12.742 Marine Chemistry: Dissolved Gases and Air-sea exchange
Lecture 8

Overview

The fluxes of gases between the ocean and atmosphere play a pivotal role in the marine geochemistry and biogeochemical cycles of many elements and/or species (e.g., CO_2, O_2, DMS or dimethylsulfide, etc.). Unlike on land, quantifying gas exchange rates at sea is a difficult task, and considerable effort has been devoted to estimating gas fluxes (usually some indirect approach). At the simplest level, estimating the flux of a gas across the air-sea interface requires two basic types of information: 1) the disequilibrium between the concentrations of gas in the air and surface seawater (the thermodynamic driving force) and 2) the rate at which the disequilibrium is removed (the kinetic rate). The formulation of air-sea gas exchange thus is very reminiscent of many other transport problems (e.g., thermal diffusion) and irreversible thermodynamics (out side the scope of this class).

Gas Solubilities

To start with, we want to know something about how much gas is dissolved in water and whether those concentrations are in equilibrium with the air above. Air is composed of a mixture of gases, the more significant of which are listed below:

Gas	Content by volume
N_2	78.08%
O_2	20.95%
Ar	0.934%
CO_2	280+ ppm
Ne	18.18 ppm
He	5.24 ppm
Kr	1.14 ppm
Xe	0.087 ppm
H_2	0.5 ppm
CH_4	2 ppm
N_2O	0.5 ppm

The above are presented "exclusive of water vapour". (Bear in mind that water exerts a vapour pressure that is a function of temperature.) ***Dalton's Law of Partial Pressures*** states that the pressure exerted by the individual gases is additive, and therefore their abundances may be expressed as ***partial pressures*** and treated independently of one another.

Exclusive of any chemical or biological reactions within the ocean or atmosphere, gases tend to dissolve into seawater in proportion to their partial pressure. This fact is usually referred to as ***Henry's Law***.

$$[A(aq)] = \frac{K_{eq}}{RT} P_A$$

Here *A(aq)* is the aqueous activity of the gas (the concentration), usually expressed in terms of molar units per unit volume of water (*e.g.,* cc(STP)/l). Also, P_A is the partial pressure of the gas, R and T are the usual, and K_{eq} is the Henry's law coefficient. While this is fine for the laboratory, a more useful measure is the ***Bunsen Solubility Coefficient,*** which relates the concentration to the partial pressure more directly:

$$[A(aq)] = \beta_A P_A$$

Be prepared to work between units like µmol/kg, µmol/l, cc(STP)/g, *etc.* These are all molar quantities, with one important exception: when the divisor is in volumetric terms, the ratio is not really molar, as the volume of water (and seawater) is dependent on temperature (and salinity). Hence *the internationally adopted (WOCE) standards of measurement are* µmol/kg.

For example, oxygen used to be given in units of "ml/l", that is ml(STP) of oxygen per litre of water. Since there are 22.4 x 10^3 ml in a mole, and since there are approximately (depending on the temperature and salinity) 1.025 kg in a litre of seawater, you can derive that

$$1 \text{ ml/l} = 43.6\ \mu\text{mol kg}^{-1}$$

so that an oxygen concentration of 6.6 ml/l would be equivalent to 287 µmol kg^{-1}.

The solubility of a gas in water may be broken down into three aspects. In a quasi-thermodynamic treatment, one may regard the heat of dissolution being the sum of three heats:

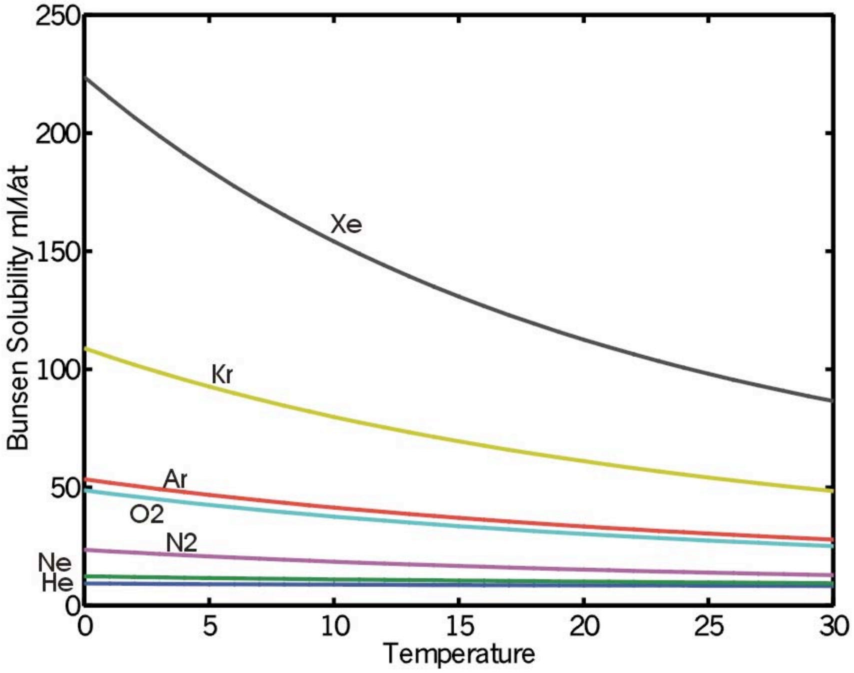
1. The work required to create a cavity in the solvent (solvent dependency)
2. The work required to contain the solute in the cavity (solute dependency)
3. The energy gained by solute-solvent interaction (solute-solvent dependency)

In general, the third appears to be the most significant factor for most gases, with the larger, more polar (or polarizable) gases being the more soluble.

For a more thermodynamics that one would care to see, the reader is referred to the following paper:
Molecular thermodynamic model for the solubility of noble gases in water. A. Braibanti et al., *J. Phys. Chem.* **98**, 626-634 (1994)

Solubilities are most strongly dependent on temperature. In general, gases are less soluble at higher temperatures. This may be regarded as a direct consequence of the latter two terms in the energy budget mentioned above: as temperature increases, it becomes more difficult to contain the gas (solute) and the solute-solvent attraction is increasingly disrupted by thermal agitation. Below is a plot of bunsen solubilities for a number of atmospheric gases.

Note that in addition to being more soluble overall, the slope and curvature of the temperature dependence *increases* for the "heavier", more soluble gases.



Isotope Effects in Solution

The heavier isotopic species of gases are generally more soluble. This can be rationalized by considering the different thermodynamic components discussed above. The second factor appears most likely to be the dominant isotopic differentiator, although the third must also contribute. Some general aspects of isotope effects of gas solution in seawater are summarized below. Note that there is a correspondence with fractional mass difference (the larger the fractional mass difference, the greater the isotope effect). However, the effect becomes far less distinct with increasing solubility, largely because of the smaller relative contribution of the second thermodynamic factor.

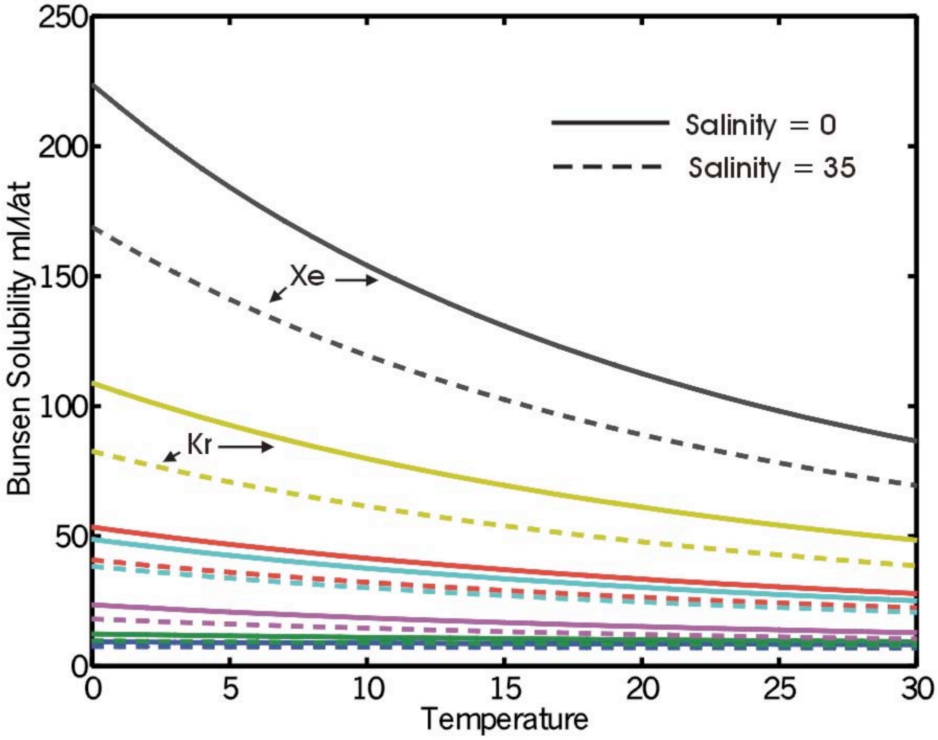
Gas	Molecular Wt	Isotope Ratio	Mass Difference	Isotope Effect
Helium	4	^{3}He/^{4}He	28.6%	-1.5%
Neon	20.2	^{20}Ne/^{22}Ne	9.5%	-0.5%
Oxygen	32	^{18}O/^{16}O	6.1%	+0.1%
Argon	40	^{40}Ar/^{36}Ar	10.5%	+0.05%

Note also the sign changes due to whether the heavier isotope is in the denominator or numerator.

Solubilities depend on salinity as well. This is known as "salting out", and results from the interference of ionic strength with the solute-solvent attraction. It is often described by the ***Setschenow Relation*** which is

$$\ln\left(\frac{\beta_0}{\beta_S}\right) = k_S S$$

where the subscript 0 refers to zero salinity, and S is the salinity. k_S is the constant of proportionality. However, more complex (higher order) terms are often used in solubility functions nowadays. Below is an example of the difference between fresh and salt water.



Solubilities are determined in the laboratory under carefully controlled conditions, and often reported as semi-empirical "thermodynamic" functions. Weiss, for example, uses the following form:

$$\ln \beta = A_1 + A_2\left(\frac{1}{T}\right) + A_3 \ln T + S\left[B_1 + B_2 T + B_3 T^2\right]$$

which nothing more than a convenient function that fits the observed laboratory temperature and salinity dependence reasonably well.

The Stagnant Film Model

The exchange of most gases between the atmosphere and ocean may be regarded as limited by molecular diffusion. The simplest model is to think of a stagnant film on the liquid side at the boundary between the two phases (air and water).

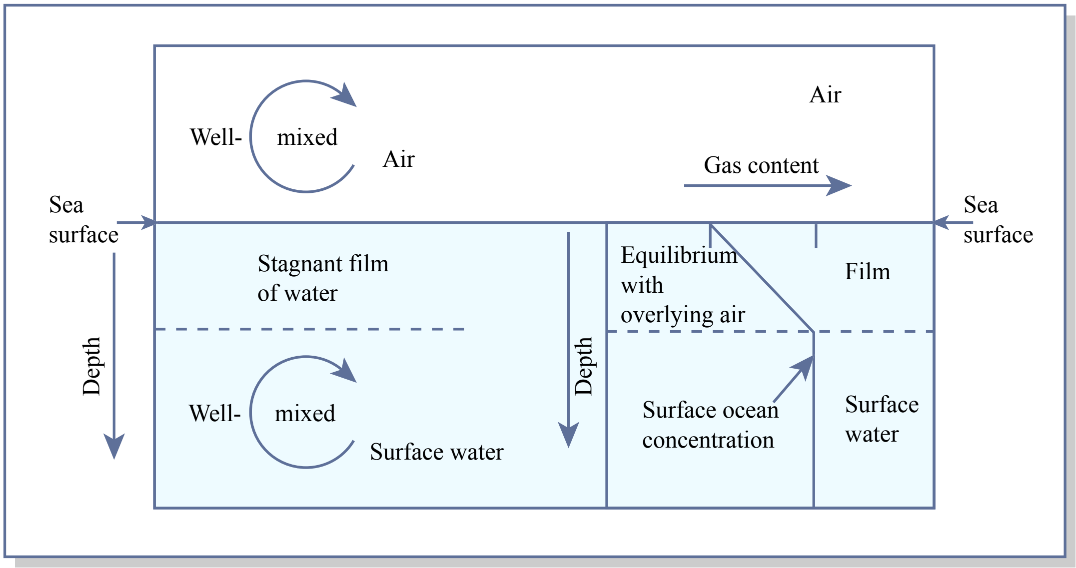


Figure by MIT OCW.

To escape (or invade) the gas must diffuse across this layer. Thus the flux would be given by

$$F = -D\frac{dC}{dz} = -D\frac{\Delta C}{\Delta z} = -D\frac{(C - C_0)}{\Delta z}$$

where D is the molecular diffusivity. Note that this predicts a linear dependence of gas exchange rate on the molecular diffusivity of the gas (a function of temperature and salinity). Also, expect the film thickness to be a function of viscosity (hence T and S) and state of turbulence.

The above formulation is an example of the "divide and conquer" approach to geochemistry: you separate the problem into gas or species dependent part, and a solvent or medium dependent part. The gas part is $D(C-C_0)$ and the medium part is the Δz. The latter, the layer thickness, should be a function of the viscosity of the water and the degree of turbulence.

Radon has a half-life of about 4 days, and to all intents and purposes, has a zero concentration in the atmosphere. It is produced in seawater by radioactive decay of ^{238}U chain nuclides, in particular its immediate parent ^{226}Ra. If ^{222}Rn were not a gas, it would be in secular equilibrium with its parent:

$$A_{222} = A_{226}$$

Secular equilibrium is a situation where the rate at which a radionuclide decays is exactly equal to the rate at which it is produced. This occurs within decay chains, and means that the parent and daughter *activities* become equal. The concentration and activity are related by

$$A = \lambda N$$

where λ is the radioactive decay constant. But when we look in the water column near the ocean surface, ^{222}Rn is less abundant than you would expect from the activity of ^{226}Ra. That is, you have $A_{222} < A_{226}$.

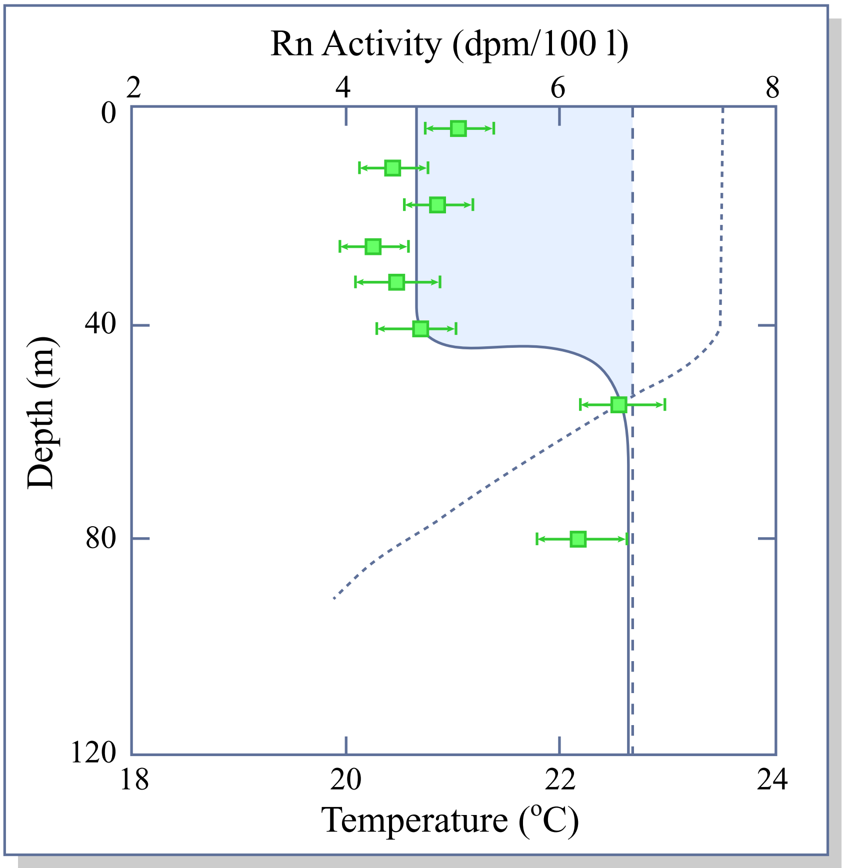


Figure by MIT OCW.

In the figure above, the dashed line is the activity of ^{226}Ra, and the dotted line is the temperature. The shaded region highlights the deficit of ^{222}Rn, which is strongly associated with the region of uniform temperature known as the ***Mixed Layer*** (the surface layer of the ocean effectively stirred to uniformity by the winds and thermal convection). If we think of the mixed layer as a column with unit area and depth *H*, the vertically integrated production rate of ^{222}Rn is the water column height times the ^{226}Ra activity:

$$\mathrm{Pr}od = HA_{226}$$

Now according to our stagnant film model, the loss of Rn due to gas exchange is

$$F = D_{222}\frac{\Delta C}{\Delta z} = \frac{D_{222}}{\lambda_{222}\Delta z}A_{222}$$

The gas exchange rate (D/Δz) is expressible in units of length/time, e.g., traditionally in cm/hr or m/day. This can be seen by substituting in the units for diffusivity and the stagnant film thickness and cancelling them out (or alternatively for the form on the far right side of the equation above, the diffusivity, the activity, the decay constant, and the stagnant film thickness). Thus it appears like a "velocity", and is often referred to as the **piston velocity** k times the concentration difference.

$$F = k\Delta C$$

For example, using mks units, we have the units of piston velocity as:

$$k = \frac{m^2 s^{-1}}{m} = \frac{m^2 s^{-1}}{s^{-1} m} s^{-1} = m\ s^{-1}$$

That is, piston velocity indeed has units of velocity (cm/hr, m/s, furlongs/fortnight, etc). It can be thought of as the speed of an imaginary piston which is pushing gas out of (or into) the water column.

When considering the mixed layer budget for Rn, the loss rate includes both gas exchange and the loss due to radioactive decay:

$$Loss = F + HA_{222} = \left(\frac{D_{222}}{\lambda_{222}\Delta z} + H\right)A_{222}$$

and insisting that in the steady-state situation, Production = Loss, we have

$$HA_{226} = \left(\frac{D_{222}}{\lambda_{222}\Delta z} + H\right)A_{222}$$

or by solving for Δz, we get

$$\Delta z = \frac{D_{222}A_{222}}{\lambda_{222}(HA_{226} - HA_{222})}$$

So that substituting the known quantities:

$$\lambda_{222} = 2.1\times10^{-6} s^{-1}$$
$$D_{222} = 1.4\times10^{-9} m^2 s^{-1}$$
$$H = 40 m$$
$$A_{222} = 4.7 dpm/100l$$
$$A_{226} = 6.7 dpm/100l$$

gives $\Delta z \approx 40 \times 10^{-6}\,m$, which should be the thickness of this hypothetical boundary layer.

Now this is all well and good, and I'm sure you find that learning about the gas exchange rate of a heavy, radioactive noble gas is a laudable achievement, but what about more important gases, like oxygen or CO_2? How do we obtain regional or global estimates of the fluxes? Thus there are two fundamental questions that arise:

1. ***How does the gas exchange rate depend on the type of gas?***
2. ***How does the gas exchange rate vary, for a given gas, with environmental factors?***

The second question depends on complicated details of the fluid: turbulence, viscosity, etc, and we'll be talking about that later in the lecture. The first question, if the thin film model were correct, would be easy: the gas exchange rate varies linearly with the molecular diffusion coefficient. We would then use the gas exchange rate measured "directly" with the Rn deficit technique described above along with laboratory measurements of molecular diffusivity, such as the ones listed (in units of 10^{-9} m^2s^{-1}) below to estimate the gas exchange rate for a given species.

Gas	**Mol Wt**	**D @ 0°C**	**D@25°C**
He	4	4.60	7.31
Ne	20	2.33	4.03
N_2	28	1.40	2.88
O_2	32	1.45	2.53
Ar	40	1.58	2.47
CO_2	44	1.0	1.9
N_2O	44	1.0	2.0
Kr	84	0.87	1.85
Xe	131	0.64	1.49
Rn	222	0.57	1.33

Note that the diffusivity is a function of temperature, often expressed in the following equation:

$$D = D_0 e^{-E_a/RT}$$

where E_a is the activation energy, T is the absolute temperature, and D_0 is the diffusivity at *infinite* temperature.

A definitive publication on gas diffusivities in seawater and water is: Jahne, B., G. Heinze and W. Dietrich (1987) Measurement of the diffusion coefficients of sparingly soluble gases in water. *J. Geophys. Res.* **92**, 10767-10776.

As you may guess from the tone of this discussion, the stagnant film model turns out to be not very good, especially as we would expect that this putative stagnant film is unlikely to remain in place under strongly turbulent conditions normally encountered in the open ocean. Wave action and bubble production will ensure that the layer is destroyed rather quickly. This has significant impact on the transport of gases, as we shall see. Thus we have to look at another model.

The Replacement Film Model

The problem with the stagnant film model is that it doesn't work very well. Bear in mind that molecular diffusivities vary by a factor of about 5-10 (depending on temperature) between gases like Rn and He. If we don't have the dependence of gas exchange rate on diffusivity *right*, then we run a serious risk of being substantially off in our estimate of other gas exchange rates.

It is hard to imagine that a stagnant film could exist under higher sea states. The next evolutionary step in our modelling of gas exchange is to consider the *replacement film model*. The concept is that the laminar boundary layer is continuously torn apart and replaced with slabs of fluid below. In this model, "renewal events" occur bringing fresh subsurface water to the air-water interface. These patches of water then gain (loss) gas across the air-water interface via diffusion thus reducing ΔC. At the next renewal event, which occurs on average with a time-scale τ, the surface water with modified concentrations is driven back into the ocean interior driving a net flux between the bulk air and water. To estimate the flux of material associated with this process, consider the diffusive penetration of material into an infinite slab. The diffusive flux into a semi-infinite space goes as:

$$F(t) = \Delta C\sqrt{\frac{D}{\pi t}}$$

Note that the flux goes down with time as the surface patch becomes equilibrated with the air. To find the average flux over the time-period that the patch is at the surface (0 to θ), one would need to integrate and then divide by θ.

$$F = \frac{1}{\theta}\int_0^\theta F(t)dt = 2\Delta C\sqrt{\frac{D}{\pi\theta}}$$

Thus in the surface renewal model the piston velocity is $k = 2\sqrt{D/\pi\theta}$. Now we don't actually know the surface renewal time-scale θ, but we know it is related to the viscosity (the more viscous the fluid, the slower the slab is replaced), so that we can relate the gas flux to a constant and the viscosity (ν) as

$$k \propto \sqrt{\frac{D}{\nu}} \propto Sc^{-1/2}$$

Now the interesting thing is that the factor $\frac{\nu}{D} = Sc$ is a dimensionless number used in chemical engineering literature to refer to the relative importance of molecular diffusion and viscosity dissipation in physical systems. It is called the ***Schmidt Number*** (*Sc*) and is larger for the more slowly diffusing gases, and smaller for the more mobile ones. Piston velocity for the film replacement model scales as $Sc^{-1/2}$ and can be used to estimate the air-sea flux for any gas F_C if we know the air-sea gas exchange coefficient (or piston velocity) for a reference gas and temperature (k_0):

$$F = k_0\left(\frac{Sc}{Sc_0}\right)^{-0.5}\Delta C \quad \text{and} \quad k = k_0\left(\frac{Sc}{Sc_0}\right)^{-0.5}$$

This model appears to be the most successful in relating the gas exchange rates of differing gases. The table below is a list of various *Sc* numbers for different gases at a variety of temperatures.

T(°C)	**He**	**Ne**	**Ar**	**O_2**	**Kr**	**Xe**	**Rn**	**H_2**	**CH_4**	**CO_2**
0	378	767	520	477	2045	2700	3168	633	1908	1922
5	292	578	361	345	1477	1929	2234	472	1399	1396
10	230	445	266	263	1090	1408	1610	360	1047	1036
20	150	276	165	168	626	793	885	219	618	**600**
30	102	180	115	117	380	472	516	141	385	369

As you can see from the table above, more mobile gases like He have a lower *Sc* and the slower movers, like Rn, have much higher *Sc.* Note that we have highlighted CO_2 at *Sc*=600. You will often find gas exchange rate measurements referenced to this standard.

It turns out that there have been a number of tests of the appropriateness of the replacement film model for oceanographic gas exchange experiments. They have tended to ask a more general question: what is the value of *n* in the general gas exchange equation?

$$F = k_0 \left(\frac{Sc}{Sc_0} \right)^{-n} \Delta C$$

Experiments point to n= 0.5 for most oceanic conditions. In the case of the stagnant film model, we had n=1, but as we said, the s.f.m. doesn't work. However, sophisticated theoretical derivations (and some experiments seem to hint at it) indicate that n should increase to 2/3 (0.667) at low wind speeds ("smooth wall" conditions). This makes sense in that the ideal of a stagnant film might be more closely approached under those conditions.

General Gas Exchange Models

Now that we have discussed how the gas exchange rate depends on the gas in question, how does it depend on other things? There are a number of factors:

Chemical Reaction

Since the flux of gas into the water ultimately governed by fickian diffusion in the boundary layer,

$$F = -D\frac{\partial C}{\partial z}$$

then chemical reactions within the thin boundary layer may serve to sharpen gradients of some gases, thereby increasing the fluxes of those gases. This kind of enhancement certainly occurs for extremely reactive compounds, particularly photo-reactive species. This might also be the case for CO_2 since it converts to bicarbonate and carbonate.

$$CO_2 + H_2O \Leftrightarrow H_2CO_3$$

It is possible to assess the significance of this by comparing the time constant of this buffering reaction, which is of the order of a minute, with the time it takes for a molecule to transit the boundary layer via molecular diffusion, which is related to

$$T \approx \frac{L^2}{D}$$

and using typical values ($L \approx 40 \times 10^{-6} m^2$ and $D \approx 2 \times 10^{-9} m^2 s^{-1}$) which substituted in the above yields $T \approx 1\, s$. Thus a CO_2 molecule spends far too little time in the boundary layer to be affected by chemical reaction whilst there. Laboratory measurements confirm this. *However*, the book is still not closed on this case, as films present at the sea surface may concentrate catalysts, in particular carbonic anhydrase, which may speed up the chemical reaction. Although measurements of bulk seawater do not show sufficient carbonic anhydrase concentrations to catalyse CO_2 gas exchange, measurements have yet to be made on surface films.

Wind Speed

Wind stirring at the ocean surface produces turbulence in the water, which shear the boundary layer, thinning it, and speeding its replacement and removal of material from the sea surface. Further, the creation of waves effectively increases surface area, thereby increasing gas fluxes. Because it is relatively quantifiable, wind speed has been used as a primary variable in studying gas exchange rates. There is no clear theory relating wind speed directly to gas exchange rates (GER), except in the general sense that the GER should increase, probably in a stronger fashion than linearly with wind speed. Thus wind-speed *vs* gas exchange rate relationships have been strictly *empirical*, that is the relationships are actually statistical regressions of some simple function against the (usually very noisy) data. The two primary relationships used are

- A tri-linear regression suggested by Liss & Merlivat (1986) which breaks the wind-speed range into three sub-ranges characterised by three different linear relations, with progressively increasing slope for increasing wind speed
- A quadratic regression used by Wanninkhof (1992)

Below is a figure which compares these formulations with a compilation of data presented by Liss and Watson (1998) originally provided by Merlivat (priv. comm.).

Figure removed due to copyright restrictions.
Watson, A. J. and Liss, P. S. "Interactions Between the Marine Biota and Climate via the Carbon and Sulphur Biogeochemical Cycles." *Phil Trans Roy Soc B* 353 (1998): 41-51.

The data presented above show that both relationships have the same general form, but that the Liss-Merlivat formulation must be multiplied by a factor (1.4 to 1.6) to match the data accumulated since its publication. It should also be noted that there are large error bars and systematic differences between the various estimates and approaches, and that the Liss-Merlivat data were originally most dependent on gas-exchange rate determinations made in lakes and rivers, which in turn may underestimate open-ocean rates. We will discuss the differences between these basic techniques later.

Sea State

Sea state must place a role in gas exchange, but is more difficult to quantify on any large scale. Clearly wave-height and wave-type are critical, as well as fetch and wave spectra. By comparing "continuous" records from moored oxygen probes with meteorological data that included wave-height measurements, Wallace and Wirrick (1992) noted a stronger short term correlation between gas exchange and wave height than with wind speed. Recently techniques using scattering of laser-light have made meaningful determinations of RMS wave slope both in the laboratory (wind tunnels and flumes) and most recently at sea. This provides direct measurements on very local scales, and provides the opportunity to look at actual mechanisms. Also, radar backscatter and sea "brightness" measurements from satellites hold considerable promise of large-scale, regional averages of sea-surface state. This is very exciting because it may permit us to obtain truly large-scale or even global averages of gas exchange rates. Such methods, however, are still under development, and will require "sea-truthing".

Bubbles

Bubbles are created in the ocean largely by breaking waves ("white caps"), and do two important things. Firstly, they can enhance gas exchange by

- Increasing the effective surface area available for gas exchange (the surface of the bubble itself adds to the contact area between air and water)
- The passage of bubbles upward and downward transports gas in large amounts vertically
- The bubbles tend to stir the surrounding liquid, making more turbulence

Secondly, they provide a mechanism whereby gases can be supersaturated in water. Bubbles can be forced downward by roller-type circulation cells in the upper ocean (often called "Langmuir Cells"), and can be carried downward several metres. Bubbles are often "seen" (using sonar back-scatter) as deep as 5-10 m. Since hydrostatic pressure increases at a rate of 1 atmosphere per 10 m depth, these bubbles, if left down there will completely dissolve. Complete dissolution of such bubbles will result in an enrichment of especially the less soluble gases. For example, the trapping and dissolution of 1 ml of air bubbles in a kg of seawater would result in the following approximate supersaturations for water at 20°C:

Gas	Abundance in Air	Concentration in Water (cc/ml)	Water/Air Ratio	Δ (%)
He	5.24×10^{-6}	3.8×10^{-8}	0.0075	14
O_2	0.21	5×10^{-3}	0.024	4.2
Ar	9.3×10^{-3}	2.5×10^{-4}	0.026	3.7
Xe	8.7×10^{-8}	8.9×10^{-9}	0.099	1.0

In the table above we show Δ, the ***saturation anomaly*** (the percentage deviation from solubility equilibrium). For He, we would have

$$\Delta He \equiv \left(\frac{C(He)}{C_0(He)} - 1 \right) \times 100\%$$

where C_0 is the solubility equilibrium concentration. The effect is strongest for the least soluble gases (esp. He) and the contrast is greater at lower temperatures, because of the strong solubility-temperature dependence for the more soluble gases. Typically, surface water helium supersaturations are of the order of 3-4%, suggesting that of order 0.2 to 0.3 ml/kg of air is trapped, and that contributions of air trapping to gases like oxygen are between 1 to 2% at most.

However, things are not as simple as this, since not all bubbles completely dissolve. Large bubbles not only live longer (and hence are more likely to eventually resurface), but enjoy greater buoyancy. The history of a bubble undergoing compression and decompression will in general be very complicated, as gas transport from the bubble under compression will alter the gas composition significantly. Moreover, the export of gas from the bubble will be diffusionally limited, with mass transport being a complex function of solubility and molecular diffusivity. In general, one has the mass transport being proportional to D^S where S is 0.5 for a "clean" (uncontaminated, or pure) fluid, and S = 0.67 for "dirty" (more typical) oceanic environs. The net mass flux for a given gas is thus a complicated function of bubble trajectory, size and population. These are not well known, and general relationships have only recently been discussed in the literature. Below is a general bubble size *vs.* population plot

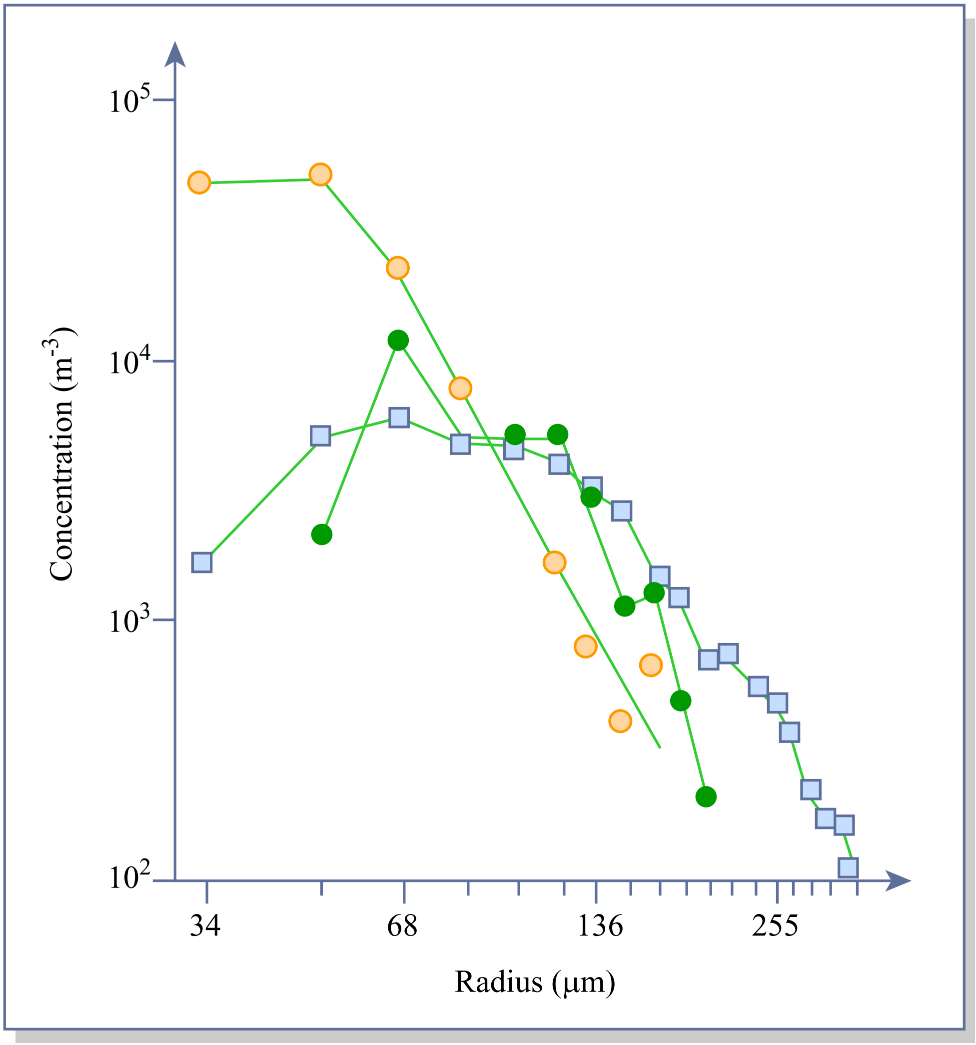


Figure by MIT OCW.

Bear in mind that although the population drops off logarithmically with increasing size, the *volumetric* contribution of such bubbles varies as the cube of the radius: $V = \frac{4}{3}\pi r^3$.

Surface Films

Surface films have been shown to be ubiquitous, not only in eutrophic/neritic coastal waters, but to a lesser extent in the oligotrophic open ocean. They can have a pronounced effect on fluid turbulence, and hence the structure of the microlayer and wave spectra. They arise from the surface concentration of dissolved organic matter, including degraded biopolymers and geopolymeric materials. Phytoplankton exudates such as polysaccarides are potent surfactants (surface active materials). Material is concentrated in the surface microlayer by their hydrophobic character, as well as by Langmuir circulations (long roll-like cells) that concentrate this material near convergence zones. These films are effective in thickening the boundary layer (increasing the viscosity), dampening turbulence, and suppressing the amplitude of short-wavelength (capillary) waves. This can be seen in the pronounced reduction of wave-slope by surfactants:

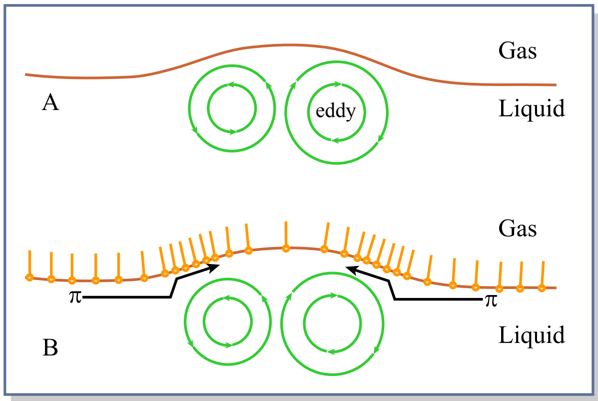


Figure by MIT OCW.

The net effect is that ***surface films suppress gas exchange***. This was first noted and documented thoroughly in laboratory gas-exchange experiments. The critical point here is that the onset of motions important for gas exchange is "pushed forward" to higher wind speeds: it takes more energy to create the boundary layer conditions necessary to enable rapid gas exchange. The other point is that *natural* surfactants (note the coastal water points) are very effective in suppressing gas exchange. This strongly suggests that the scatter in the empirical data for gas exchange as a function of wind speed may be driven by variability in the presence of organic films.

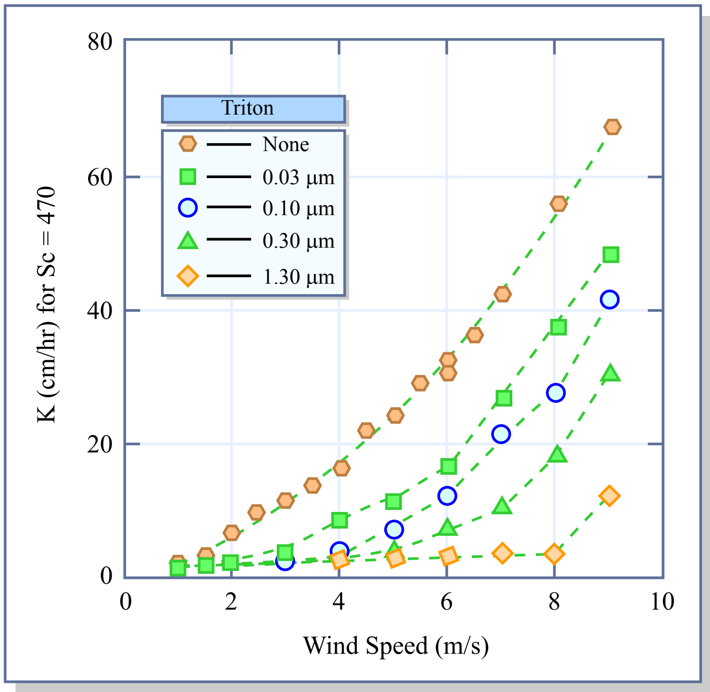


Figure by MIT OCW.

Gas Exchange Residence Times

This is an important concept in geochemistry, akin to the residence time of an element in the ocean. Simply put, it is the response time of the upper ocean to a change in the atmospheric composition of a gas. The rule of thumb is that

The response time for a gas in the ocean mixed layer is the depth of the mixed layer divided by the piston velocity for that gas.

That is:

$$T = \frac{H}{k}$$

where H is the mixed layer depth. For helium ($Sc \sim 150$) in a 100 m mixed layer with a wind speed of about 10 m s^{-1} the time constant will be

$$T = \frac{100\,m}{40\ cm\,h^{-1}} = 250\,h = 10.5\ d$$

That is, the He concentration of the mixed layer would respond on a time-scale of 10 days to a perturbation. Similarly, for Xe ($Sc \sim 750$), the time constant would be 24 days.

The Carbon Dioxide Exchange Time-Scale

Now it turns out that this is not the whole story for CO_2. Because the bulk of CO_2 exists in the carbonate-bicarbonate buffer system, then to affect that inventory, you have to move a much larger amount of CO_2 than what you would infer from the $[CO_2]_{aq}$ alone. For isotopic exchange, the time-scale lengthens considerably to:

$$T = \left(\frac{H}{k}\right) \times \frac{[\Sigma CO_2]}{[CO_2(aq)]}$$

Since the ratio of CO2 (aq) to total inorganic CO2 is roughly 1:100 to 1:200, the timescale for carbon isotopic exchange is roughly 10 years!! The time-scale for CO2 itself is less because adding CO2 changes seawater pH and carbonate system speciation:

$$T = \left(\frac{H}{k}\right) \times \frac{1}{R} \times \frac{[\Sigma CO_2]}{[CO_2(aq)]}$$

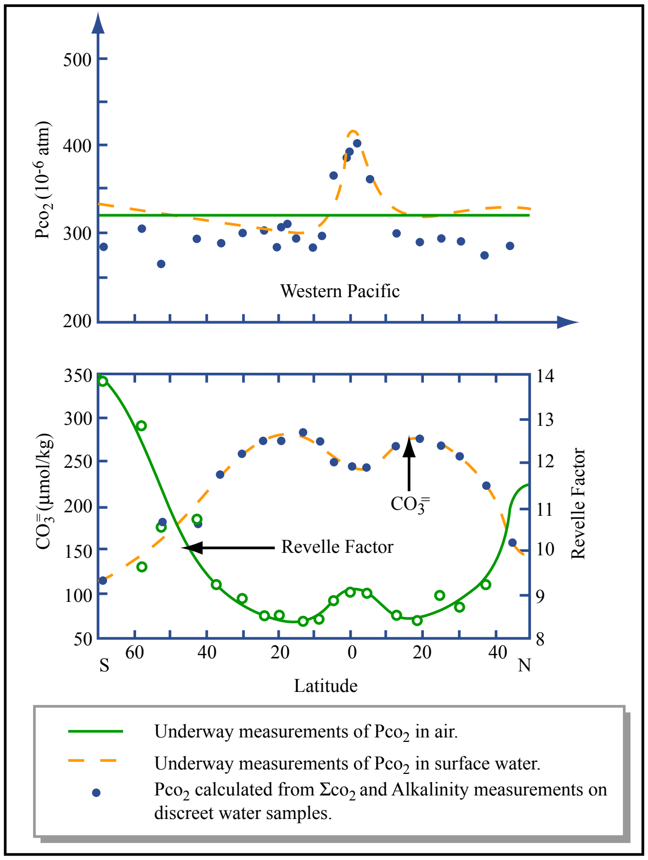


Figure by MIT OCW.

$$R \equiv \frac{\partial[CO_2(aq)]}{[CO_2(aq)]} \times \frac{[\Sigma CO_2]}{\partial[\Sigma CO_2]}$$

where the factor R is the "***Revelle Factor***" and is related to the ratio of the fractional aqueous CO_2 concentration change to total carbonate change. We will discuss this later in the course, but suffice it to say that R ~ 10 in the surface ocean. In the 100 m, 20°C mixed layer discussed above, the time constant for CO_2 would be

$$T = \left(\frac{100\ m}{20\ cm\,h^{-1}}\right) \times \frac{1}{10} \times 150 = (21d) \times (15) \approx 0.9y$$

That is, in addition to being a mediocre diffuser, CO_2 has such a large chemical inertia that it's time constant for exchange close to a year, *i.e.,* about 10 times slower than other gases. This has a significant effect, for example, in the Gulf Stream, where water is carried northward in the current, and cooled much more rapidly than the CO_2 can exchange (i.e., be taken up due to increased solubility). As a result, the CO_2 becomes greatly undersaturated as water goes northward.

Radiocarbon Time-scales

Radiocarbon has an even longer time scale of exchange than CO_2. This is because you must move the isotope through the entire buffer system to make any change. Thus the gas exchange rate is:

$$\frac{T_{GE}\left(C^{14}O_2\right)}{T_{GE}\left([CO_2]_{aq}\right)} = \frac{[\Sigma CO_2]}{[CO_2]_{aq}} \approx \frac{2200}{12} \approx 180$$

$$\therefore T_{GE}\left(C^{14}O_2\right) \approx 10.4\ years$$

where we have been careful to distinguish the physical gas exchange rate for CO_2 (the denominator in the above equation) from the buffered gas exchange rate for CO_2. Thus the gas exchange time-scale for radiocarbon is increased by a ratio of nearly 200, raising it to a decade! See *Broecker and Peng* for a more thorough discussion of these matters.

Measuring Gas Exchange Rates

Measuring gas exchange rates is a difficult task for a number of reasons. These reasons will emerge as we discuss the various approaches that have been used. Primarily they are

- It is difficult (or impossible) to measure gas fluxes "directly"
- It is impossible to replicate the natural environment
- You may perturb the processes you are measuring
- Gas fluxes are variable on a large variety of space and time scales
- Not all relevant control variables are measured or measurable

These difficulties manifest themselves in a large amount of scatter in results. This doesn't mean the results are bad, just that there are significant challenges in making such measurements. These challenges have been met in a variety of ways, and we'll discuss some of the approaches.

The measurement strategies break down into two basic groups: laboratory and field determinations. The latter could be further subdivided on the basis of scale into open ocean and "mesocosm" experiments, and on the basis of technique into "direct" and "indirect" determinations. These are summarised as follows:

Laboratory Measurements:
These offer a high degree of control over physical, chemical and biological conditions and allow the investigator to systematically explore the basic processes involved in gas exchange. These are powerful techniques for building intuition and understanding about basic processes, but provide no direct constraints on the natural "numbers" because it is not possible to replicate the natural environment on the appropriate scales, or to "scale up" the effects due to complicated processes that occur within the experiments.

Experiments typically occur in "wind tunnels" which may be linear, but can also be toroidal. The latter are used to overcome "finite fetch" problems associated with the linear machines, but all are subject to geometric limitations (e.g., orbital or resonance circulation modes excited in the chambers). It is possible to argue that laboratory measurements may systematically *under*- or *over*-estimate gas exchange rates, depending on the facility. We will not dwell on this technique, except to mention that there have been superb studies on the effect of surfactants, etc on gas exchange, e.g., by the Woods Hole group headed by Nelson Frew.

Field Measurements

Mesocosm

Another approach is to measure gas exchange rates in small bodies of water. Studies have been done in wave pools, ponds, lakes, rivers, and estuaries. This allows a degree of control, and the possibility of measuring more "control variables" than in the open ocean. Such an approach is a compromise between the laboratory and field experiments, but suffers from the many of the problems of both.

Open Ocean

There are four basic approaches to open ocean measurements. These include:

1. **Direct flux measurements (eddy-correlation methods):** These involve trying to measure the turbulent gas flux directly. They are enormously challenging because they require extremely precise, rapid measurement schemes, and are often characterised by the "noise" being as large as (or larger than) the "signal".
2. **Tracer release experiments:** These constitute a powerful emergent technique where multiple tracers are released and monitored as they are affected by gas exchange. This experimentally demanding, but very rewarding. The experiments, however, are limited to intermediate, rather than very large scales.
3. **Tracer balance techniques:** This involves calculating the gas exchange from the mass balance of some "clock" tracer, such as ^{222}Rn. You are limited to the time-scale and spatial characteristics of the tracer, but they often provide good integral constraints on the processes.
4. **Remote (Proxy) measurements:** Actually not a "real" measurement technique, but an approach to extrapolate "local" measurements via some algorithm to the global scale using satellite measurements.

Dual Tracer Release Experiments

The most obvious way to measure gas exchange rates is to release a tracer gas in the mixed layer of the ocean, and track its decrease with time as it outgasses to the atmosphere. This sounds easy, but it’s not. As soon as you release a patch of material into the ocean, mixing and stirring tend to spread it out, and you have to sample over increasingly larger areas to sum up what is in the water. This is subject to considerable errors. The next best thing is to release *two* tracers, one which is *not* volatile, and one which is. Then you can use the ratio of the two tracers to tell you the gas exchange rate. The problem is that there is at present no ideal “non-volatile” tracer, so a “less volatile” tracer is used, and corrections are made for its loss by gas exchange. The two most commonly used tracers are ^{3}He (a stable, inert gas without much oceanic background concentration) and SF_6 which is essentially inert, has no natural source, and diffuses *much* more slowly than ^{3}He. The technique has been applied in small water bodies (lakes, rivers, *etc.*) and has recently been used at sea. Please read the Watson *et al.* Reference about this technique.

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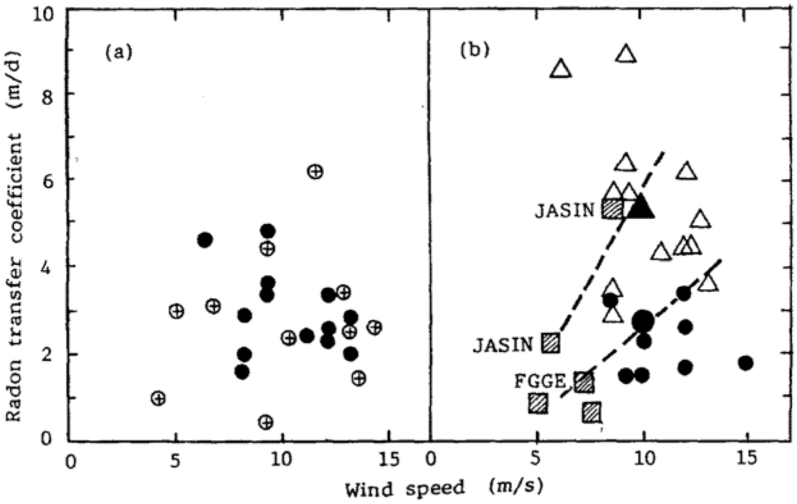
You are already familiar with a tracer balance technique: the Radon Deficit Technique. This balances gas exchange rates against a known clock: the radioactive production (and decay) of ^{222}Rn. The problem with this technique is that it is a "local" and "short term" measurement: the short half-life of the tracer (4 days) means that it has a short memory. Even then, one finds variability that probably arises because the time-scale is comparable to the meteorological time-scale. As geochemists, we are really interested in techniques that tell us about gas exchange on time-scales ranging from the seasonal to the annual/decadal.



It would have been much better if it were much longer or much shorter!

Gas Exchange Rates Using Natural Radiocarbon

Radiocarbon, as we mentioned before, has a much longer gas-exchange time-scale, and hence provides us with a much longer term average. Radiocarbon (^{14}C) is radioactive with a half-life of 5730 a. Radiocarbon atoms are born from nuclear reactions caused by cosmic rays in the atmosphere. In the atmosphere they immediately combine with oxygen to become $^{14}CO_2$. A lot of this $^{14}CO_2$ ends up in the oceans, because the oceans represent a huge carbonate reservoir. Since this $^{14}CO_2$ must gas exchange into the oceans, we can use the observed distribution of $^{14}CO_2$ in the oceans to infer the rate of gas exchange *on a global scale*. This calculation simply rests on the assumption that

The rate at which $^{14}CO_2$ enters the oceans must be balanced by the rate it decays in the ocean.

The rate $^{14}CO_2$ enters the ocean:

To estimate the rate radiocarbon enters the ocean, we apply our gas exchange equation:

$$F_{in} = k\Delta C$$

Now how do we calculate ΔC? This is the difference between the (bulk) surface water concentration and solubility equilibrium. The latter is easy to calculate:

$$C_0 = \left(\frac{^{14}C}{^{12}C}\right)_{atm} \alpha_{14-12}\left[CO_2\right]_0$$

That is, the equilibrium concentration of radiocarbon dioxide would be the isotopic ratio of carbon in the atmosphere, times the solubility isotope factor, times the equilibrium concentration of CO_2. The solubility isotope factor arises from the fact that $^{14}CO_2$ is about 1.5% more soluble than normal CO_2. We will make the simplifying assumption that the surface carbon dioxide concentration is very close to equilibrium with the atmosphere, so that we have

$$C_0 = 1.015 \times \left(\frac{^{14}C}{^{12}C} \right)_{atm} \left[CO_2 \right]_{Surf}$$

The surface radiocarbon dioxide concentration is not such a simple thing to find. We have been talking about ***natural radiocarbon***, whereas the atmosphere (and to some extent, the surface ocean) has been flooded with radiocarbon produced by *atmospheric nuclear weapons testing* in the 1950s and 1960s. In addition, mankind has also been burning fossil fuels at a great rate, and fossil fuels have no radiocarbon, so that we have been diluting the atmospheric carbon dioxide inventory with dead carbon, lowering the radiocarbon ratio in the atmosphere. This his known as the *Suess Effect*. The problem is that we did not have many good measurements of radiocarbon in surface waters before the bomb testing, and *none* prior to the industrial revolution.

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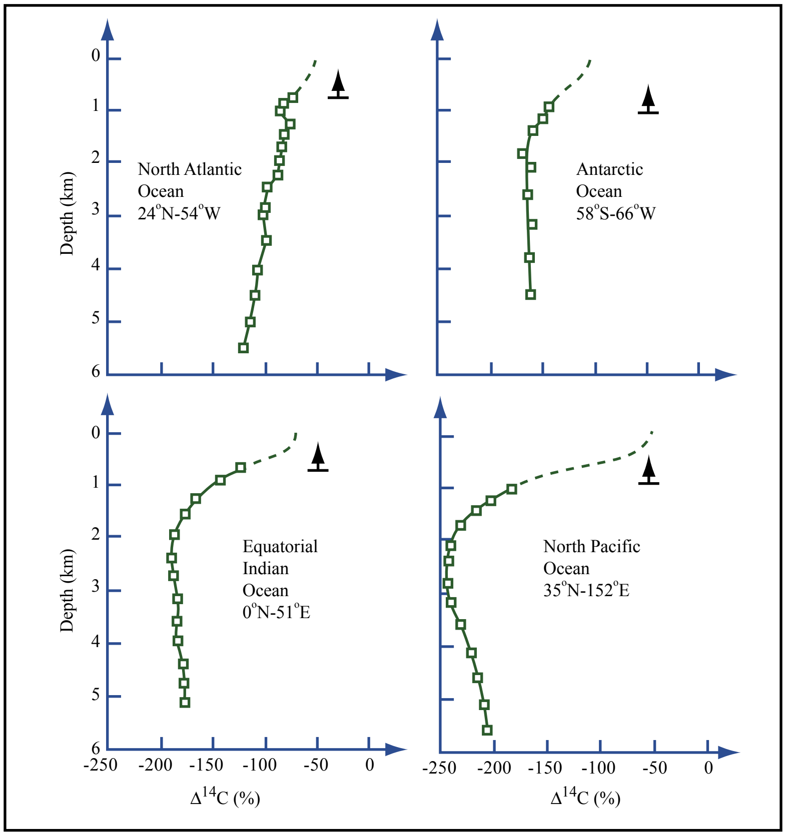

Figure by MIT OCW.

Above is a plot of atmospheric radiocarbon ratio anomaly (in permil) as a function of time. The ratio anomaly is referenced to the pre-anthropogenic atmospheric ratio. This can be measured in tree-rings back many hundreds of years, and shows that the effects, particularly of bomb-radiocarbon are substantial. We must, therefore, infer the pre-anthropogenic surface water radiocarbon ratio from other means. These include using ^{13}C ratios (fossil fuels have very characteristic ratios compared to ocean water), and using "oceanic consistency" arguments.

In a very crude sense, the arguments used are to "extrapolate" the radiocarbon concentrations from older waters where the anthropogenic influence is very small to surface waters.

Another approach is to measure radiocarbon in banded corals. These corals put down annual layers of calcium carbonate which can be counted backward just like tree-rings. It turns out that they obtain their carbonate (with a small and documentable isotope shift) from the inorganic carbon in seawater. Thus they act as recorders of surface water radiocarbon.

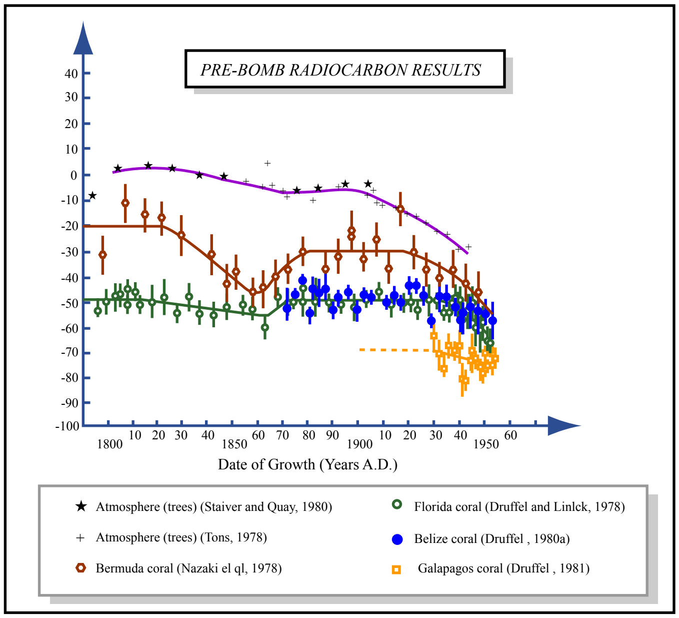

Figure by MIT OCW.

You can clearly see the Suess Effect in the records! In any case, we come up with an average surface water radiocarbon ratio of about 0.95 times the atmospheric ratio.

$$\left(\frac{^{14}C}{^{12}C}\right)_{Surf.} = 0.95\left(\frac{^{14}C}{^{12}C}\right)_{Atm.}$$

So now we have:

$$C_{Surf} = 0.95\times\left(\frac{^{14}C}{^{12}C}\right)_{Atm}\left[CO_2\right]_{Surf}$$

And we can write the incoming flux as

$$F_{in} = k\left(C_{Surf} - C_0\right)$$

$$F_{in} = k\left\{0.95\left(\frac{^{14}C}{^{12}C}\right)_{Atm}\left[CO_2\right]_{Surf} - 1.015\left(\frac{^{14}C}{^{12}C}\right)_{Atm}\left[CO_2\right]_{Surf}\right\}$$

$$F_{in} = -0.065k\left(\frac{^{14}C}{^{12}C}\right)_{Atm}\left[CO_2\right]_{Surf}$$

where the minus sign indicates flux *into* the ocean.

Calculating the Oceanic Loss Rate of Radiocarbon

The other side of the balance equation is the loss rate of the radiocarbon in the oceans due to radioactive decay. This is the radioactive decay equation.

$$F_{Loss} = -\lambda N$$

where N is the number of radiocarbon atoms per unit area of the ocean. (Remember that the gas flux calculated above is per unit area as well). If we have a water column of the ocean (average depth 3800 m) with 1 m^2 area, we have a net volume of 3800 m^3. The total amount of radiocarbon in this volume is

$$N = 3800\times\left(\frac{^{14}C}{^{12}C}\right)_{Ocean}\left[\Sigma CO_2\right]_{Ocean}$$

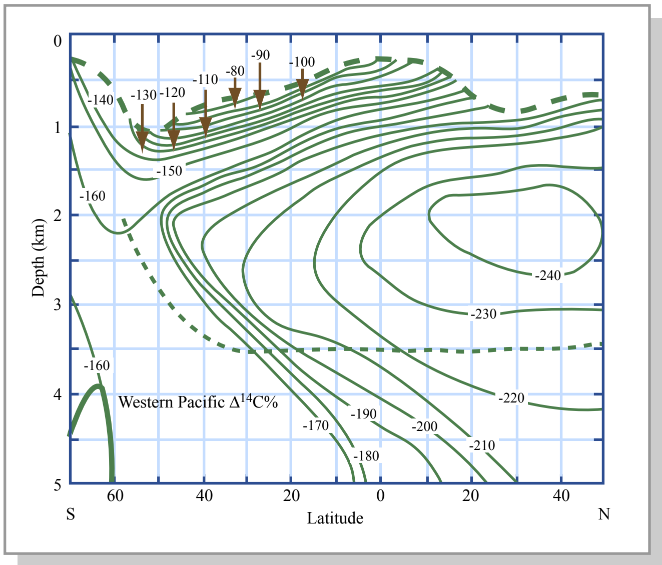

Figure by MIT OCW.

Examination of the profiles shown on page 5 of these notes, plus oceanographic sections such this one gives a mean oceanic isotopic ratio of about 0.83 times the atmospheric ratio,

that is

$$\left(\frac{^{14}C}{^{12}C}\right)_{Ocean} = 0.83\left(\frac{^{14}C}{^{12}C}\right)_{Atm}$$

which gives us

$$N = 3154\left(\frac{^{14}C}{^{12}C}\right)_{Atm}\left[\Sigma CO_2\right]_{Oceans}$$

which leads to

$$F_{Loss} = -0.385\left(\frac{^{14}C}{^{12}C}\right)_{Atm}\left[\Sigma CO_2\right]_{Oceans}$$

where we have used the decay constant for radiocarbon (1/8200 y^{-1}).

Putting The Fluxes together:

Now we say that the two fluxes are balanced

$$F_{in} = F_{Loss}$$

$$-0.00176k\left(\frac{^{14}C}{^{12}C}\right)_{Atm}\left[CO_2\right]_{Surf} = -0.385\left(\frac{^{14}C}{^{12}C}\right)_{Atrm}\left[\Sigma CO_2\right]_{Oceans}$$

which can gives

$$k = 220\frac{\left[\Sigma CO_2\right]_{Oceans}}{\left[CO_2\right]_{Surf}} m/y$$

Using typical surface water CO_2 concentrations of 12 μmol/kg and water column ΣCO_2 concentrations of 2200 μmol/kg, we obtain

$$k = 40{,}000\ m\, y^{-1}$$

or

$$k = 460\ cm\, h^{-1}$$

Now to calculate the mean global gas exchange rate relative to *Sc* = 600, we get a value of about 20 cm/h.

Estimating Gas Exchange Rates from the Uptake of Bomb-Radiocarbon

Looking at coral records of radiocarbon allow us to track the surface ocean response to the bomb radiocarbon transient. This response can be seen in the records, such as those reported by Druffel and Suess.

Which can be compared to atmospheric “forcing” as in the diagram below.

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This allows us to make an additional estimate of the exchange rate. This approach is rather model-dependent, but you can at least see in principle how this might be done: you essentially monitor the annual change of radiocarbon inventory in the surface layers in response to the changing input by gas exchange. This input will vary with time according to the *difference* in radiocarbon ratio between the atmosphere and the surface ocean.

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References:

For some general discussion on gas exchange, you could look in Broecker and Peng, but the treatment of gas exchange models is dated, and downright wrong in places. You could look in Libes’ book for a better, if elementary treatment. Below are some reference papers in the field.

Liss, P.S. and A.J. Watson (1998) Report Group 1 – physical processes in the microlayer and the air-sea exchange of trace gases. In *The Sea Surface and Global Change*. Ed. P.S. Liss and R.A. Duce. Cambridge (ISBN 0521 56273 2) pp1-33.

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Wallace, D.R.W. and C.D. Wirrick (1992) Large air-sea gas fluxes associated with breaking waves. *Nature* **356**,694-696.

Wanninkhof, R. (1992) Relationship between wind speed and gas exchange over the ocean. *J. Geophys. Res.* **97**, 7373-7382.

An excellent assortment of articles can be found in a symposium publication entitled “Air-Water Gas Transfer” B. Jahne and E.C. Monahan (Ed.) AEON Verlag (1995). They tend to be rather specialised, but in composite provide you with recent overview of the cutting-edge issues in gas exchange science