appears to be about 0.7 parts per million (ppm) measured over the oceans [Bolin and Keeling, 1963]. Local and temporal variations may be much greater than this according to temperature, amount of vegetation, season, industrial activity, and volcanism. The general increase has often been attributed to human activities involving the combustion of ever larger quantities of hydrocarbon fuels; consequently the prospect of gradual industrialization over most of the earth evokes predictions of huge carbon dioxide concentrations in the atmosphere. However, carbon dioxide released to the atmosphere is continually being mixed with other reservoirs--the oceans, soil, biosphere--and the oceans, being the largest reservoir for carbon dioxide, are especially important in withdrawing excess carbon from the atmosphere.

In view of the possibility of long term climatic changes due to variations in carbon dioxide concentration in the atmosphere, it is of particular interest to determine how great such variations may become. An upper limit may be calculated by assuming that man will consume the total supply of fossil fuels remaining in the earth. This paper will be concerned with the quantitative exchange of carbon between the earth's natural reservoirs, and particularly with the rate at which an excess of carbon dioxide in the atmosphere caused by combustion products will decay with time. To do this, the four-reservoir model of exchange and the exchange rate constants established from radiocarbon data will be used [Plesset and Dugas, 1966].

FOSSIL FUEL RESOURCES

Statistics on the amount of fossil fuel (that is, fuel derived from geologic deposits of organic matter, including coal, petroleum and gas) thus far produced on earth are given in Table 1. Data prior to 1961 were obtained from Hubbert (1962) and statistics for recent years were gathered from the world production tables published by the Bureau of Mines (1963-1966).

Numerous estimates of the amount of fossil fuel remaining in the earth have been made. There are wide discrepanices between estimates, with the later ones generally being larger than earlier ones, reflecting more thorough geological surveys, improved recovery methods and more experience with proven reserves. Recent figures from the U.S. Geological Survey [Averitt, 1968 and Hendricks, 1965] for the petroleum and natural gas resources remaining in place in the world are also given in Table 1. The estimates were obtained by classifying sedimentary basins of the world, including the continental shelves, then applying known productivity factors of similar U.S. basins. Note that "ton" as used throughout this paper refers to the metric ton (1000 kg or 2200 lb). When original data were given in barrels, they have been converted here to metric tons assuming an average specific gravity for crude oil and natural gas liquids of 0.92.

World coal resources were not included in U.S.G.S. estimates, so a prior estimate of Weeks [1960] is given in the table. It includes all grades of anthracite, bituminous, and lignite, even though they may be in narrow seams or deep deposits that are not now commercially exploitable. Some large claims for coal resources in USSR and China are included, although they have not been verified. It is agreed by most authorities that these two countries contain a major portion of the coal remaining in the earth.

Table 1

CARBON RELEASABLE FROM FOSSIL FUELS

Resource	World Production to 1967	Remaining World Resources	Carbon Ultimately Releasable (10^9 tons)
Coal	115×10^9 tons	7270×10^9 tons	2250
Petroleum	27×10^9 tons	1460×10^9 tons	244
Natural gas	9.5×10^{12} cu m	864×10^{12} cu m	342
Natural gas liquids	1.17×10^9 tons	121×10^9 tons	39
Total			2875
Shale Oil	--	481×10^9 tons	370
Total			3245

Very little shale oil is being produced in the world at present (none in the U.S.) because it cannot compete economically with petroleum. However, it is estimated that there is a potential of over three trillion barrels of oil contained in the world's reserves of shale [Bureau of Mines, 1965]. Whether it will become economical to mine and process this oil shale will depend on how rapidly petroleum reserves are consumed and the rate at which alternate energy sources (such as nuclear) are expanded. Since the future of the shale oil industry is still fairly uncertain, two values for the total carbon ultimately releaseable have been determined: one assumes all shale oil reserves will be consumed, and one that disregards shale oil altogether.

In order to add the fuel resources listed in Table 1, each has been reduced to the common base of tons of carbon ultimately releaseable. This conversion involved the expected recovery rate for each resource originally in place, and the average carbon content of the recovered fuel. The factors which were used in this conversion are listed in Table 2. They are, of course, subject to revision as technology progresses and demand changes. It is presumed that all of the carbon in a fuel as produced will eventually be oxidized and reach the atmosphere as carbon dioxide, even though it may be wasted, temporarily stored, or inefficiently consumed.

Table 2

RECOVERY RATE AND CARBON CONTENT OF HYDROCARBON FUEL RESOURCES

Resource	Fraction of Resource Recoverable	Average Carbon Content (%)
Coal	½	
Petroleum	¼	64
Natural gas	½	78
Natural gas liquids	½	64
Shale oil	all*	77

*Resource is estimated in terms of recoverable oil rather than oil in place.

Adding the releasable carbon for fuel already consumed and remaining resources gives the total for all time of 2875 billion tons (or 3245 billion tons if shale oil is included). This represents 4.9 times (or 5.5 times) the amount of carbon in the atmosphere before 1900.

CARBON EXCHANGE MODEL

After the method previously developed [Plesset and Dugas, 1966], four reservoirs of carbon dioxide will be considered to exchange as indicated schematically in Fig. 1. The equations for exchange of carbon among the four reservoirs under equilibrium conditions (that is, before significant hydrocarbon fuel consumption begins) are:

$$-K_{ad}N_a - K_{am}N_a - K_{ah}N_a + K_{da}N_d + K_{ma}N_m + K_{ha}N_h = 0 \qquad (1)$$

$$-K_{ha}N_h + K_{ah}N_a = 0 \qquad (2)$$

$$-K_{ma}N_m - K_{md}N_m + K_{am}N_a + K_{dm}N_d = 0 \qquad (3)$$

$$-K_{da}N_d - K_{dm}N_d + K_{ad}N_a + K_{md}N_m = 0 \qquad (4)$$

where

N_i is the amount of carbon in reservoir i under equilibrium conditions (see Fig. 1).

Subscripts refer to the four reservoirs:
a - atmosphere
h - humus
m - mixed layer of oceans
d - deep sea

K_{ir} is the exchange rate constant for exchange of carbon between reservoir i and r as determined by radiocarbon data and multiplied by the appropriate fractionation factors (see Table 3).

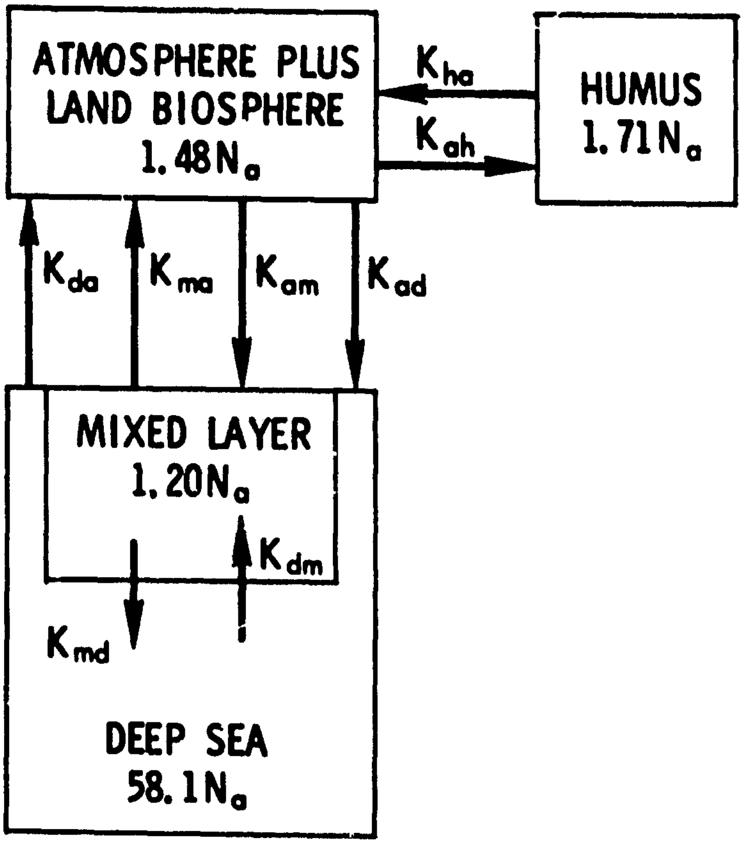

Fig. 1 Four-reservoir model of the earth's carbon exchange system. Amount of carbon in each reservoir is given relative to that in the atmosphere alone, N_a.

Table 3

EXCHANGE RATE CONSTANTS FOR CARBON IN (YEARS)$^{-1}$

Exchange Rate Constant	$\eta = 1$	$\eta = 10$
K_{ah}	2.91×10^{-3}	2.91×10^{-3}
K_{am}	1.78×10^{-2}	3.65×10^{-2}
K_{ad}	1.78×10^{-2}	3.65×10^{-3}
K_{ha}	2.52×10^{-3}	2.52×10^{-3}
K_{ma}	8.85×10^{-4}	8.44×10^{-3}
K_{md}^{*}	2.75×10^{-2}	5.12×10^{-2}
K_{da}	8.85×10^{-4}	8.44×10^{-4}
K_{dm}	1.34×10^{-4}	3.02×10^{-4}

*Note that incorrect values of k_{md} were given in the referenced paper [Plesset and Dugas, 1966].

The ratio of exchange rates between atmosphere-mixed layer and atmosphere-deep sea is denoted by

$$\eta = K_{am}/K_{ad}$$

Since this ratio has not been well-established by experimental data, exchange rate constants are given for two values of η in Table 3. If one assumes that the exchange rate is directly proportional to the surface area exposed, then $\eta = 3$ is the appropriate value, at least for the Atlantic Ocean where the areas of deep sea upwelling near the poles amount to about one-fourth the ocean area [Craig, 1963]. However, it is generally thought that K_{ad} tends to be larger than K_{am} at high latitudes, because of the stronger winds and more turbulent sea conditions and ˜ = 1 appears more nearly correct. We shall use here values of ˜ = 1 and 10 to determine the effect of varying amounts of exchange between deep sea and atmosphere. ˜ = ∞ corresponds to the so-called chain model in which no direct exchange between deep sea and atmosphere occurs.

In the non-equilibrium condition, that is, after pollution begins, we denote the amount of carbon in reservoir i by $N_i{}^*$, a function of time. The non-equilibrium equations will then be analogous to the steady state, with the addition of a term, p(t), which represents the rate of addition of carbon to the atmosphere. It is convenient to use in place of the $N_i{}^*$, the following variables:

$$x = N_a{}^* - N_a \; ; \quad u = N_m{}^* - N_m$$

$$y = N_h{}^* - N_h \; ; \quad v = N_d{}^* - N_d$$

The non-equilibrium equations then become

$$\frac{dx}{dt} = -\left(K_{ah} + K_{am} + K_{ad}\right)x + K_{ma}u + K_{da}v + K_{ha}y + p(t) \qquad (5)$$

$$\frac{dy}{dt} = -K_{ha}y + K_{ah}x \qquad (6)$$

$$\frac{du}{dt} = -\left(K_{ma} + K_{md}\right)u + K_{am}x + K_{dm}v \qquad (7)$$

$$\frac{dv}{dt} = -\left(K_{da} + K_{dm}\right)v + K_{ad}x + K_{md}u \qquad (8)$$

Since we do not know the rate at which carbon fuel will be consumed in the future, we must extrapolate the function p(t) from present data. For the past few years world production of hydrocarbon fuels has been increasing by over 4 percent per year, although the rate of increase has not been steady as shown in Table 4.

Table 4

RECENT WORLD PRODUCTION OF HYDROCARBON FUELS*

	World Production			Calculated
	Coal	Natural Gas	Crude Petroleum	Carbon Released
Year	(10^9 tons)	(10^9 cu m)	(10^9 tons)	(10^9 tons)
1959	2.53	431	1.04	2.53
1960	2.64	479	1.12	2.67
1961	2.49	513	1.19	2.66
1962	2.55	547	1.30	2.79
1963	2.66	621	1.39	2.97
1964	2.76	680	1.50	3.14
1965	2.81	723	1.62	3.28
1966	2.84	763	1.75	3.42

*Production data from Bureau of Mines [1963-1966]. Natural gas liquids are neglected, since they represent less than 2 percent of the total.

As long as the exponential rate of increase continues, the amount of carbon released to the atmosphere each year will have the form

$$p(t) = \alpha P_o(e^{\gamma t} - 1); \qquad 0 < t < t_1 \qquad (9)$$

We shall assume t_o to be the year 1900, when the industrial revolution was gaining momentum and effluents to the atmosphere were becoming significant. The amount of carbon in the atmosphere at that time, P_o, is estimated to have been about 590 billion tons. Evaluating the constants in Eq. (9) to correspond with a 4 percent annual increase and the production data for 1966 gives:

$$p(t) = .000471 \, P_o \, (\epsilon^{.0392 \, t} - 1); \qquad 0 < t < t_1 \qquad (10)$$

It is improbable that the exponential rate of increase in fuel consumption will continue unabated until fuel supplies are completely exhausted. It seems more likely that fuel consumption will continue exponentially for some time, then level off as fossil fuel becomes scarce and other types of energy are developed. Eventually the hydrocarbon fuels will cease to be significant as the last of the reserves become uneconomical to recover. The leveling-off portion of the curve may be approximated by a hyperbolic tangent function:

$$p(t) = c \tanh bt; \qquad t_1 < t < t_{max} \qquad (11)$$

The values for constants c and b will depend on the estimated fuel consumption rate for many years in the future. If the rate of consumption reaches a maximum of ρ times the current value, which was 3.42 billion tons per year in 1966, then c becomes $.00578\rho P_0$. For (tanh bt) to approach a value of one within about 200 yr, b must be at least 0.01. The equation for p(t) will then be

$$p(t) = .00578\rho P_0 \tanh (.01\ t); \qquad t_1 < t < t_{max} \qquad (12)$$

Larger values of b will cause the consumption rate to reach its maximum value sooner. Figure 2 illustrates the rate of carbon addition to the atmosphere according to the scheme described above for ρ = 5, 10, 20. The exponential function is used to approximate the first portion of the curve and the tanh function approximates the latter half. The intersection of the two curves determines t_1. Addition of carbon is assumed to drop sharply to zero at t_{max} when all fossil fuel resources are exhausted. The area under each composite curve represents the total amount of carbon added over all time due to combustion of fossil fuel, and in each case must be equal to the original supply ($4.9\ P_0$). Thus the integral determines the value of t_{max}.

$$\int_0^{t_{max}} p(t)dt = \alpha\ P_0 \int_0^{t_1} (e^{\gamma t} -1)dt + \rho a\ P_0 \int_{t_1}^{t_{max}} (\tanh bt)dt = 4.9\ P_0 \qquad (13)$$

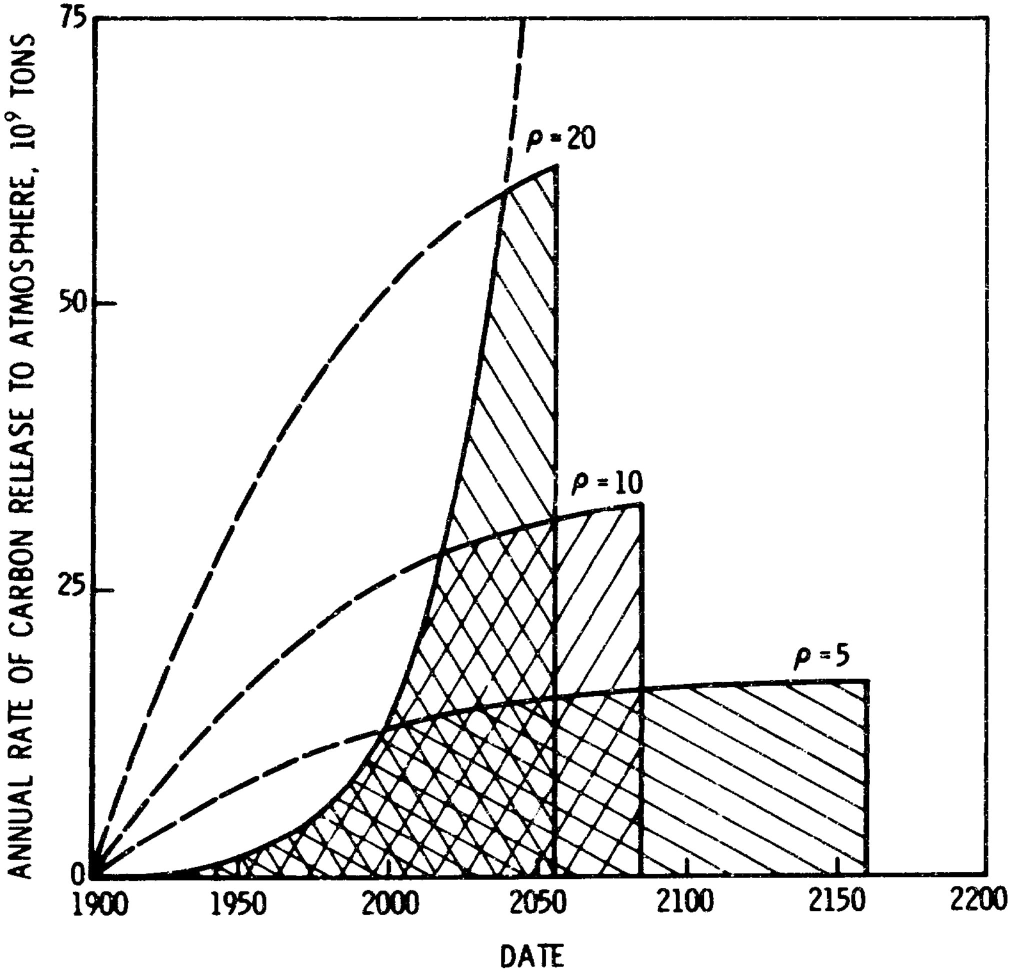

Fig. 2 Rate of addition of fossil fuel carbon to the atmosphere according to the composite schedule described in the text. Total carbon released to atmosphere in each case is 2875 billion tons.

RESULTS

The rise and decay of excess carbon in the four reservoirs was calculated by numerically integrating Eqs. (5) through (8) using several assumptions as to the rate of consumption of fuel, total supply of fossil fuel, and amount of mixing between deep sea and atmosphere.

Figure 3 illustrates the changes in carbon concentration in each reservoir as excess carbon is added according to the schedule for $\rho = 10$. When the addition of carbon to the atmosphere stops (fuel resources exhausted), the carbon concentration in each reservoir gradually approaches a new equilibrium value, with over 90 percent of the excess accumulating in the deep sea. In the case illustrated, the atmosphere-land biosphere combined reaches a maximum carbon excess at nearly the same time as the peak fuel consumption. The mixed layer reaches a maximum about half as great a few years later. The excess carbon in the humus is even less and delayed somewhat longer than the mixed layer, but over the long run it retains a slightly greater quantity of carbon.

It was assumed that the exchange between land biosphere and atmosphere is fairly rapid, so that the ratio of carbon in these two reservoirs remains essentially constant. Figure 4 illustrates the carbon content of the atmosphere alone for three different fuel consumption rates. It can be seen that the maximum carbon content and the time at which it is reached are highly sensitive to the value of ρ. The equilibrium value is independent of ρ, however, depending only on the total amount of fuel consumed; thus th carbon content decays to a value about 8 percent above normal in each case.

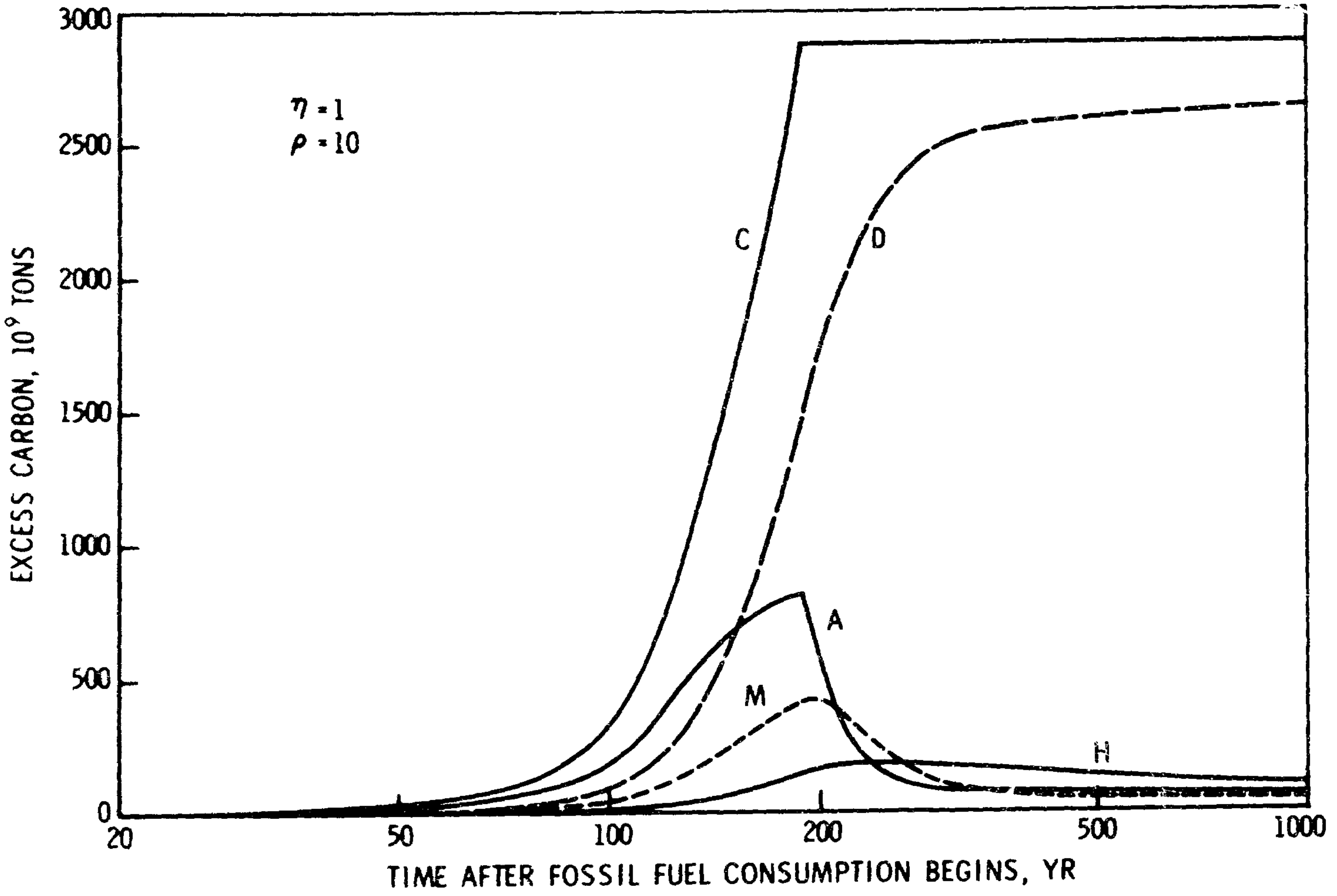

Fig. 3 Excess carbon in the earth's four reservoirs during and after consumption of all fossil fuel: C) cumulative carbon addition to the atmosphere from fossil fuel, A) atmosphere plus land biosphere, H) humus, M) mixed layer of the oceans, D) deep sea.

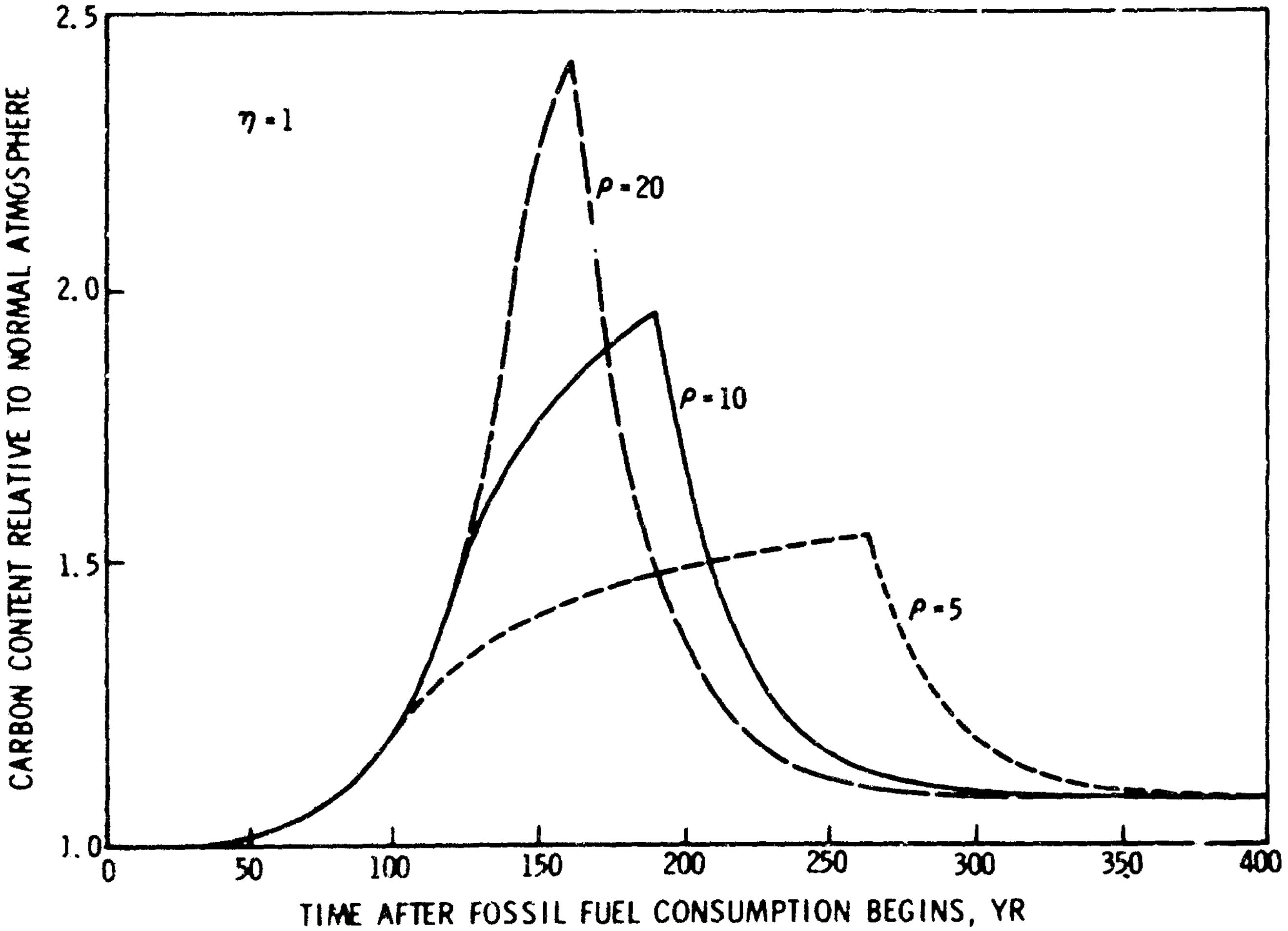

Fig. 4 Carbon content of the atmosphere for various projected fuel consumption schedules. Carbon content of atmosphere at $t = 0$ is assumed 590 billion tons.

A change in τ has very little effect on the time variation of carbon in the atmosphere (Fig. 5). Changing τ has a greater, but opposite, effect in the mixed layer and also shifts the time of peak carbon content. The mixed layer reaches its maximum carbon content at $t = 196$ or 192 years for $\tau = 1$ or 10, respectively, while the atmosphere reaches its maximum at $t = 189$ years in either case, giving delay times of 7 years for $\tau = 1$ or 3 years for $\tau = 10$.

The inclusion of shale oil extends the total fossil fuel supply slightly (10 years for $c = 10$), but as Fig. 6 shows, it has a relatively minor effect on the carbon content of the atmosphere. The ultimate equilibrium value after all fuel is consumed is about 10 percent higher than if shale oil were not included.

We may conclude that the atmospheric carbon concentration is not highly sensitive to the discrepancies in estimating total fuel resources, nor to variations in direct exchange between atmosphere and deep sea, but that the rate of future fuel consumption is much more critical to the transient carbon distribution.

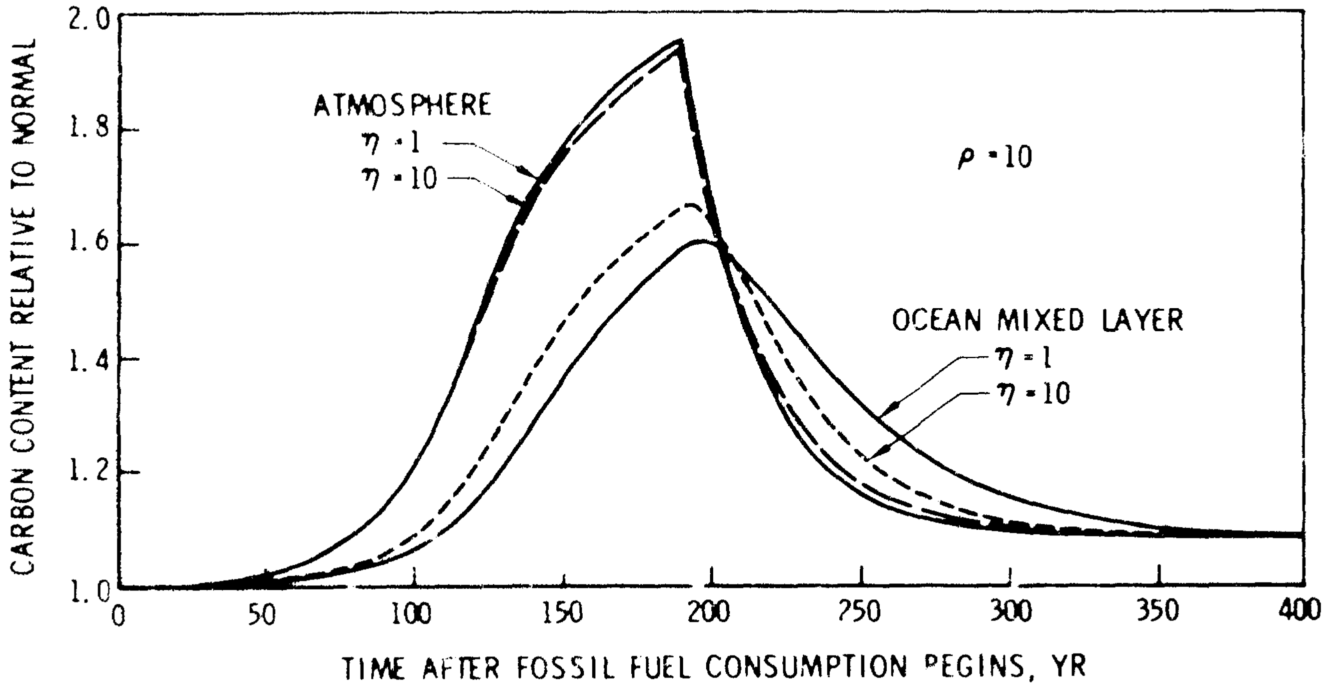

Fig. 5 Comparison of carbon content of the atmosphere and oceans for $\eta = 1$ and 10.

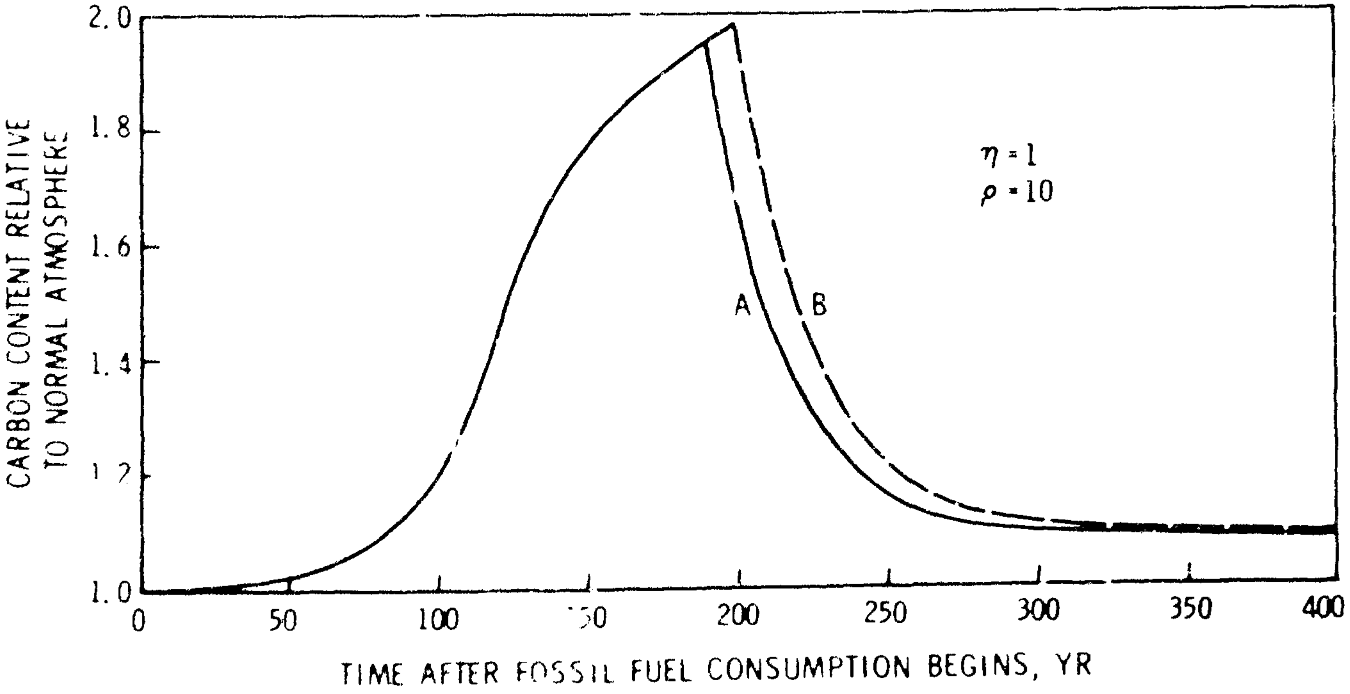

Fig. 6. Carbon content of the atmosphere during and after consumption of all fossil fuels: A) assuming no shale oil is used, B) including all shale oil.

DISCUSSION

According to the model of carbon exchange described here, about 40 percent of the carbon released so far by combustion of fossil fuel should have remained in the atmosphere. This is in reasonable agreement with the data of Keeling and Waterman [1968], whose measurements indicate that the increase in atmospheric carbon dioxide corresponds to about half the carbon fuel consumed to date. The model further indicates that the natural exchange processes among carbon reservoirs cannot operate fast enough to maintain equilibrium as long as the current and projected rates of fossil fuel consumption prevail. Thus, it may be expected that the atmosphere will continue to accumulate nearly half of the carbon released until fuel consumption rates decline or the fuel supply is exhausted. It is impossible to predict with any confidence the maximum carbon dioxide concentration that will be reached, since that depends on future rates of hydrocarbon fuel consumption. Obviously the scheme presented here for describing future consumption rates is only one of many possibilities. However, within the constraints of the known recent consumption rates and the remaining supply, it would seem that future consumption rates could not deviate greatly from those presented here. In any case, it appears that the equilibrium concentration of carbon in the atmosphere that is eventually reached after all fossil fuel is consumed will be about 8 percent above the pre-1900 normal.

REFERENCES

Averitt, Paul, U.S. Department of the Interior, Geological Survey News Release, April 20, 1968.

Bolin, B., and C. D. Keeling, Large Scale Atmospheric Mixing, J. Geophys. Res., 68 (13), 3899-3920, 1963.

Bureau of Mines, U.S. Department of the Interior, Bull. #630, Mineral Facts and Problems (1965).

Bureau of Mines, U.S. Department of the Interior, Minerals Yearbook, 1963-1966.

Callendar, G. S., On the Amount of Carbon Dioxide in the Atmosphere, Tellus, 10, 243-248, 1958.

Craig, H., The Natural Distribution of Radiocarbon: Mixing Rates in the Sea and Residence Times of Carbon and Water, in Earth Science and Meteoritics, edited by J. Geiss and E. D. Goldberg, pp. 103-114, North Holland Pub. Co., Amsterdam, 1963.

Hendricks, T. A., Resources of Oil, Gas, and Natural Gas Liquids in the U.S. and the World, U.S. Geological Survey circular #522 (1965).

Hubbert, M. K., Energy Resources, National Academy of Sciences - National Research Council Publication 1000-D, Washington, D.C., 1962.

Keeling, C. D., and L. S. Waterman, Carbon Dioxide in Surface Ocean Waters, J. Geophys. Res. 73 (14), 4529-4541, 1968.

Plesset, M. S., and D. J. Dugas, Decay of a Disturbance in the Natural Distribution of Carbon-14, The RAND Corporation, RM-5'00-TAB, November 1966.

Weeks, L. G., The Next Hundred Years Energy Demand and Sources of Supply, GeoTimes, 5, (1), 18-21 and 51-55, 1960.