

Gas exchange rates between air and sea¹

By W. S. BROECKER and T.-H. PENG, *Lamont-Doherty Geological Observatory of Columbia University, Palisades, New York 10964*

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ABSTRACT

Gas exchange rate studies carried out in the laboratory suggest that the stagnant film model is adequate to relate the transfer coefficients of most gases between the atmosphere and sea to an accuracy of $\pm 15\%$. Estimates of the average film thickness prevailing for the world ocean based on the distribution of natural radiocarbon, bomb-produced radiocarbon, and radon are in good agreement. Radon data from the BOMEX area and from station PAPA lend support to Kanwisher's suggestion that gas exchange rates should vary in proportion to the square of the wind velocity. These observations permit a number of generalizations regarding the potential of the ocean as a source and sink for trace gases to be made. They also permit the more complicated situation for carbon dioxide to be assessed.

Introduction

The ability to predict rates of gas transfer between various regions of the ocean surface and atmosphere is necessary to the understanding of the cycles of a number of trace atmospheric gases. For some of these gases the ocean is a potential sink; for others the ocean has been proposed as a natural source. If we are to develop the capability to make long range forecasts of the effect of pollution on concentrations of these gases, we must be able to establish their air-sea transfer rates. In order to do this it is necessary to measure not only the concentration difference across the air-sea interface but also the transfer coefficient governing the exchange.

Although experiments carried out in the laboratory are useful in establishing the order of magnitude of these rates and their dependence on wind velocity, temperature, gas solubility, diffusion rate and aqueous chemistry, the complexity of open ocean conditions precludes accurate absolute estimates by this means alone. It is necessary to measure some parameter in the "real" ocean which can be linked directly to the gas exchange process. To date only two such methods have been successfully employed. Both involve the exchange between the air and

sea of a natural radioactive trace gas. One of these is $C^{14}O_2$ and the other is Rn^{222} . In this paper the results obtained by these methods are reviewed. In addition, new radon results from the Atlantic GEOSECS study are presented.

Evaluation of gas exchange model

Before commencing with a discussion of these isotopic methods a brief discussion of models of gas exchange is in order. Dankwerts (1971) in his recent book has given a general review of the subject based largely on chemical engineering studies of industrial processes involving the uptake of reactive gases such as NH_3 , CO_2 , and SO_2 . He compares the reliability of the classical stagnant film model (see Fig. 1) with that of the more recent film replacement models and concludes that, at least for the purposes of the processes studied by chemical engineers, the models give equally satisfactory results. Choices among them can be made only in connection with the relative ease of mathematical computation. As oceanographers have used exclusively the stagnant film model in their calculations, it is consoling to know that it provides an adequate first order approximation to the much more complex processes actually taking place.

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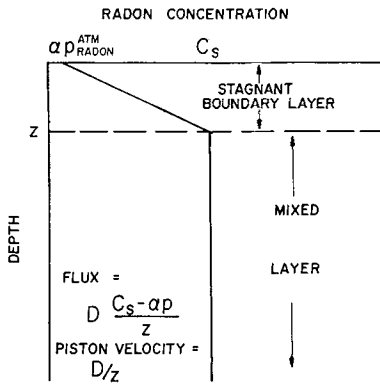


Fig. 1. Stagnant boundary layer model of gas exchange. The rate of transfer of gas between water and air is controlled by the thickness of a thin layer of water through which gas is transferred only by molecular diffusion. The overlying air and underlying water are assumed to be well mixed. In the flux equation, D is the molecular diffusivity of gas, z is the thickness of the film, C_s is the concentration of the gas at the bottom of the film, α is the solubility of the gas, and p is the partial pressure of the gas in the air.

Briefly, the stagnant film model assumes that the rate limiting step to transfer between air and water is molecular diffusion through a hypothetical stagnant water film. The air above this film is assumed to be well mixed (i.e., a measurement made 10 m above the sea surface from a ship would give the gas concentration

Table 1. Comparison of film thicknesses obtained from the laboratory agitation in fresh and sea water

Agitation	Gas	Film thicknesses (μ)
<i>Fresh water</i>		
High	Rn ²²²	97
	O ₂	102
	CO ₂	83
Low	Rn ²²²	236
	O ₂	285
	CO ₂	233
<i>Sea water</i>		
High	Rn ²²²	138
	O ₂	156
	CO ₂	129
Low	Rn ²²²	261
	O ₂	337
	CO ₂	311

Table 2. Diffusivities of dissolved gases in water^a

All values are in 10^{-5} cm²/sec

Temp. °C							
	0	5	10	15	20	25	30
H ₂	2.24	2.61	3.03	3.49	4.01	4.58	5.21
N ₂	0.95	1.11	1.29	1.49	1.71	1.96	2.23
O ₂	1.17	1.36	1.57	1.80	2.06	2.35	2.66
He ^c	3.07	3.57	4.14	4.78	5.48	6.26	7.12
Ar ^c	0.88	1.02	1.18	1.36	1.56	1.78	2.03
Rn	0.67	0.79	0.91	1.05	1.20	1.37	1.56
CO ^b	0.98	1.14	1.32	1.53	1.75	2.00	2.27
CO ₂	0.94	1.08	1.25	1.43	1.64	1.86	2.11
CH ₄ ^b	0.98	1.14	1.32	1.53	1.75	2.00	2.27
N ₂ O	1.16	1.35	1.56	1.80	2.07	2.36	2.69
H ₂ S	0.87	1.02	1.18	1.36	1.56	1.78	2.03
SO ₂	0.85	0.99	1.15	1.34	1.54	1.77	2.02

^a These values are interpolated from some measured diffusion constants by the equation $\log D = (-1010/T) + B$ (Himmelblau, 1964), where T is the absolute temperature, B is a constant and varies from gas to gas. The constant B for various gases is evaluated in terms of measured values of D at known temperatures as summarized by Himmelblau (1964). The maximum uncertainty is 20%.

^b Measured values of D are not available. The interpolation is based on theoretical prediction by Wilke & Chang's (1955) equation at 25°C.

^c These values at 25°C are approximately 2.5 times higher than those given by Boerboom & Kleyn (1969).

in the air immediately above the sea surface). The top of the stagnant film is assumed to have a gas concentration at equilibrium with the overlying air (i.e., $[\text{gas}]_0 = \alpha p^{\text{atm}}$ in Fig. 1). Similarly the water below the stagnant film is assumed to be well mixed. The concentration of the gas as measured in a sample from one meter below the surface is assumed to typify that at the base of the film. The thickness of the film (and hence the rate of gas exchange) is dependent on the degree of agitation of the sea surface by wind and wave motion; the higher the state of agitation the thinner the film and the more rapid the exchange rate. Kanwisher (1963) has shown in laboratory experiments that the rate of exchange (and hence the reciprocal of the film thickness) is roughly proportional to the square of the wind velocity.

In order to check the adequacy of this model in predicting the gas exchange rate of one gas from measurements of the exchange rate of another, one of us (THP) made measurements

of the film thickness values obtained by exchanging three different gases in a laboratory container agitated by recirculating the water (see Peng, 1973, for details). The degree of agitation was adjusted so that film thicknesses approximating more quiet oceanic conditions were obtained (in one set of experiments z was about 100 and in the other, 250 microns). As shown in Table 1 the agreement among results for O_2 , CO_2 , and Rn^{222} both for fresh water and for sea water is satisfactory, although these gases are not done simultaneously in one container. The uncertainties in the molecular diffusion data alone (see Table 2) could account for the differences observed. Although this set of experiments cannot be used to verify the reliability of the model for all sea states and all gases it is consistent with the conclusion of the chemical engineers that for accuracies to $\pm 15\%$ the film model should be reliable for chemically inactive gases (the CO_2 experiments summarized above were for solutions where CO_2 rather than HCO_3^- was the dominant carbon species; the sea water used was acidified).

It should be noted at this point that the stagnant film model predicts that the transfer coefficients (piston velocities, see Fig. 1) for various gases will be proportional to their respective molecular diffusion coefficients. The film replacement models, on the other hand, predict dependency on the *square root* of the diffusivity. As the gases of interest (CO_2 , CO , CH_4 , N_2O , SO_2 , Rn^{222} , ...) show only a range of 1.5 in their rates of diffusion, the maximum difference between the results obtained by using stagnant film model and those by using the film replacement model to predict the rate of exchange of one gas from that of another is a factor of $\sqrt{1.5}$ or about 1.2. At the present state of our knowledge such errors are not of great significance.

Bolin (1960) was the first to present a modification of the stagnant film model to include the enhancement in exchange rate resulting from the reaction of CO_2 with carbonate ion to form two bicarbonate ions. Although Quinn & Otto (1971) show that Bolin's assumption of constant pH within the film is not correct they point out that for situations where the CO_2 partial pressure difference between gas and water is small his formulation is adequate. As this condition is met almost everywhere in the ocean Bolin's model can be used. More

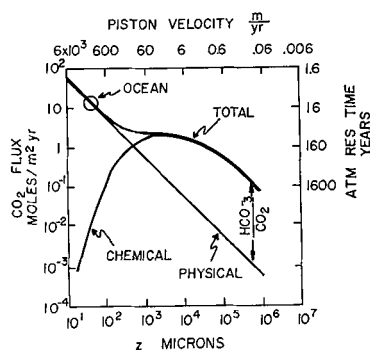
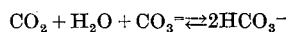


Fig. 2. Chemical enhancement of oceanic CO_2 gas exchange rate resulting from the chemical reaction



For the range of film thicknesses observed in the ocean the effect is small. The calculations are based on the formulation by BOLIN (1960).

general formulations such as that of Quinn & Otto (1971) prove prohibitively complex.

The effect of chemical enhancement on the exchange rate for CO_2 gas as a function of film thickness for sea water is shown in Fig. 2. At very low film thicknesses the chemical enhancement is negligible. For very large film thicknesses the chemical pathway dominates. The ratio of chemically supported to pure physical transport through the film approaches the ratio of HCO_3^- to CO_2 in the solution. For sea water this ratio averages 150. The transition from the region where physical transport dominates to that where chemical transport dominates is characterized by a lack of sensitivity of gas exchange rate to film thickness, the main mechanism being diffusion of CO_2 coupled with reaction with CO_3^{2-} ion to form two HCO_3^- ions.

The film thickness at which chemical enhancement becomes important depends on the time constants for the reaction pathways which convert CO_2 to HCO_3^- . These increase not only with temperature but also with pH (and perhaps, as suggested by Berger & Libby (1969) with the presence of natural catalysts). For waters in contact with the air the pH of the water rises with alkalinity. Hence the greater the bicarbonate ion content of the water the greater the reaction rate and the lower the stagnant film thickness at which chemical enhancement becomes important. Bolin (1960) concluded that the average film thickness

Table 3. Summary of chemical enhancement on CO_2 exchange rates

z (μ)	Alk. ^a (mM/l)	$F_{No\ ENH}^{Pred. b}$ (M/m ² yr)	$F_{ENH}^{Pred. c}$ (M/m ² yr)	F_{Obs}^d (M/m ² yr)	$F_{Obs} - F_{No\ ENH}$	$F_{Obs} / F_{No\ ENH}$
					$F_{ENH} - F_{No\ ENH}$	$F_{ENH} / F_{No\ ENH}$
<i>Fresh H₂O</i>						
83	1.64	8.8	9.6	10.8	2.5	1.13
83	2.32	8.8	9.7	11.6	3.1	1.20
83	2.80	8.8	9.8	12.2	3.4	1.25
233	0.64	3.1	4.6	5.0	1.3	1.10
233	1.30	3.1	4.9	5.1	1.1	1.04
233	2.40	3.1	5.4	6.2	1.4	1.15
<i>Sea H₂O</i>						
129	2.41	4.9	7.2	9.6	2.0	1.33
311	2.24	2.1	6.0	6.3	1.1	1.05

^a z = film thickness, Alk. = alkalinity.

^b $F_{No\ ENH}^{Pred.}$ = predicted CO_2 flux without chemical enhancement.

^c $F_{ENH}^{Pred.}$ = Predicted CO_2 flux with chemical enhancement.

^d $F_{Obs.}$ = observed CO_2 flux.

for the sea fell well within the region where the enhancement is negligible. If so, then the task of relating air-sea $C^{14}O_2$ exchange rates to those of other gases becomes much easier.

To test whether any serious problem exists in this connection the gas exchange experiments mentioned above were extended to include solutions with alkalinities close to that for sea water. They were carried out under conditions identical to those for solutions free of any alkalinity. As summarized in Table 3 the predicted *enhancement* (based on Hoover & Berkshire's (1969) solution to Bolin's (1960) equations and the stagnant film thicknesses obtained for CO_2 in alkalinity-free solutions) and the observed *enhancement* differ by a factor of three (column 6 in Table 3). Whether this reflects an inadequacy in the experiment, an error in the reaction rates adopted, or some inadequacy in the film model is not clear. Lately Liss (1973) reported similar results under a different experimental method. In any case, since the film thickness developed in the laboratory experiments is much greater than that of the mean ocean, use of the observed enhancement, rather than the theoretical enhancement, affects the results by only 10%. Thus, although the situation for CO_2 exchange in alkaline solutions needs more study, the film model (with no correction for chemical enhancement) should still be adequate for our present purposes.

Film thickness estimates based on radiocarbon data

With this background in mind let us turn our attention to the techniques used to measure the apparent stagnant film thicknesses which exist in the sea. Our first good estimate came from the distribution of natural radiocarbon between the air and sea. Since radiocarbon is generated within the air and decays largely within the sea there must be a net transport of C^{14} atoms (as $C^{14}O_2$) from the atmosphere to the sea. If, as has been documented by C^{14} measurements on tree rings, the C^{14}/C^{12} ratio in the atmosphere has been nearly constant over the last 2000 years, then the system must be close to steady state. If so, the rate of decay of C^{14} within the sea must be matched by the net transport of C^{14} through the sea surface. The C^{14}/C^{12} ratio in atmospheric CO_2 prior to the industrial revolution and nuclear testing was nearly uniform over the globe. In the warm surface ocean the C^{14}/C^{12} ratio in the dissolved inorganic carbon also appears to have been quite uniform (see summary by Broecker & Li, 1970). Further, as shown by Takahashi (1961) and by Keeling et al. (1965a, 1965b) the partial pressure of CO_2 in the warm ocean is uniform to within 10% and averages very close to that in the air. In the polar oceans (especially the Antarctic) the C^{14}/C^{12} ratios are lower than in the warm ocean. Also the CO_2 pressures are

lower. Because these differences are not well mapped and since the polar oceans constitute only about 10% of the sea surface, these differences from the warm surface ocean have generally been ignored. The surface ocean has, for the purposes of the calculation, generally been assumed to be homogeneous in its C^{14}/C^{12} ratio, and its CO_2 partial pressure to be equal on the average to the atmosphere (if the carbon cycle was at steady state prior to the industrial revolution). The error associated with this assumption stems mainly from the lower C^{14}/C^{12} ratios in the Antarctic. Were they included, a somewhat greater film thickness would be obtained for the average world ocean. Although difficult to estimate, this correction should not exceed 40%.

Based on the assumption of steady state in the C^{14} and C cycles and uniform C^{14}/C^{12} ratio in air and surface sea, the amount of C^{14} entering the sea must balance the decay of C^{14} within the sea:

$$A \frac{D}{z} [CO_2]_{mix} \left[\frac{C^{14}}{C} \Big|_{atm} \frac{\alpha C^{14} O_2}{\alpha CO_2} - \frac{C^{14}}{C} \Big|_{mix} \right] = V [\sum CO_2]_{ocean} \frac{C^{14}}{C} \Big|_{ocean} \lambda \quad (1)$$

Thus,

$$\frac{D}{z} = \frac{[\sum CO_2]_{ocean} V}{[CO_2]_{mix} A} \times \frac{\left[\frac{C^{14}}{C} \Big|_{ocean} / \frac{C^{14}}{C} \Big|_{atm} \right] \frac{\alpha C^{14} O_2}{\alpha CO_2}}{1 - \left[\frac{C^{14}}{C} \Big|_{mix} / \frac{C^{14}}{C} \Big|_{atm} \right] \frac{\alpha C^{14} O_2}{\alpha CO_2}} \lambda \quad (2)$$

Taking the mean total dissolved carbon content of the ocean, $[\sum CO_2]_{ocean}$, to be 2.3 moles/m³, the mean dissolved CO_2 gas content of the surface mixed layer, $[CO_2]_{mix}$, to be 1.2×10^{-2} moles/m³, the mean depth, V/A , of the ocean to be 3 800 m, the mean C^{14}/C ratio in the ocean to be 0.84 that at the top of the stagnant film, i.e., $(C^{14}/C)_{atm} \cdot (\alpha C^{14} O_2 / \alpha CO_2)$, while the mean ratio in the mixed layer to be 0.96 this value, and the radioactive decay constant, λ , for C^{14} to be $1/8 250 \text{ yr}^{-1}$, the transfer coefficient (or piston velocity) of CO_2 , D/z , is calculated to be 1 800 m/yr. Taking the molecular diffusivity of CO_2 to be $5 \times 10^{-2} \text{ m}^2/\text{yr}$, the mean film thickness of the world ocean is calculated to be

Table 4. Ocean atmosphere exchange rates based on the distribution of natural radiocarbon

Reference	CO_2 Atm. res. time (yrs)	Equiv. film ^a thickness (microns)
Arnold & Anderson (1957)	14	46
Craig (1957)	7 ± 3	23 ± 10
Revelle & Suess (1957)	~ 7	~ 23
Bolin & Erikson (1959)	5	17
Broecker (1963)	8 ^b	25
Craig (1963)	15 ± 5	50 ± 17

^a Assume D_{CO_2} at 20°C = $1.6 \times 10^{-5} \text{ cm}^2/\text{sec}$, $[CO_2]_{mixed\ layer} = 1 \times 10^{-5} \text{ M/l}$, Atmospheric $CO_2 = 2.41 \times 10^{18} \text{ g}$, Ocean area = $3.6 \times 10^{18} \text{ cm}^2$.

^b Equivalent atmospheric residence time calculated from original exchange rates.

30 microns. Results of calculations made by a number of authors are summarized in Table 4. The critical factor in this calculation is the difference between the C^{14}/C^{12} ratio in atmospheric and surface ocean carbon. The estimate given by Broecker & Li (1970) is $4 \pm 1\%$. The ratio in the surface ocean is based on observations on pre-nuclear testing of sea water and shells. The atmospheric estimate is based on a host of tree ring data. The average has been corrected for the effect of industrial CO_2 (a correction of 1% to the measured difference of 5%). The result of this calculation is a film thickness of 30 ± 10 microns. Since the greatest possibility for error lies in the direction of lower film thickness (the average air-sea C^{14}/C^{12} difference could conceivably lie within the error of zero but certainly does not exceed 8%), a much more conservative estimate would be that the film thickness is less than 60 microns.

An alternate means of using $C^{14} O_2$ is to consider the distribution of C^{14} produced by nuclear testing between air and sea. This C^{14} , like that produced by cosmic rays, originates in the atmosphere and reaches the sea by gas exchange. A large number of measurements on atmospheric CO_2 since the onset of this contamination in 1954 provides a good estimate of the temporal and geographic variations in the bomb $C^{14} O_2$ content of CO_2 invading the sea. By measuring the depth integrated amount of bomb-produced C^{14} accumulated by any given portion of the sea it is possible to determine the average rate of CO_2 invasion (and hence film

Table 5. *Ocean-atmosphere gas exchange rates based on the distribution of radiocarbon produced by nuclear testing*

Reference	CO ₂ Atm. res. time (yrs)	Equiv. film ^a thickness (microns)
Rafter & Fergusson (1957)	2	7
Münnich & Roether (1967)	—	24
Bien & Suess (1967) ^b	25	83
Nydal (1967)	4.5 ± 1	15
Nydal (1968)	5–10	17–33
Young & Fairhall (1968)	4–6	13–20
Rafter & O'Brien (1970)	12	40

^a Assumed figures for calculations are the same as Table 4.

^b Bien & Suess (1967) assumed the surface ocean to be part of atmospheric reservoir.

thickness) over the last decade or so. Münnich & Roether (1967) calculate film thickness ranging from 16 to 72 microns for the North Atlantic. Since the vertical distribution of C¹⁴ at any given locality is influenced by horizontal transport the rates obtained by this method could be somewhat too high in some areas (where a net horizontal influx of C¹⁴ has occurred) and too low in others (where a net horizontal loss of C¹⁴ has occurred). In any case, the average film thickness of 24 microns is certainly consistent with the result obtained for the entire ocean from natural C¹⁴. Other such estimates are summarized in Table 5. The average film thickness is seen to be 30 ± 25 microns by the bomb C¹⁴ method.

Film thickness estimates based on radon data

Broecker & Peng (1971) proposed a second isotopic method which would yield gas exchange rates for local areas of the sea integrated over several days (as opposed to large segments of the ocean integrated for many years by the C¹⁴O₂ methods). Radon gas (half life 3.85 days) generated within the sea by the decay of dissolved radium is in part lost to the atmosphere before it undergoes radioactive decay. The magnitude of this loss provides a measure of the stagnant film thickness. This is done by matching the loss rate of radon through the

stagnant boundary film with the difference between the depth integrated Ra²²⁶ and Rn²²² activities (if no loss occurred the integrated activities of parent and daughter in the water column would be identical). The equation can be written as:

$$D \frac{(C_S - \alpha P^{\text{atm}})}{z} = \lambda \int_0^\infty (C_E - C_x) dx \quad (3)$$

where C_E , C_x , C_S are, respectively, the concentration of radon at radioactive equilibrium with the dissolved radium, the concentration measured at some depth, x , within the surface ocean and the concentration at the base of the stagnant boundary film (i.e., as measured at the top of the mixed layer), α is the solubility of radon and P^{atm} is the partial pressure of radon in the air. For convenience the water column deficiency integral is replaced by the product of the surface deficiency times an appropriate characteristic depth, \bar{h} , i.e.,

$$\int_0^\infty (C_E - C_x) dx = (C_E - C_S) \bar{h} \quad (4)$$

Since the atmospheric burden of radon is very small (i.e., $C_S \gg \alpha P^{\text{atm}}$), eqs. (3) and (4) can be solved for the film thickness as:

$$z = \frac{D}{\lambda \bar{h}} \frac{1}{(C_E/C_S - 1)} \quad (5)$$

The radon model assumes that the effects of horizontal transport are negligible and that sea state conditions remain constant for more than a mean lifetime of a radon atom (i.e., ~6 days). Since especially the latter assumption will frequently be violated, care must be taken in interpreting results. Averages of profiles measured over a period of weeks will prove more indicative than single profiles. Where comparisons with meteorological parameters are to be made, weather data for at least a week prior to the radon measurements should be considered. If, for example, a storm causes an unusually efficient purging of radon from the mixed layer, the return of the radon profile to its "normal" value will require at least one week (the half recovery time will be $C_S/C_E \times 3.85$ days where C_S/C_E is the "normal" fraction of equilibrium between the surface radon and radium activities).

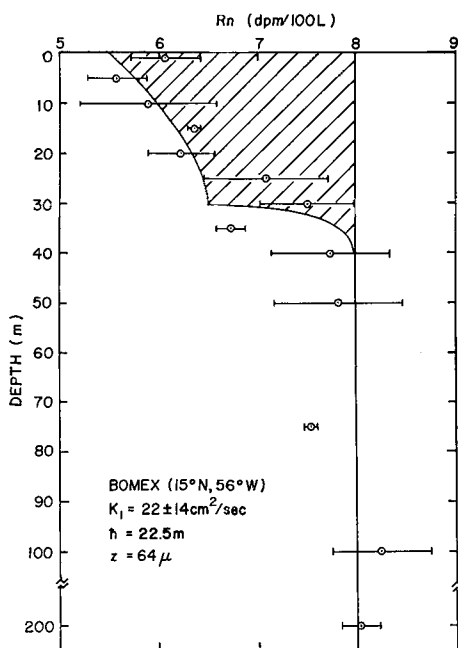


Fig. 3. Radon profile taken in the North Atlantic Ocean during BOMEX project in the summer of 1969. The shaded area indicates the net radon loss to the atmosphere. See PENG et al. (1973) for details.

Only two long series of marine radon profiles have been made to date. One was in the trade wind area off Barbados (Broecker & Peng, 1971) and the other in the winter North Pacific (Peng et al., in press). Composite profiles of the results of these two studies are reproduced in Fig. 3 and Fig. 4. For the BOMEX area where wind velocities averaged 13 knots (7 m/sec) a film thickness of 64 microns was obtained. For the North Pacific where the wind velocity averages 22 knots (12 m/sec) a film thickness of 20 microns was obtained. As predicted by Kanwisher (1963) the film thicknesses for these two stations are consistent to the inverse relation of the squares of the wind velocities (i.e., $64/20 \cong (12)^2/(7)^2$).

An upper limit on the film thickness expected for the ocean can be obtained from the results for Canadian Lake 227 in the Experimental Lakes Area southeast of Kenora, Ontario. Schindler et al. (1972) spiked the epilimnion of this 300 meter diameter lake with Ra^{226} and observed the extent of radon loss. They obtained a film thickness of about 300 microns. As the

wind velocity over this tree-shielded water body did not exceed 2 knots (3 m/sec) during the period of observation, the observed film thickness must reflect a limit imposed by the instabilities created by evaporative and thermal effects. As will be seen from the GEOSECS data summarized below, the largest value of film thickness observed in the Atlantic was about 150 microns.

The average scalar wind for the world ocean is estimated to be about 15 knots from the "Atlas of Climatic Charts of the Oceans", prepared by McDonald of the US Weather Bureau. The wind velocity in the chart is given as average wind contour according to the seasons. The average square wind of the season is obtained by taking the average of the square wind profiles from the contour along the longitude across the ocean. The world average scalar wind is the square root of the mean square wind of four seasons. Using the BOMEX and PAPA data as calibrations, we would estimate the average film thickness to be 46 microns. This compares favorably with the 30 ± 10 micron value obtained from the distribution of

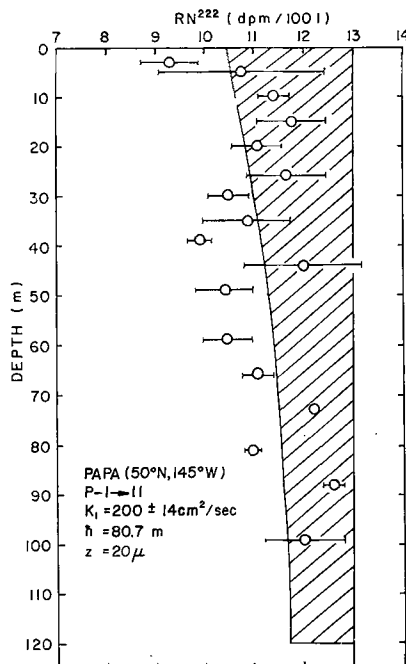


Fig. 4. Radon profile taken in the North Pacific Ocean Station PAPA in January and February of 1972. See Peng et al. (1973) for details.

Table 6. Summary of collection dates, geographic coordinates, \bar{h} and z for Western Atlantic GEOSECS stations

Station No.	Lat.	Long.	Collection date (1972)	$\frac{C_S}{C_E} - 1$	Mixed layer thickness (m)	\bar{h} (m)	z (μ)
15	69° N	20° W	8/15	0.60	13	13	44
16	72° N	08° W	8/16	0.35	10	10	104
18	70° N	0° W	8/22	0.41	35	40	26
22	62° N	14° W	8/27	0.08	55	58	98
24	54° N	34° W	9/7	0.8	5	11	51
25	48° N	40° W	9/10	0.9	27	27	24
28	39° N	44° W	9/15	0.35	32	34	55
30	32° N	51° W	9/20	< 0.2	35	33	106
32	24° N	54° W	9/24	0.4	35	20	88
34	18° N	54° W	9/28	0.4	35	32	55
36	16° N	53° W	10/11	0.4	30	30	59
39	08° N	43° W	10/17	0.4	20	24	73
40	03° N	38° W	10/19	0.1	90	80	87
41	02° N	37° W	10/20	< 0.12	100	60	97
42	0° N	37° W	10/21	0.16	90	60	73
46	0° S	34° W	10/23	< 0.13	75	60	89
48	05° S	28° W	10/25	< 0.10	80	70	100
49	07° S	28° W	10/29	< 0.13	—	50	107
49	07° S	28° W	10/29	< 0.13	—	50	107
50	08° S	34° W	11/5	0.45	55	46	34
52	09° S	33° W	11/5	0.24	70	73	41
53	12° S	27° W	11/7	0.35	30	45	43
54	15° S	28° W	11/8	0.40	20	25	68
55	18° S	31° W	11/11	0.50	30	30	44
57	24° S	35° W	11/15	0.43	40	43	34
58	27° S	37° W	11/18	0.60	22	25	40
59	30° S	39° W	11/20	0.24	50	50	49
60	33° S	42° W	11/22	0.34	58	57	28
61	36° S	45° W	11/24	0.28	80	75	26
71	42° S	50° W	12/8	0.53	60	32	31
79	55° S	50° W	12/17	0.37	20	8	126

natural C^{14} and the 30 ± 25 micron value obtained by using the distribution of bomb-produced C^{14} . If linear relation between the exchange rate and the wind speed is assumed, the film thickness is estimated to be about 59 microns from BOMEX data, and 31 microns from PAPA data (using 14 knots world average scalar wind which is obtained from linear wind profiles). These values are also comparable to those obtained from the distribution of C^{14} . Thus we can say with some confidence that the world average for a parameter characterizing the rate of exchange has been determined.

The only regional study of gas exchange rates yet attempted is currently in progress as part of the GEOSECS program. At the time this paper was prepared the Atlantic portion of this study had just been completed. The map in

Fig. 5 shows the stations at which gas exchange rates were determined. Table 6 gives the collection date, the geographical coordinates, the value of $C_E/C_S - 1$, the value of the mixed layer thickness, the value of \bar{h} , and the corresponding film thickness for each of these stations. Six profiles of the actual radon versus depth data are shown in Figs. 6 to 11. Because the laboratory Ra^{226} measurements are not yet available, the value of C_E was estimated by averaging the results for sub-mixed layer samples on a regional basis. In order to eliminate the effects of salinity variation the results have all been normalized to 35.00%. Also as shown in Fig. 12, Ra^{226} and SiO_2 covary in thermocline waters. Thus any increase of Ra^{226} with depth below the mixed layer can be taken into account by normalizing all submixed layer results to zero

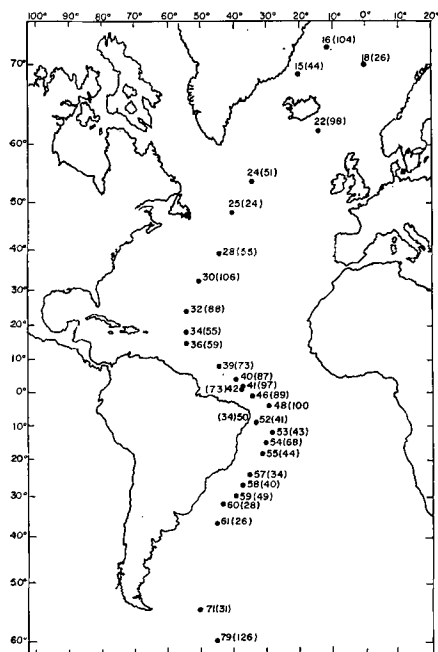


Fig. 5. Map of GEOSECS Stations where the radon profiles were taken. The number in the bracket indicates the film thickness in microns determined at the station.

silica content (the silica content of the mixed layer was not observed to exceed $1 \mu\text{m}/\text{kg}$).

The error of $\pm 7\%$ assigned to each measure-

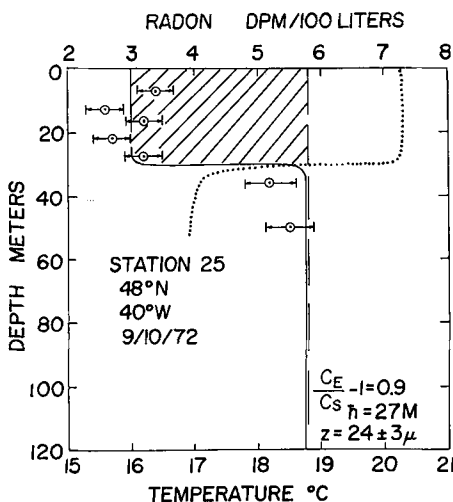


Fig. 6. Radon profile at Atlantic GEOSECS Station No. 25. The dotted curve is the temperature profile taken at the same station to show the thickness of the mixed layer.

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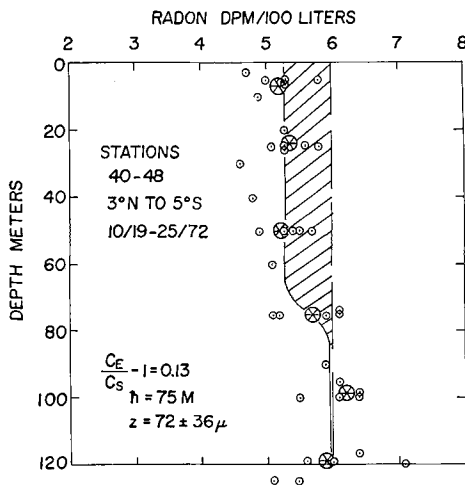


Fig. 7. Composite radon profile for Atlantic GEOSECS Stations Nos. 40-48. Small circles are individual measurements, and big circles are the average of the measurements at the same depth.

ment stems largely from a variability in the efficiencies of the individual counting cells. The statistical counting error and uncertainty in blank and background together do not account for more than a 3% error. Because of this relatively large error and the small magnitude of the deficiencies (i.e., in $C_E - C_S$) the uncertainties in the individual film thickness estimates average $\pm 30\%$.

The results, as summarized in the histogram

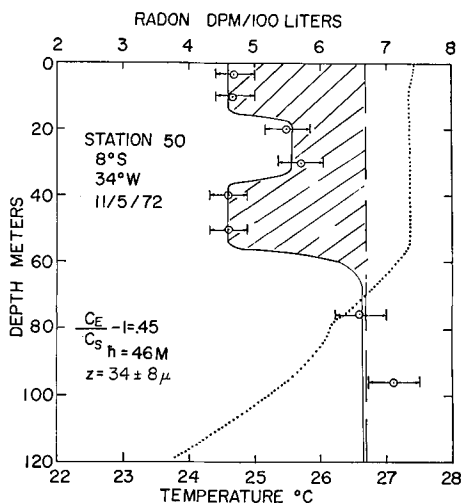


Fig. 8. Radon profile at Atlantic GEOSECS Station No. 50.

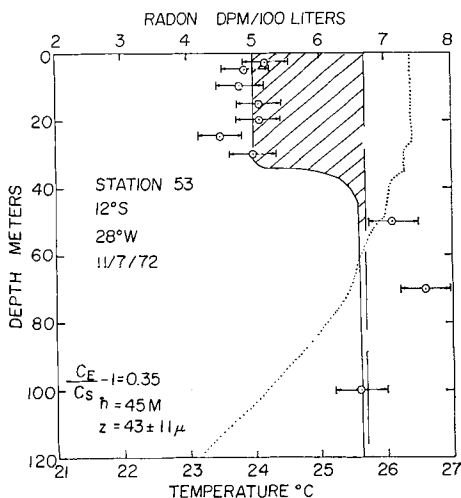


Fig. 9. Radon profile at Atlantic GEOSECS Station No. 53.

in Fig. 13 range from 24 microns to 126 microns. The average is 63 with a standard deviation of about 30 microns. Although meteorological data were obtained they were not yet available at the time this paper was written. It should be pointed out that all high latitude measurements are for relatively calm summer conditions. Thus the fact that the results average on the high side of the ocean average is not unexpected.

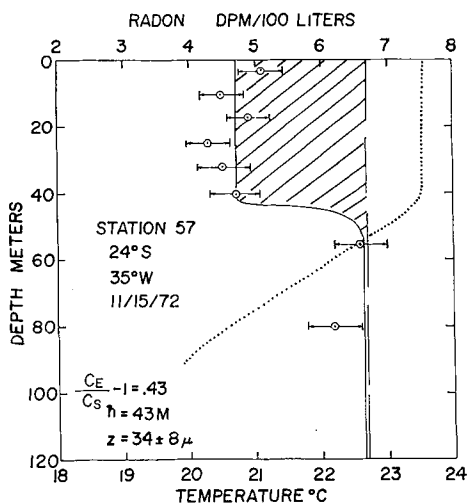


Fig. 10. Radon profile at Atlantic GEOSECS Station No. 57.

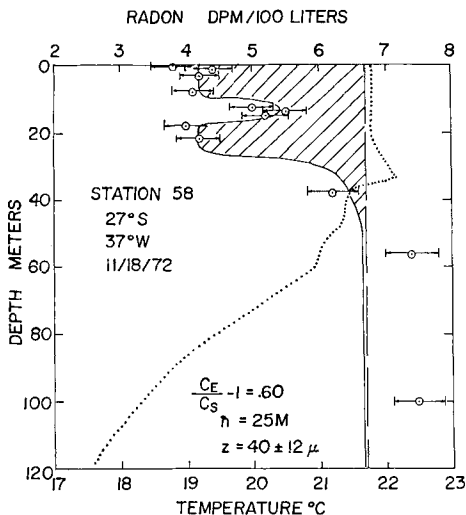


Fig. 11. Radon profile at Atlantic GEOSECS Station No. 58.

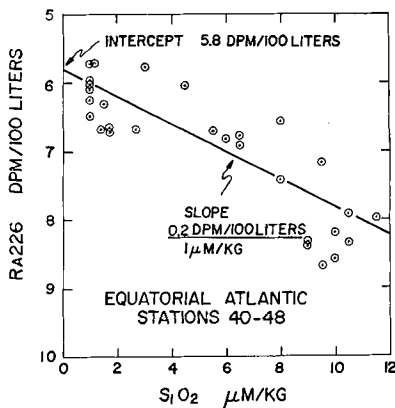


Fig. 12. Linear relationship of Ra^{226} and SiO_2 in the thermocline waters.

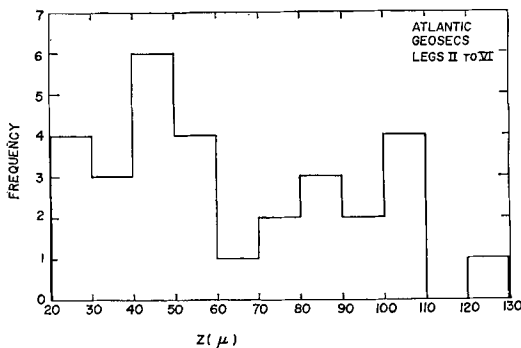


Fig. 13. Histogram showing the distribution of film thicknesses determined in the Atlantic Ocean during GEOSECS cruises.

Table 7. *Solubility of gases in water*^a

Gas	Temp. (°C)							Note
	0	5	10	15	20	25	30	
H ₂	0.0215	0.0204	0.0196	0.0188	0.0182	0.0175	0.0170	(b)
N ₂	0.0235	0.0209	0.0186	0.0169	0.0155	0.0143	0.0134	(b)
O ₂	0.0489	0.0429	0.0380	0.0342	0.0310	0.0283	0.0261	(b)
He	0.00946	—	0.00901	—	0.00868	—	0.00852	(c)
Ar	0.0573	—	0.0434	—	0.0367	—	0.0313	(c)
Rn	0.509	—	0.331	—	0.242	—	0.179	(c)
CO	0.0354	0.0315	0.0282	0.0254	0.0232	0.0214	0.0200	(b)
CO ₂	1.71	1.42	1.19	1.02	0.878	0.759	0.665	(b)
CH ₄	0.0438	0.0399	0.0362	0.0325	0.0290	0.0255	0.0221	(d)
N ₂ O	1.28	—	0.876	—	0.611	—	0.451	(c)
H ₂ S	4.67	3.98	3.40	2.95	2.58	2.28	2.04	(b)
SO ₂	79.8	67.5	56.7	47.3	39.4	32.8	27.2	(b)

^a The values are the volumes of gas at STP absorbed by one volume of water when the pressures of the gas amount to 760 mmHg.

^b Based on *Handbook of Chemistry and Physics*; Chemical Rubber Publishing Co.

^c Calculated from Henry's law constant *K* given in *Handbook of Chemistry and Physics*.

^d Given by Atkinson & Richards (1967) for sea water having a salinity of 36‰. The values for fresh water should be slightly higher.

Application to trace gas geochemistry

Based on this mean film thickness we can compute the mean residence times of various gases in the atmosphere (with respect to transfer to the mixed layer) and in the mixed layer (with respect to transfer to the atmosphere). The atmospheric residence time, τ_{atm} , is defined as:

$$\tau_{\text{atm}} = \frac{M_{\text{atm}}}{R_{\text{inva.}}} = \frac{P(\text{atm}) 3 \times 10^5 \left(\frac{\text{moles}}{\text{m}^2 \text{atm}} \right)}{P(\text{atm}) \alpha \left(\frac{\text{moles}}{\text{m}^3 \text{atm}} \right) \frac{D}{z} \left(\frac{\text{m}}{\text{yr}} \right)}$$

$$= \frac{3 \times 10^5}{\alpha D/z} (\text{yr}) \quad (6)$$

where M_{atm} is the amount of gas in the atmosphere per unit area, $R_{\text{inva.}}$ is the invasion rate of gas into the ocean, P is the partial pressure of the gas in the air, and α is the solubility. It is obvious that τ_{atm} is in inverse proportion to solubility (see Table 7) and to molecular diffusivity (see Table 2). Gases like N₂, O₂, CO, H₂, NO, Ar, CH₄, and C₂H₄ with "normal" solubilities ($\alpha \approx 1$ mole/m³ atm) and diffusivities ($D/z \approx 1$ 000 m/yr) reside in the air about 300 years (τ_{atm}) before having a chance to take "vacation" in the sea. CO₂, which has an unusually high solubility ($\alpha \approx 40$

moles/m³ atm and $D/z \approx 1$ 000 m/yr), requires only 8 years.

Residence time in the mixed layer, τ_{mix} , is also defined as:

$$\tau_{\text{mix}} = \frac{M_{\text{mix}}}{R_{\text{evas.}}} = \frac{P(\text{atm}) \alpha \left(\frac{\text{moles}}{\text{m}^3 \text{atm}} \right) h(\text{m})}{P(\text{atm}) \alpha \left(\frac{\text{moles}}{\text{m}^3 \text{atm}} \right) \frac{D}{z} \left(\frac{\text{m}}{\text{yr}} \right)}$$

$$= \frac{h}{D/z} (\text{yr}) \quad (7)$$

where M_{mix} is the amount of gas in the surface mixed layer per unit area of the ocean, $R_{\text{evas.}}$ is the evasion rate of gas from the ocean, and h is the thickness of the mixed layer. Clearly, τ_{mix} is inversely proportional to the molecular diffusivity of the particular gas. In addition, it depends on the mixed layer thickness. Based on many tens of thousands of BT and XBT measurements the mean mixed layer thickness for the North Pacific Ocean has been shown to be 80 m (Bathen, 1972). For gases with "normal" diffusivities the mixed layer residence time turns out to be about one month ($\tau_{\text{mix}} \approx 80/1$ 000 ≈ 0.08 yr ≈ 1 month). CO₂ again requires special discussion. Although CO₂ gas dissolved in the mixed layer is exchanged with the atmosphere roughly once each

Table 8. *Effect of a ten percent increase in atmospheric CO₂ content on mixed layer chemistry (in a borate-free ocean)*

	Before	After
$p_{\text{CO}_2}^{\text{atm}}$ (atm)	3.0×10^{-4}	3.3×10^{-4}
$[\text{CO}_2]$ (M/l)	1.0×10^{-5}	1.1×10^{-5}
$[\text{HCO}_3^-]$ (M/l)	172×10^{-5}	175×10^{-5}
$[\text{CO}_3^{2-}]$ (M/l)	24.0×10^{-5}	22.6×10^{-5}
$2[\text{CO}_3^{2-}] + [\text{HCO}_3^-]$ (equiv./l)	220×10^{-5}	220×10^{-5}
$\frac{[\text{HCO}_3^-]^2}{[\text{CO}_2][\text{CO}_3^{2-}]}$	1.23×10^3	1.23×10^3

month, it also exchanges with the far larger pool of dissolved HCO_3^- and CO_3^{2-} . Complete isotopic exchange of C^{13} or C^{14} between mixed layer and atmosphere requires 150 times longer than exchange for CO_2 gas alone (i.e., about 12 years).

Carbon monoxide, oxygen, nitrous oxide, hydrogen and presumably other gases are being produced within the sea (see other papers this volume). It is important to establish their contribution to the total atmospheric input of these gases. From the information given here it is possible to make an estimate of the supply rate of any such gas to the atmosphere from the sea provided the average partial pressure difference between the mixed layer and atmosphere is known. For normal gases an amount equal to the mixed layer excess is supplied to the atmosphere each month.

Except for areas of unusually high rates of gas exchange and/or unusually thin mixed layers, diurnal effects due to a combination of gas exchange and plant productivity should be small. On the average only 2% of the excess gas contained by the mixed layer could be lost during the 12 hour dark period when photosynthesis is inoperative. Also the pattern of radon deficiency within the mixed layer suggests that vertical mixing is sufficiently rapid to prevent the establishment of large gradients of excess gas content within the mixed layer.

It is also unlikely that measurable oxygen excesses within the mixed layer will be generated by plants. The average rate of photosynthesis in the surface ocean produces about 1.5×10^{-2} moles of O_2 per square meter of ocean surface per day (much of this is consumed by respiration within the mixed layer). Gas ex-

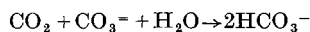
change leads to a transfer of about 0.75 moles of O_2 per square meter of ocean surface per day. Thus even if none of the O_2 were consumed by animals and bacteria only a 2% excess in the oxygen partial pressure of the surface sea over that for the atmosphere would be needed to expel the excess photosynthetic O_2 to the air. Thus the p_{O_2} in surface water would be expected to generally lie within a few percent of equilibrium with the atmosphere.

Except for gases with very high solubilities (SO_2 , CO_2 , NO_2 , ...) the sea does not offer an effective sink for anthropogenic gases. Entry into the sea would require many hundreds of years.

From the information given here it is possible to show that the mixed layer of the sea achieves chemical equilibrium with CO_2 in the atmosphere in about 1.5 years. Since the replacement time of the mixed layers as the result of mixing with underlying water is on the order of a decade, gas transfer of CO_2 across the air-sea interface is *not* the rate limiting step in the removal of fossil fuel CO_2 from the air. The 1.5 year time constant for chemical equilibrium is determined by the product of the gas exchange time constant (~ 1 month) and the ratio of the carbonate ion content to the dissolved CO_2 gas content of mixed layer water (~ 20);

$$\tau_{\text{chem equil}} \approx \frac{[\text{CO}_3^{2-}]}{[\text{CO}_2]} \tau_{\text{gas exch}}$$

The reason is as follows. Fossil fuel derived CO_2 is taken up by the sea by chemical combination with carbonate ion to form bicarbonate ion.



If the atmospheric CO_2 content rises 10% then in order for chemical equilibrium with the mixed layer to be reestablished the dissolved CO_2 content of the mixed layer must rise 10% and the CO_3^{2-} ion content must fall by *roughly* 10% (the exact drop is somewhat less because the rise in bicarbonate content partially rebalances the equilibrium product; see the example in Table 8). The time required for the carbonate ion content to adjust will be in direct proportion to the $\text{CO}_3^{2-}/\text{CO}_2$ ratio in the mixed layer. Thus we have three quite different time constants for the CO_2 system in the mixed layer.

Table 9. *Effect of a 2°C drop in temperature of the world ocean surface temperature on mixed layer chemistry (in a borate-free ocean)*

The mixed layer of the sea is assumed to average 80 m in thickness

Temperature (°C)	17	15
$[\text{HCO}_3^-]^2$	1.44×10^3	1.48×10^3
$[\text{CO}_2][\text{CO}_3^-]$		
$p_{\text{CO}_2}^{\text{atm}}$ (ppm)	320	318
$[\text{CO}_2]$ (M/l)	1.17×10^{-5}	1.24×10^{-5}
$[\text{CO}_3^-]$ (M/l)	19.5×10^{-5}	18.3×10^{-5}
$[\text{HCO}_3^-]$ (M/l)	181×10^{-5}	183×10^{-5}
$2[\text{CO}_3^-] + [\text{HCO}_3^-]$ (equiv./l)	220×10^{-5}	220×10^{-5}
M_{CO_2} atm (M/m ²)	171	170
M_{CO_2} surf sea (M/m ²)	0.94	0.99
ΣCO_2 [M/l]	201.7×10^{-5}	202.5×10^{-5}

$$\tau_{\text{gas exch}} = 1 \text{ month}$$

$$\tau_{\text{chem equil}} \cong \frac{[\text{CO}_3^-]}{[\text{CO}_2]} \tau_{\text{gas exch}} = 1.5 \text{ years}$$

$$\tau_{\text{isotopic equil}} = \frac{[\text{HCO}_3^-] + [\text{CO}_3^-]}{[\text{CO}_2]} \tau_{\text{gas exch}} \cong 12 \text{ years}$$

Another question of importance to atmospheric chemistry is the response time of the chemistry of the oceanic mixed layer to temperature changes. We know that part of the annual and part of the secular change in the CO_2 content of the atmosphere documented by Pales & Keeling (1965) at Mauna Loa, Hawaii, must be the result of changes in sea surface temperature. Heating causes a net transfer of CO_2 from mixed layer to air and vice versa. The reason is that the equilibrium constant for the above reaction, i.e.,

$$K = \frac{[\text{HCO}_3^-]^2}{[\text{CO}_2][\text{CO}_3^-]}$$

and solubility both decrease with increasing temperature. Again the primary adjustment will be in the carbonate ion content. The time constant for adjustment will be roughly the product of the gas exchange time constant and the ratio of CO_3^- to CO_2 (i.e., about 1.5 years). Thus it is not surprising that annual temperature changes and secular changes in mean annual sea surface temperature are recorded by the atmosphere (see example in Table 9).

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Conclusions

(1) The stagnant film model adequately serves to relate the exchange rates of most gases between the atmosphere and surface sea.

(2) The mean stagnant film thickness for the world ocean is estimated to be 50 ± 30 microns by the radon method. As predicted by Kanwisher (1963), it appears to vary in inverse proportion to the square of the wind velocity. Using both C^{14} and Rn^{222} , the world average is 40 ± 30 microns.

(3) From a knowledge of the wind velocity, mixed layer thickness and partial pressure difference between air and surface sea, the net transfer rate of most gases can be predicted to $\pm 30\%$.

(4) The average residence time for transfer from atmosphere to mixed layer is 300 years for gases with normal solubilities. For CO_2 it is about 8 years.

(5) The average residence time for transfer from the mixed layer of the sea to the atmosphere is about 1 month. CO_2 is a special case because of the interaction of CO_2 with the far larger reservoirs of HCO_3^- and of CO_3^- ion. The chemical equilibration time is about 1.5 years and the isotopic equilibration time about 12 years.

(6) Diurnal changes within the mixed layer cannot in general involve gas exchange. Where observed, they are more likely the result of diurnal biological effects resulting from day to night photosynthesis to respiration changes.

(7) Oxygen should remain within a few percent of saturation in the mixed layer.

(8) The rate limiting step for removal of anthropogenic CO_2 from the air is vertical mixing within the sea rather than transfer across the air-sea interface.

Acknowledgements

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СКОРОСТИ ОБМЕНА ГАЗОМ МЕЖДУ ВОЗДУХОМ И МОРЕМ

Изучение скоростей обмена газом, проведенное в лаборатории, показало, что пленочная модель удовлетворительно описывает коэффициенты переноса большинства газов между атмосферной и морем и дает точность $\pm 15\%$. Оценки средней толщины пленки для мирового океана, основанные на распределении естественного радиоактивного углерода, образующегося при ядерных взрывах, и радона хорошо согласуются между собой. Данные по

радону с BOMEX и со станции PAPA подтвердили предположение Канвишера, что скорости обмена газом пропорциональны квадрату скорости ветра. Эти наблюдения позволяют провести дальнейшие обобщения, если рассматривать потенциал океана как источник или сток трассеров. Они позволяют также оценить более сложную ситуацию с углекислым газом.