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Gas Exchange Measurements in Natural Systems

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Abstract

Our direct knowledge of the rates of gas exchange in lakes and the ocean is based almost entirely on measurements of the isotopes ^{14}C, ^{222}Rn and ^3He. The distribution of natural radiocarbon has yielded the average rate of CO_2 exchange for the ocean and for several closed basin lakes. That of bomb produced radiocarbon has been used in the same systems. The ^{222}Rn to ^{226}Ra ratio in open ocean surface water has been used to give local short term gas exchange rates. The radon method generally cannot be used in lakes, rivers, estuaries or shelf areas because of the input of radon from sediments. A few attempts have been made to use the excess ^3He produced by decay of bomb produced tritium in lakes to give gas transfer rates. The uncertainty in the molecular diffusivity of helium and in the diffusivity dependence of the rate of gas transfer holds back the application of this method. A few attempts have been made to enrich the surface waters of small lakes with ^{226}Ra and ^3H in order to allow the use of the ^{222}Rn and ^3He methods.

While these studies give broadly concordant results, many questions remain unanswered. The wind velocity dependence of gas exchange rate has yet to be established in field studies. The dependence of gas exchange rate on molecular diffusivity also remains in limbo. Finally, the degree of enhancement of CO_2 exchange through chemical reactions has been only partially explored.

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These remaining uncertainties have relevance to some of the key applications of our knowledge regarding gas exchange rates to environmental problems. For example, as our knowledge of the gain or loss of CO_2 from lake surfaces depends on ^3He or ^{222}Rn based gas exchange rates, the degree of enhancement of CO_2 relative to these gases must be understood. Another example is the uptake of fossil fuel CO_2 by the sea. Improvements over the current 1-D models of the ocean require a knowledge of the regional and seasonal dependence of CO_2 exhange rates. Here the wind velocity dependence becomes important.

Introduction

Despite a long history of interest in the process of gas exchange there is still no theory which allows the rate of transfer of a gas across an air-water interface to be reliably predicted from basic data such as the velocity of the wind over the water and the degree of turbulence in the water. Instead, environmental scientists and chemical engineeers interested in this phenomena must depend on empirical calibrations for each system of interest. In natural systems these calibrations are based on measurements of the flux of some natural or artificial tracer gas across the interface. The most widely used tracer gases are those bearing a naturally radioactive isotope. The reason is that the radiodecay often creates a situation where its flux can be estimated.

In the absence of a broadly accepted theory an ambiguity arises with regard to the appropriate parameter to be used in describing the results of such measurements. It is generally accepted by workers in the field that the concentration of the gas in the upper few molecular layers of the water is equal to the partial pressure of the gas in the overlying air

times the solubility of the gas. This assumption leads to the commonly used piston velocity concept. The ratio of the net flux of gas (units moles/cm^2 sec) to the concentration difference between the upper few molecular layers and the body of the fluid (units moles/cm^3) has the dimensions of velocity (units cm/sec). While piston velocity is the least model dependent parameter currently in use for the defining of the gas exchange rate it does have one major drawback. In many situations the tracer gas is merely a vehicle to gain information about the transfer rate of the environmental gas of interest. Because all models of gas exchange have a molecular diffusivity dependence, the piston velocity for the gas of interest will not be equal to the piston velocity for the tracer gas. The oldest, simplest and most commonly used model for gas exchange is the stagnant film model (Lewis and Whitman 1924). In this model the resistance to transport is envisioned as a thin layer of unstirred water at the interface. The resistance is defined by the thickness of this layer. The thickness of the stagnant film (units cm) is given by the molecular diffusivity of the gas (units cm^2/sec) divided by the piston velocity (units cm/sec). Were the model valid it would provide a formulation of the tracer gas results applicable to any gas. The problem is that theory (Deacon 1977) and wind tunnel experiments (Jahne et al., 1979 and Ledwell 1982) suggest that the stagnant film model is not adequate and that the piston velocity depends inversely on the 0.41 to 0.67 power of the molecular diffusivity rather than on the first power. To date, our knowledge of gas exchange in natural systems has not been greatly affected by these considerations. Except for helium, the gases of interest have diffusivities differing from one another by no more than a factor of two (see Table 1).

Thus, if for example, the 0.5 power of diffusivity were adopted in no case (except He) would the error incurred by going from one gas to another will be more than 40%. As our measurements of gas exchange rates are rarely any better than ±30%, the lack of an adequate theory has as yet not presented any serious problems.

As much of the research on gas exchange rates in natural systems has been motivated by an interest in the natural cycles of carbon and its isotopes ^{13}C and ^{14}C, rates of gas transfer are often expressed as the unidirectional invasion flux of CO_2 from the atmosphere into the water body of interest. As the CO_2 pressure in the atmosphere is nearly uniform geographically and changes only slowly with time, this mode of presentation proves handy to carbon cycle geochemists. For example, the average unidirectional flux of CO_2 from air to sea is thought to be about 20 moles/m^{2}yr. This corresponds to a mean stagnant film thickness of about 40 microns and to a mean unidirectional piston velocity of about 3 meters/day.

With this background in mind, we will proceed to consider the various methods which have been employed to measure gas exchange rates in natural systems. As these methods are well described in the literature, we will not consider the details of the experimental procedures or the mathematics of the models employed. Rather, we stress the strengths and limitations of each approach.

The Natural Radiocarbon Method

For the ocean and for several closed basin lakes it has been possible to estimate the rate of CO_2 exchange with the atmosphere by making a mass balance for ^{14}C (Craig 1957; Broecker and Peng 1974). This technique gave

us the first accurate estimate of the mean CO_2 exchange rate between ocean
and atmosphere. Since the amounts of ^{14}C carried to the sea by rivers and
lost from the sea to its sediments are small compared to the amounts gain-
ed by CO_2 exchange with air and lost by radiodecay within the sea, the
situation is quite simple. The net flux of ^{14}C across the air sea inter-
face must nearly match the decay of ^{14}C within the sea. As the ocean has
been well surveyed for both ΣCO_2 concentration (Takahashi et al., 1980;
Takahashi et al., 1981) and $^{14}C/C$ ratio, (Stuiver and Ostlund 1980;
Ostlund and Stuiver 1980; Stuiver et al., 1981; Broecker and Peng, 1983)
the amount of ^{14}C decaying in the sea is well known. The uncertainties in
this method come from an imprecise knowledge of the $^{14}C/C$ ratio
distribution in surface water (Broecker 1963). The flux of ^{14}C atoms into
the sea depends on difference in the $^{14}C/C$ ratio for atmospheric CO_2 and
that for mean surface water ΣCO_2 (corrected for equilibrium isotope
fractionation effects using ^{13}C) and on the rate of CO_2 exchange. If the
former is known, the latter can be calculated. The problems associated
with the $^{14}C/C$ ratio in surface water are as follows,

1) As it differs from that in the atmosphere by only about 5%, a 1%
error in its mean value will lead to a 20% uncertainty in the ex-
change rate.

2) The natural $^{14}C/C$ ratio in the ocean's surface waters ranges from
about 4% lower (in temperate zones) to as much as 10% lower (in the
Antarctic) than that in the atmosphere. Thus, not only must the
geographic averaging be done correctly but also this distribution
should be weighted regional differences in for wind speed and
temperature (parameters on which the gas exchange rate depends).

3) Anthropogenic effects (i.e. fossil fuel burning and nuclear weapons testing) have altered the $^{14}C/C$ ratio in the atmosphere and surface ocean. The perturbation from nuclear weapons testing began in 1954 and by 1957 was detectable in the surface ocean. It is avoided by using only measurements on water samples collected before 1957 or on shell and coral samples grown before 1957. The fossil fuel effect for the ocean as of 1957 is estimated to have been quite small (~1.0%). These estimates are based on the $^{14}C/C$ record from tree rings and atmosphere-ocean mixing models. The results of these calculations are consistent with direct measurements on ring-dated corals (Druffel 1980; Druffel 1981; Druffel 1982) and on shells from museum collections (Broecker 1963).

The main residual uncertainties are for the Antarctic. Its surface waters have the lowest $^{14}C/C$ ratios. It experiences the highest mean wind speeds. It is the coldest. For this region of the ocean the pre-1957 data set is the weakest. No corals grow at high latitudes. Antarctic shell collections are sparse. Because of this our ^{14}C based estimate could be in error by as much as 25%.

It should be kept in mind that this natural ^{14}C based measurement tells us nothing about regional or seasonal effects and that it applies to the preanthropogenic CO_2 content of the atmosphere which is thought to have been about 265 ppm (today's is about 340 ppm or about 1.3 times the preanthropogenic value).

Our best estimate for the unidirectional CO_2 invasion rate based on the distribution of natural ^{14}C is 16 ± 3 moles CO_2/m^2yr. Translated to today's p_{CO_2} value this would be about 21 moles CO_2/m^2 yr.

Bolin (1960) explored the possibility that the rate of CO_2 invasion into the sea might be enhanced by the reactions which transform CO_2 to HCO_3^-. He concluded that although this reaction did contribute, the physical flux of CO_2 (i.e., that in the absence of chemical reaction) would be only about 6% lower than the observed flux of CO_2. While Hoover and Berkshire (1969) and Peng (1973) provide evidence based on laboratory studies that the inorganic reaction enhancement effect might be somewhat larger than estimated by Bolin, definitive measurements have yet to be made. It is also possible that organic rich films might alter the situation. Thus the possibility that ^{14}C based fluxes provide overestimates of the exchange rates of other gases must be kept in mind.

Libby and Berger (1969) performed experiments on stored sea water samples which they interpreted as providing evidence for an enhancement in CO_2 exchange rate resulting from the presence of the natural enzyme, carbonic anhydrous. Recently Goldman and Dennett (1983) have performed experiments which they interpret to demonstrate that significant enhancement due to this mechanism does not occur in natural systems.

The natural radiocarbon method has also been applied to lakes in closed basins (Walton and Broecker 1959). In this case the input of ^{14}C from rivers cannot be neglected. Also because of water diversion and agricultural modifications of the vegetation and soils in the basins of these lakes the assumption of steady state for the carbon and radiocarbon budgets is shaky. As more reliable CO_2 invasion estimates for the same lakes have been made from studies of the build up of radiocarbon from nuclear testing it is not worth pursuing the problems associated with these estimates (Thurber and Broecker 1970; Peng and Broecker 1980). They are mainly of historic interest.

The Bomb-Produced Radiocarbon Method

The buildup of bomb-produced ^{14}C in the sea and in closed basin lakes provides a measure of the CO_2 invasion rate into these water bodies (Münnich and Roether 1967). The driving force for this input is well documented. From direct measurements we have a good knowledge of both the temporal trend in atmospheric CO_2 content and of the temporal trend in ^{14}C/C ratio for atmospheric CO_2 (see figure 1). From these observations the equilibrium concentration of [14]CO_2 in the upper few molecular layers of the surface ocean can be estimated as a function of location and time. To obtain the CO_2 invasion rate it is necessary only to meassure the inventory of bomb ^{14}C atoms in the water body and the ^{14}C/C ratio in its surface waters at one time (provided the prenuclear ^{14}C distribution is known). In the absence of firm prenuclear data a time history of the nuclear ^{14}C effect must be obtained.

Estimates of this type have been made for the ocean as a whole (based on the GEOSECS global data set; Broecker et al., 1980) and for several lakes in the Great Basin of the western United States (Peng and Broecker 1980). The result obtained for the ocean (adjusted to the 1980 atmospheric p_{CO_2} is 23±5 moles/m^2 yr. Those for the Great Basin lakes are summarized as follows: 5 moles/m^2yr for Pyramid Lake, 15 moles/m^2 yr for Walker Lake and 30 moles/m^2 yr for Mono Lake.

While this method could conceivably be applied to lakes with outlets, care would have to be taken to determine how much ^{14}C and ΣCO_2 entered from rivers. Also the ratio of carbon replacement time via river input to carbon replacement time via CO_2 invasion must be small enough so that a measurable impact of bomb ^{14}C invasion can be seen in the lake's ^{14}C/C ratio.

While this method might also be used in rivers and estuaries, the results will always be quite fuzzy because of uncertainties in other elements of the carbon and ^{14}C budget for these systems.

The Radon Method

All natural waters contain ^{226}Ra. This radium produces ^{222}Rn by radiodecay. During their mean lifetime of 5.5 days those radon atoms born in the wind stirred mixed layer of a water body have a chance to escape to the overlying air. In certain circumstances the extent of this loss can be measured and the evasion rate for radon calculated. The open ocean proves ideal for this task (Broecker 1965; Broecker and Peng 1971, 1974). The overlying air is nearly radon free (hence, no significant correction for invasion of radon need be made). Lateral transport from adjacent shallow water sediments is generally negligible. The underlying thermocline is well defined and well stratified insuring that radon produced in the thermocline is not being mixed in significant amounts into the wind mixed layer (Peng et al., 1974; Kromer and Roether 1980).

Lakes, rivers, estuaries and coastal waters are generally unsuitable for radon studies. Continental air contains significant and variable amounts of radon. Hence, an air to water radon flux correction must be made. More damaging is the input of radon produced in the sediments underlying these water bodies. Even in systems with strong thermoclines, the lateral transport of radon released from sediments contacted by the mixed layer water is important. Rarely are these systems large enough so that radon atoms cannot reach their centers. Rarely can the sediment flux be adequately documented so that a correction can be made.

Despite the immunity from airborne radon and sediment derived radon the open ocean application of the radon method suffers two major difficulties.

1) the ratio of signal to measurement error ranges from 10 in the most favorable circumstances to as low as 2 in the least favorable circumstances.

2) constant wind conditions never prevail for several radon mean lives; hence the radon inventory in the ocean mixed layer is never at steady state.

To date these difficulties have been countered by averaging the results from many different times and places (Peng et al., 1979). While this averaging procedure precludes the determination of the wind velocity dependence of gas exchange rate in a given area it does permit regional and seasonal average values to be obtained.

A summary of the film thicknesses and piston velocities obtained in various regions of the ocean is given in table 2. The global average piston velocity obtained in this way is 2.8 m/day. If this result is used to calculate the CO_2 invasion rate (using a diffusivity dependence of 0.67 and an atmospheric CO_2 content of 340 ppm) a flux of about 16 moles/m^{2}yr is obtained. While this value is somewhat lower than that obtained from ^{14}C studies. The difference lies within the range of uncertainty. As mentioned above it is possible that the CO_2 value is somewhat larger due to chemical reaction between CO_2 and OH^- ion in the boundary layer. Thus, the difference between the ^{14}C and [222]Rn based transfer coefficients might upon further study prove to be real.

The Helium Method

Continental surface waters in the northern hemisphere contain significant amounts of tritium. The trace isotope [3]He is generated by the decay of this tritium. Because of this production the [3]He/[4]He ratio in these waters must be slightly higher than in the overlying atmosphere. If the ratio difference could be measured it would provide a measure of the rate

of helium evasion. The problem with this method is that for most surface waters the gas replacement time (by exchange with the atmosphere) is only a few days. On this time scale, a water with a tritium content of 50 TU (typical for contemporary temperate latitude northern hemisphere surface waters) the expected increase in $^3He/^4He$ ratio is only a few tenths of one percent. This is comparable to the uncertainty in the measurements. Hence, this potentially useful method has received little attention (Torgerson et al., 1977; Weiss et al., 1978).

Were the experimental accuracy to be improved permitting the use of ^3He then a new problem would emerge. While the diffusivity of helium is poorly known it is surely several times higher than that for the other gases of interest. Thus, not only would its diffusivity relative to that for CO_2 and O_2 have to be determined, but also the molecular diffusivity dependence of gas exchange would have to be better defined (see Torgerson et al., 1982).

The Oxygen Method

The oldest of the gas exchange tracer methods is that involving O_2 (Streeter and Phelps 1925). Many continental and coastal surface waters receive such large amounts of reduced substances (organic matter, industrial wastes...) that their oxygen content is reduced well below the saturation value. In such cases were a means available to estimate the rate at which oxygen is utilized in the water, then the invasion rate of O_2 could be estimated. As the latter is possible only in special cases, this method has received little geochemical application. It has been used almost exclusively by sanitary engineers and industrial chemists in rather specialized applications. It seems possible that it could be given for

broader application especially n river systems where no natural tracer method applies.

The work of Schurr and Ruchti (1977) is especially interesting in this regard. By monitoring O_2 continuously over many days in several Swiss rivers these authors were able to show that the phasing of the diurnal O_2 cycle relative to that of the diurnal radiation cycle provided a measure of the O_2 resaturation time and hence of the unidirectional invasion rate of O_2. This powerful approach should be given further attention!

Tsunogai and Tanaka (1980) have used the dissolved oxygen and phosphorus budgets for Funka Bay in the island of Hokkaido to obtain estimates of the rate of dissolved oxygen invasion. They estimate film thicknesses of 45 microns for summer conditions and 12 microns for winter conditions.

The Helmet Method

Several investigators have employed helmets to measure the flux of gas into or out of waters (Copeland and Duffer 1964; Hood and Kelley 1976; Hammond and Fuller in press; Hartman and Hammond in press; Nixon personal communication; Gosink and Kelley, personal communication). This can be done by either depleting or enriching the helmet air in the gas of interest. Often the natural air-water difference can be employed. The problem with this approach is that by placing the helmet over the surface one disrupts the very process to be studied. It is generally agreed that the friction of the air moving over the water reduces the impedance to transfer over that which would be experienced were the air stagnant. It could of course be argued that wind energy is stored within the mixed layer as turbulent energy and it is this turbulent energy which reduces the

impedence to gas transfer. If so, then as along as the helmet did not al-
ter the turbulence in the underlying water, the gas exchange rate under
the helmet would be similar to that outside the helmet. Few workers in
the field accept this logic. Until those who use this method provide
evidence that it gives valid results it will have little credence.

The Purposeful Tracer Method

For rivers and small lakes it is possible to add tracers which would
permit gas evasion rates to be measured. The Lamont group has used this
approach in the Experimental Lakes Area near Kenora, Canada (Emerson 1975;
Hesslein et al., 1980; Torgerson et al., 1982). They chose to add the
radioactive parents (^{226}Ra and ^{3}H) of two tracer gases (^{222}Rn and ^{3}He).
In this way these investigators hoped to achieve a steady state concentra-
tion of the tracer gases. While successful these experiments suffered
from uncertainties created by changing mixed layer thickness, radium re-
moval onto sediments and variable wind conditions.

It is our feeling that this approach holds much promise. However,
the radioactive parent approach introduces more difficulties than it over-
comes. Gases themselves should be added. The rapid growth in the tech-
nology of gas chromatography permits the measurements of a host gases
whose concentrations are very low in natural waters. These gases are
readily added to water by diffusion through silicone tubing. They pose no
environmental hazard. Dispersion through the mixed layer (lateral and
vertical) requires no more than a day in small lakes. In rivers a con-
servative non-gaseous substance such as fluoride ion could be added con-
currently as a dispersion tracer.

The Eddy Correlation Method

For years claims have been made that the fluxes of CO_2 and O_3 could be measured by an eddy correlation technique which involves simultaneous measurement of vertical velocity and gas content. Jones and Smith (1977) attempted this for CO_2 but performed few field studies and no intercalibrations with alternate techniques. Wesley et al.(1982) have published measurements which give results one to two orders of magnitude higher than expected from other techniques. Bingham of the Lawrence-Livermore National-al Laboratory (personal communication) is currently making these measurements in areas of the sea where p_{CO_2} measurements on air and water are also available. Thus, he will be able for the first time to compare the results of the eddy correlation method directly with estimates based on radon and radiocarbon. The consensus among people knowledgeable about this approach is that only if exceedingly small CO_2 fluctuation can be measured (i.e., 0.01ppm or better) can the small CO_2 fluxes expected for water bodies be measurable. While a long shot, because of its great potential in studying the wind velocity dependence of gas exchange, it must be thoroughly explored.

Summary of Existing Information

From the data in hand we are able to make estimates of the transport coefficient of all ordinary gases in most open water systems. The errors on such estimates range from a minimum of ±20% to a maximum of a factor of three. Exceptions are gases such as SO_2 with high chemical reactivity and systems such as rapidly flowing streams where gravitationally induced turbulence is more important than wind induced turbulence in breaking down the interface resistance.

Several important pieces of information are lacking:

1) the wind velocity dependence of gas exchange in natural systems (i.e. systems with large waves).

2) the relative importance of wind stress and gravitational energy in breaking down the transport resistance in rivers and streams.

3) the role of dissolved organic matter altering the interface character in natural waters.

4) the diffusivity dependence of gas exchange rate as a function of wind velocity in natural systems

5) the possible rate of catalysts in speeding the $CO_2 + OH \rightleftharpoons HCO_3^-$ reaction in natural waters.

It is our opinion that natural tracers will not supply this information. It will come either from purposeful tracer studies or from eddy correlation measurements (if this method proves reliable).

Applications of Measurements on Natural Systems

The motivation by geochemists to obtain information regarding gas exchange rates in natural systems came initially through a desire to harness the distribution of radiocarbon to learn about the rates of thermocline and deep sea ventilation. Following close on the heals of attempts to define the CO_2 invasion rate into the sea came a variety of environmental questions requiring information about gas exchange between water and air. These included:

1) the rate of fossil fuel CO_2 uptake by the sea.

2) ocean source strength (or sink strength) for a variety of trace gases of environmental interest (CO, CH_4, N_2O, ...).

3) the rate of CO_2 supply to eutrophic lakes.

4) the rate of O_2 supply to systems receiving high sewage loading.

5) the role of the atmosphere in distributing sediment-reactive organic compounds (PCBs, DDT, ...).

In the sections which follow we reiterate a few examples from this research.

Measuring Upwelling Rates in the Equatorial Ocean

Despite extensive efforts designed to learn about the patterns and rates of ventilation of the ocean's interior our knowledge remains quite primitive. Our ignorance in this area is exemplified by the fact that the development of realistic general circulation models of the sea's operation lies at least a decade and perhaps many decades in the future. The quest for such models will be speeded and ultimately verified by information gained from tracers. While most of these studies depend mainly on the distribution of tracers within the sea a few depend on the differences in tracer concentration between air and sea.

One such application involves the source and flux of water upwelling to the surface of the equatorial Pacific Ocean. While this process is well known to marine biologists (because of the elevated nutrient constituent contents and plant productivities of equatorial waters) and to the sedimentologist (because of the imprint of the high production rate of calcite and opal in the sediments beneath the equator), details of the routes followed by the upwelling waters and the rates at which they are injected have only recently begun to emerge. Key to the progress in this area has been the surface water anomalies in CO_2 partial pressure and in $^{14}C/C$ ratio.

Figure 2 shows traverses of these two properties across the equator in the Pacific Ocean. The high CO_2 partial pressure seen in equatorial surface water is an artifact of the high ΣCO_2 content of the upwelled water (it carries excess CO_2 produced by respiration along its subsurface pathway and also because when these waters left contact with the air they had a lower temperature than that for surface waters in the equatorial zone). The low ^{14}C/C ratio for the ΣCO_2 in equatorial surface waters reflects the fact that much of upwelling water left contact with the atmosphere prior to the onset of nuclear testing and therefore does not contain an excess of ^{14}C atoms. As can be seen in figure 2 the ^{14}C anomaly extends further away from the equator than does the CO_2 anomaly. This reflects the fact that in surface ocean waters chemical equilibrium for carbon is achieved about ten times more rapidly than isotopic equilibrium for carbon. This difference is related to the ratio of the $CO_3^=$ ion content to the ΣCO_2 content of sea water. To achieve chemical equilibrium (i.e., a p_{CO_2} pressure equal to that in the air) the $CO_3^=$ content must be adjusted. To achieve isotopic equilibrium the ^{14}C content of all the dissolved inorganic carbon must be adjusted. As carbonate ion makes up only about one tenth of the ΣCO_2 in surface waters of the ocean, the CO_2 pressure signal carried to the surface by upwelling does not spread as far as the isotopic signal. It is more quickly obliterated by interaction with the atmosphere (and also by the growth of plants). Thus a knowledge of the rate of CO_2 invasion allows the calibration of flow models designed to explain the observed distributions of CO_2 pressure and ^{14}C/C ratio anomalies. The upwelling rates obtained in this way prove to be an important breakthrough in the struggle to quantify the ventilation of the ocean's interior (see Broecker and Peng 1983).

Also shown in figure 2 is a traverse of dissolved oxygen in surface water. A strong depletion in O_2 is seen centered right at the equator. This anomaly is caused by the upwelling of waters depleted in O_2 by respiration. It is narrower than even the CO_2 pressure anomaly consistent with the prediction from our knowledge of the gas exchange characteristics of O_2 and CO_2; i.e., O_2 equilibrium is achieved roughly ten times faster than CO_2 equilibrium. The time for O_2 equilibrium, τ_{O_2} is as follows,

$$\tau_{O_2} = \frac{h}{v_{O_2}}$$

where h is the mixed layer thickness and v_{O_2} is the piston velocity for dissolved oxygen. For CO_2 the equilibration time, τ_{CO_2}, is given by,

$$\tau_{CO_2} = \frac{h}{v_{CO_2}} \frac{[CO_3^=]}{[CO_2]}$$

In tropical surface water the $[CO_3^=]/[CO_2]$ ratio is about 15.

The p_{CO_2} and $^{14}C/C$ anomalies in the equatorial Pacific are the strongest in the world ocean and hence the easiest to utilize in ocean ventilation studies. Disequilibrium in CO_2 partial pressure and $^{14}C/C$ exist almost everywhere on the sea surface. At higher latitudes these anomalies change with season. As all these anomalies reflect an interplay between mixing processes in the sea and gas exchange across the air-sea interface, our knowledge of gas exchange process will eventually allow broader constraints to be made on the ventilation process.

Fossil Fuel CO_2 Uptake by the Sea at High Latitudes

Our knowledge of CO_2 exchange rates (based on the distribution of natural and bomb ^{14}C) and of ventilation rates of the temperate ocean thermoclines (based on the distribution of bomb produced tritium) clearly demonstrates that the major resistance to uptake by the sea of the excess CO_2 added to the atmosphere through fossil fuel burning is transport within the sea rather than transport across the air-sea interface (Oeschger et al., 1975). The oceans surface waters should contain about 5/6th their capacity for excess CO_2.

The situation at higher latitudes is not so clear. During the deep convection occurring in winter months, the waters brought to the surface and cooled likely do not have time to achieve CO_2 equilibrium with the air. Thus, the new waters entering the deep sea will carry a smaller fraction of their capacity for excess CO_2 than their temperate equivalents. How much smaller is currently not known. Because the deep sea will ultimateley become the largest storage reservoir for fossil fuel CO_2, it is essential to determine the extent to which deep sea source waters equilibrate with the atmosphere prior to and during the cooling events which sends them to the abyss.

To date we have no direct observations of the CO_2 chemistry of high latitude winter surface waters. Even when such results do become available we will not know how much of what we see is natural and how much is anthropogenic. Thus, we must seek some less direct means of assessing the extent to which this water takes up excess atmospheric CO_2. The most promising approach is to use the distributions of two tracer gases in subsurface waters adjacent to the source region (Broecker et al., 1975).

One would be a gas for which the atmospheric equilibration time is much less than that for CO_2 (i.e. [85]Kr or one of the freons) and one for which the atmospheric equilibration time is much greater than that for CO_2 (i.e., [14]CO_2). Surface waters leaving contact with the atmosphere should in all cases carry an atmospheric equilibrium content of the normal gases (because under mean oceanic circumstances; i.e., layer ~60 meters and piston velocity 3 meters per day the characteristic equilibration time is 20 days). Thus, the concentration of [85]Kr or freons in subsurface waters should provide a measure of the proportion of the water which left the surface prior to anthropogenic contamination (i.e., of the dilution of new with old deep water). The ratio of [14]CO_2 to the ordinary gas provides a measure of the extent of carbon isotope equilibrium in waters descending from the surface. Knowing the relative equilibration times for CO_2 and for ^{14}C/C it should then be possible to estimate the fraction of the descending water's capacity for excess CO_2 which is utilized. While this strategy is surely valid its successful implimentation requires a model which reproduced the important aspects of the mixing of "new" with "old" waters. The reason is that the anthropogenic anomalies for ^{14}C/C and for [85]Kr (or for freons) do not have identical time histories. Thus, it is important to have some idea of the age spectrum of the waters making up a given subsurface sample.

CO_2 Supply to Eutrophied Lakes

During the debate as to whether the phosphate control strategy for eutrophication abatement would prove effective one question had to do with whether lakes with very low alkalinities (and hence very low ΣCO_2 contents) could be eutrophied by the input of phosphate. The argument ran

that in such waters the inavailability of carbon would limit algal growth; hence phosphate control was unnecessary.

Schindler (1975,1977) answered this question by showing that small soft water lakes artificially fertilized with phosphate could indeed be eutrophied. He conjectured that the needed CO_2 must enter the lake from the atmosphere. To check this hypothesis Emerson et al. (1973) measured the gas transfer coefficient for the lake studied by Schindler by adding [226]Rn to the lake's epilimnion and determining the extent to which the [222]Ra produced by the decay of this [226]Ra was lost to the atmosphere. The CO_2 invasion rates calculated from this [222]Rn based transfer coefficient fell well short of providing the extra carbon needed to support Schindler's algal blooms.

Emerson (1975) solved this problem by performing experiments which showed that the rate of CO_2 invasion into the lake was several times higher than that predicted from radon. He showed that this enhancement resulted from the reaction between CO_2 and OH^- to give HCO_3^-. As the algae draw down the lakes CO_2 reserves the pH rises to quite high values (i.e., 9 to 10). The high OH^- ion concentration produced in this way greatly accelerates the uptake of CO_2 via the chemical (as opposed to thephysical) route. These experiments clearly demonstrated that carbon deficiencies do not effectively limit algal growth in soft water lakes receiving high phosphate loading.

Conclusions

Although isotopic methods have greatly expanded our knowledge of the rates of gas exchange in natural systems, we still lack any means of generalizing this information so that it can be extrapolated to specific circumstances. Herein lies the challenge of the future!

Acknowledgements

Table 1. Coefficients of molecular diffusion of various
gases in sea water*.

Gas	Molecular wt. (g/mole)	Diffusion Coefficients (10^{-5} cm^2/s)	
		0°C	24°C
He	4	~2	~4
Ne	20	1.4	2.8
N_2	28	1.1	2.1
O_2	32	1.2	2.3
Ar	40	0.8	1.5
Kr	84	0.7	1.4
Xe	131	0.7	1.4
Rn	222	0.7	1.4
CO_2	44	1.0	1.9
N_2O	44	1.0	2.0

* The sources for these estimates are given by Broecker and Peng 1983.

Table 2. Summary of the film thicknesses and piston velocities obtained during GEOSECS program using radon method (Peng et al., 1979).

	Piston velocity (m/d)	Film thickness $(10^{-6} m)$
Atlantic		
60°N – 40°N	2.9	36
40°N – 15°N	2.6	40
15°N – 15°S	2.0	51
15°S – 40°S	2.6	40
40°S – 70°S	3.3	31
Pacific		
60°N – 40°N	2.1	49
40°N – 15°N	2.7	38
15°N – 15°S	2.3	45
15°S – 40°S	3.2	32
40°S – 50°S	3.7	28
50°S – 70°S	5.8	18

Figure Captions

Figure 1. Excess ^{14}C in atmospheric CO_2 (per mil excess in the $^{14}C/C$ ratio over the 1850 value) as a function of time based on a large number of measurements on air samples from both the northern and southern hemisphere made in a number of ^{14}C laboratories (Nydal et al., 1979).

Figure 2. Transects of $^{14}C/C$ ratio in surface water ΣCO_2, of the CO_2 partial pressure in surface water and of the O_2 content of surface water across the equator in the central Pacific Ocean.
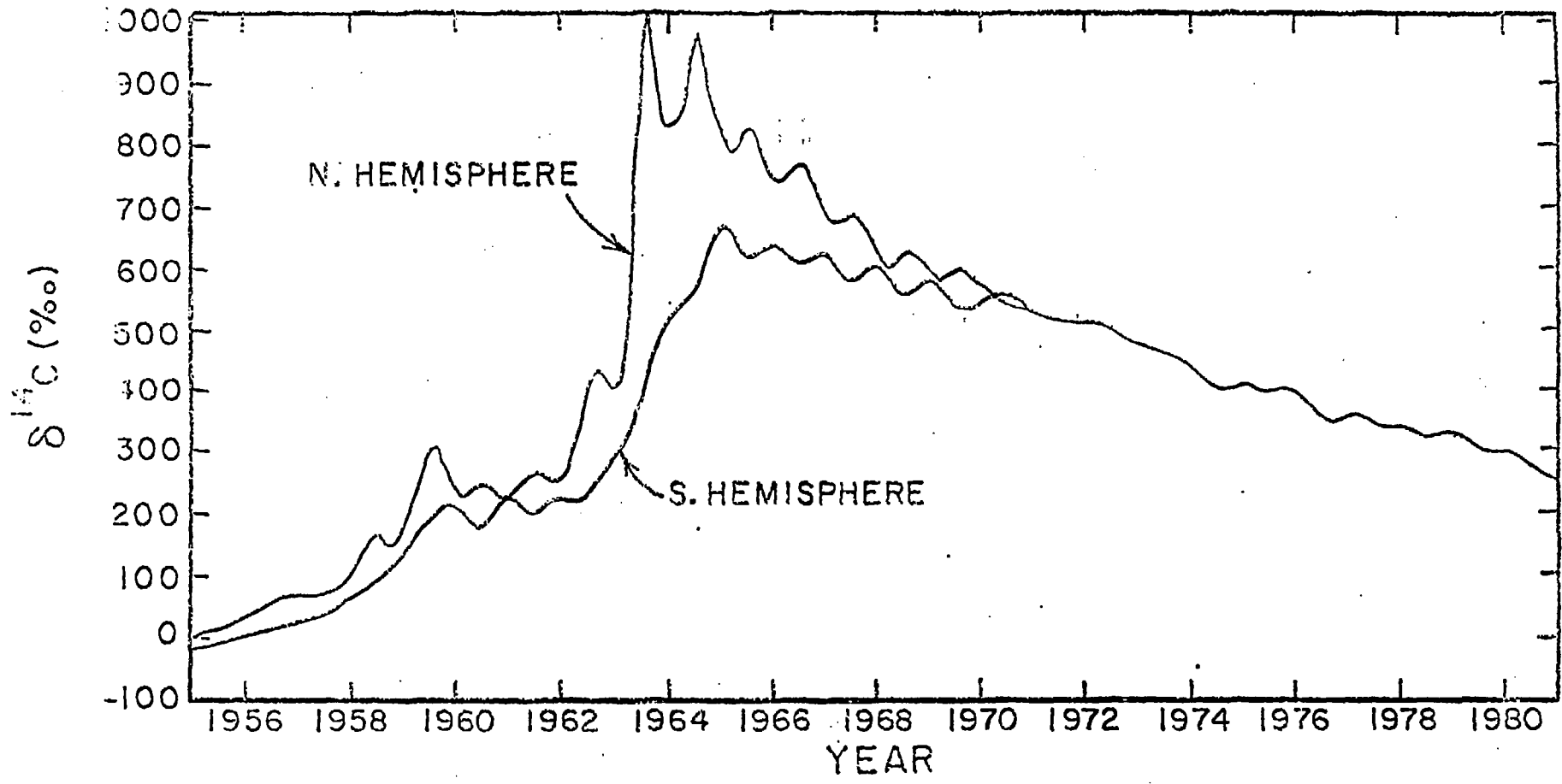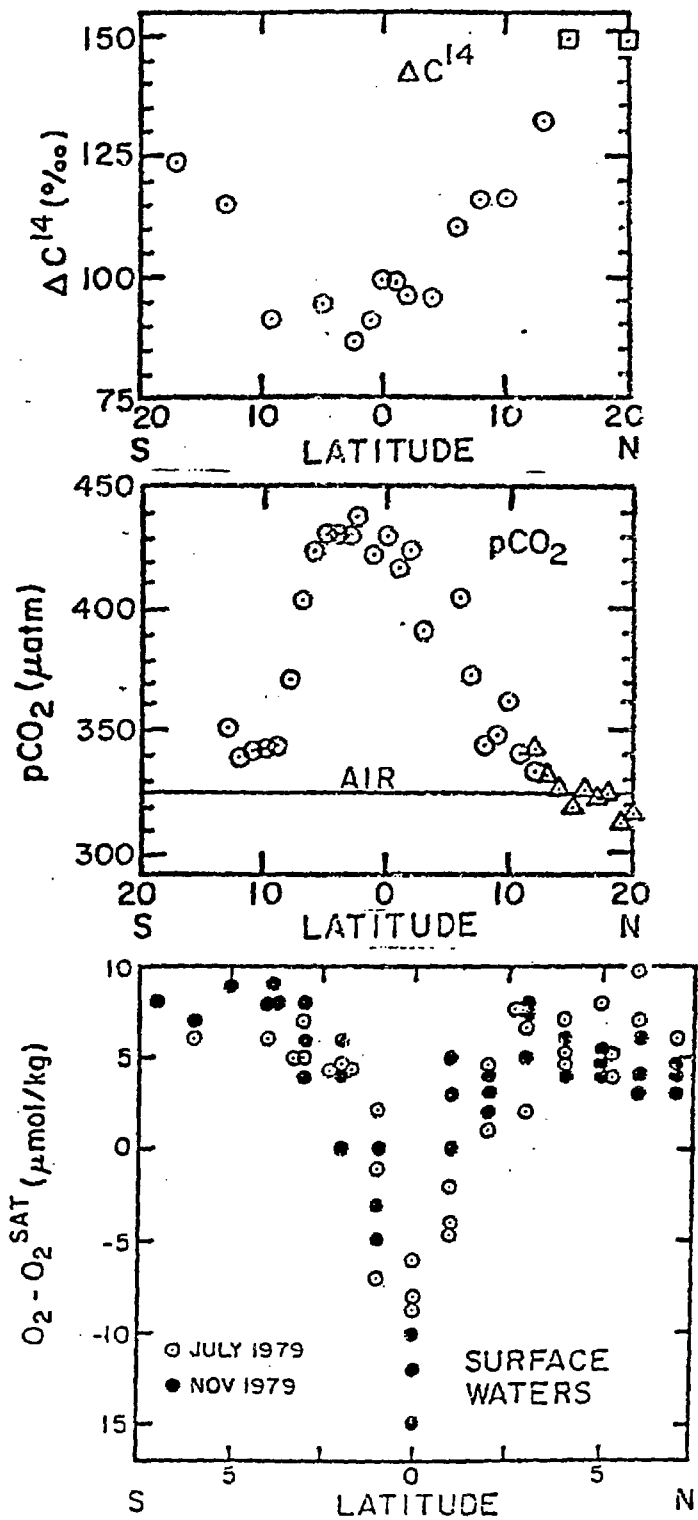
Fig 1

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