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Modelling atmosphere–ocean CO_2 transfer

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SUMMARY

Knowledge of the uptake of atmospheric carbon dioxide by the North Atlantic is important in understanding the global carbon budget. Obtaining an accurate value for the ocean sinks in the northern hemisphere temperate zone, in particular, would make it possible to be more quantitative about the enigmatic land sink in these latitudes. The global ocean sink is dominated by the North Atlantic, despite its small area in comparison with the North Pacific. Of the possible methods for calculating the uptake, potentially the most informative is that based on the gas exchange equation because information about the seasonal and spatial trends can be obtained. However, there still remain serious questions about which form of the gas exchange coefficient is appropriate to carbon dioxide. Here we summarize current knowledge of the gas exchange coefficient, including recent new evidence which supports lower gas exchange rates and which, therefore, generally supports the Liss–Merlivat prediction for less soluble gases.

In view of the uncertainties still surrounding the direct calculation, we investigate methods for calculating the basin-wide uptake by exploiting what is known about the general circulation of the North Atlantic. The uptake can be estimated by dividing it into pre-industrial steady state and anthropogenic contributions. We make a new estimate of the pre-industrial flux based on the heat budget of the North Atlantic, and also consider two earlier calculations of the same quantity. Taking a best value, adding the better-known anthropogenic flux and making small corrections, we find a value of 0.7 ± 0.15 Gt C a^{-1} for the uptake of the North Atlantic, north of 15° N, in the mid 1980s. Though larger than the gas exchange based estimates of Tans *et al.* (1990), this value is not enough to obviate the need which they deduced for a sizeable 'land-based' northern hemisphere sink for CO_2.

1. INTRODUCTION

In recent years the study of the ocean carbon cycle has been given added impetus by the concern over global change. As a first step, it would be satisfying to be able to account adequately for the fate of anthropogenic carbon dioxide; to be able to resolve the 'missing sink' problem. Ocean CO_2 studies can play an important role here, because we are much closer to being able to confidently specify the uptake of CO_2in a number of ocean regions than we are for the land surfaces. The oceans are simpler in this regard because they are more homogeneous and because the net CO_2 flux into them does not change by such a large factor through the seasonal cycle.

Recent modelling studies have focused attention on the CO_2 budget for the northern temperate latitudes. This is the region where most of the fossil fuel carbon dioxide is released, but inverse models of the atmospheric distribution (Tans *et al.* 1990; Enting & Mansbridge 1991) find that during the 1980s, there must be a sink in the natural world, having a magnitude approximately 3 Gt C a^{-1}, in the same latitudes, to account for the gradient in CO_2 concentrations between northern and southern hemispheres (which is lower than had been expected). Thus, knowing how much CO_2 is being absorbed by the northern oceans becomes critical, if only to obtain by difference (there being no other method available) the net uptake by terrestrial vegetation. The North Atlantic (including the Greenland, Norwegian and Labrador seas) is of special interest in this regard because it is a comparatively well-studied region which is, area for area, the most intense sink of carbon dioxide in the global ocean.

The most direct way to obtain the air–sea flux of CO_2 is by integration over time and space of the gas exchange equation, $F = K_v \alpha \Delta p CO_2$, where K_v is the gas transfer coefficient, α the solubility of CO_2 and $\Delta p CO_2$the air–sea difference in partial pressure of carbon dioxide. For the North Atlantic, enough $\Delta p CO_2$ data exists to make preliminary attempts at this calculation (Tans *et al.* 1990) though there are important uncertainties still, due to the natural variability of the signal (Watson *et al.* 1991*a*) as well as a paucity of data, particularly in the wintertime. In addition there is a serious conflict over what form the gas transfer coefficient should take. The problem is compounded because the gas exchange coefficient will itself be variable on short timescales as a result of its dependency on wind speeds (Etcheto *et al.* 1991), so that a reliably accurate integration of the equation requires high resolution wind and $\Delta p CO_2$ information.

It is doubtful whether data gathered by dedicated research cruises will ever be sufficient to give accurate global coverage of $\Delta p CO_2$. However, valuable data has already been obtained by opportunistic use of merchant vessels (Takahashi *et al.* 1993) and supply ships (Poisson *et al.* 1993). Later on in this decade it will be realistic to look forward to an order of magnitude increase in the amount of data available, when the efforts of several groups around the world to develop automated techniques for remote measurement of $p\mathrm{CO}_2$, are fully realized. These include unattended systems installed in the engine rooms of merchant ships (D. J. Cooper *et al.*, personal communication) and sensors designed for deployment on remote buoys (Friederich *et al.* 1995; Goyet *et al.* 1992)

To be of use in calculating absolute values for air–sea CO_2 exchange, the continuing debate over the form of the gas exchange coefficient for CO_2, K_v, must be resolved. In the meantime, models and indirect approaches provide the most accurate means of specifying the air–sea flux over ocean basins. Below we provide a status report on the situation with regard to the gas exchange coefficient (see §2), and compare model calculations for the uptake by the North Atlantic (see §3).

2. THE GAS EXCHANGE COEFFICIENT FOR CARBON DIOXIDE

(*a*) *Measurements of gas exchange*

Currently, no method exists to routinely and accurately measure gas transfer rates of carbon dioxide across the open sea surface. However, Broecker *et al.* (1985) inferred CO_2 gas exchange rate over the major oceans using the measurements of radiocarbon from the GEOSECS programme of 1972–1973. The ^{14}C was derived from the nuclear testing of 1950s and 1960s, and correction had to be made for the smaller contribution from pre-existing natural ^{14}C production. Far more detailed information is available about the exchange rates of other gases. Field observations which give a coherent variation with wind speed, such as had previously been observed in wind tunnels (Broecker *et al.* 1978; Jahne *et al.* 1984) have recently been obtained at sea both with the dual tracer technique of Watson *et al.* (1991*b*), and the older 'radon deficit' method (Emerson *et al.* 1991). These methods employ the inert, sparingly soluble gases radon, sulphur hexafluoride and helium to derive estimates of gas transfer. In fact, both methods derive evasion rates only.

Fortunately, a body of theory (Dankwerts 1951; Deacon 1977; Ledwell 1984) supported by laboratory and (very limited) field data enables us, under carefully prescribed conditions, to scale gas transfer rates measured for the inert tracers to other gases such as CO_2. For low to moderate wind speeds (no bubbles present) we can perform this scaling according to a power of the Schmidt number, $Sc = \nu/D$, where ν is the kinematic viscosity of water and D is the diffusivity of the gas in water. For very low wind speeds K_v scales as $Sc^{-2/3}$, whereas if the surface is rough but unbroken by bubbles it scales as $Sc^{-1/2}$. For these cases therefore, a single, well documented parameter encapsulates all the variation of gas exchange rates between different gases.

However, if bubbles and whitecaps are present the situation becomes more complicated: theory indicates that the solubility of the gas then becomes important. The contribution of bubbles to the total exchange is greater for poorly soluble gases than for more soluble ones (Merlivat & Memery 1983; Woolf 1993). If the bubbles are sufficiently long-lived that they tend to equilibrate and the transfer due to bubbles becomes independent of Schmidt number. In general, transfer rates become dependent on the spectrum of bubble sizes and the depth to which they penetrate in the ocean, all of which are difficult to predict. It is at present not possible to accurately predict the transfer of CO_2 under these conditions from that of other less soluble gases.

Figure 1 shows a compilation of measurements at sea by the radon deficit and dual tracer techniques, scaled to $Sc = 600$ using a $Sc^{-1/2}$ dependency and plotted as a function of wind speed measured at 10 m. We used

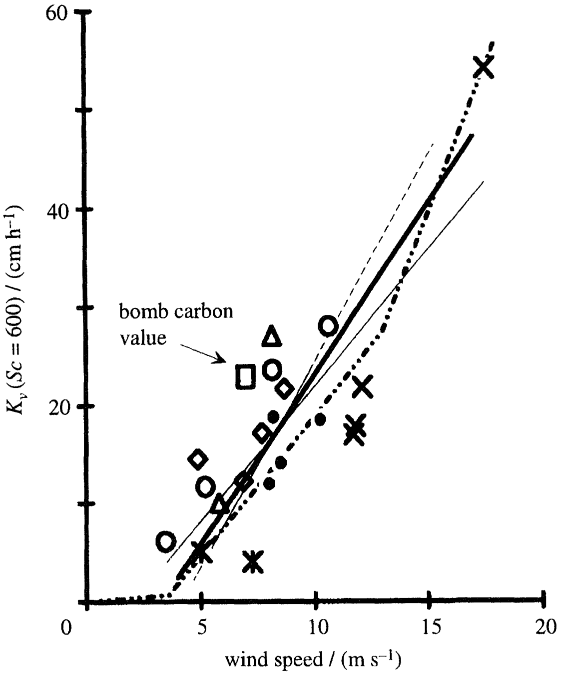

Figure 1. Gas exchange as a function of wind speed at 10 m. Except for the bomb ^{14}C value, the points are all short term averages of radon-deficit or dual-tracer data, converted to a value appropriate to a Schmidt number of 600 using $K \sim Sc^{-1/2}$. Radon deficit data: △, JASIN, North Atlantic (Kromer & Roether 1983); *, FGGE (Kromer & Roether 1983); ●, North Pacific (Emerson *et al.* 1991); ◇, recalculated Tropical Atlantic TTO/TAS data from Smethie *et al.* (1985). Averages of four periods when the wind remained steady over periods of at least three days were used. Winds were corrected to 10 m assuming a neutrally stable atmosphere.

Dual tracer data: ×, North sea, Watson *et al.* (1991*b*); ○, Georges Bank, Wanninkhof *et al.* (1993).

The lines shown are the Liss–Merlivat relation (dot-dash line) and regressions of the data. The thick line is the preferred linear regression, $K_v = 3.44$ (wind speed) $- 11.44$. This was obtained assuming that the fractional error was equally distributed between wind speed measurement and gas exchange. The two faint lines are regressions assuming all the error is in the gas exchange determination (shallower line; slope 2.74) or all in the wind speed (steeper line; slope 4.13).

only measurements taken over periods of a few days or less, during which wind speed was relatively constant. The scatter in this diagram is considerably larger than the errors on the measurements, which gives a clear indication that wind-speed is not the only factor important in determining gas exchange rates. Fetch, atmospheric stability and degree of whitecapping have all been suggested as additional factors.

It is now well documented that the mean value for bomb ^{14}C lies above most of these measurements when plotted at the global mean wind (Wanninkhof 1992; Watson 1993); on the figure, the ^{14}C value obtained by Broecker *et al.* (1985) scales to 21.8 cm h^{-1} (Wanninkhof 1992). However, the piece-wise linear formulation of Liss & Merlivat (1986) originally based on inert tracer studies over a lake, gives a mean value of only 11.7 cm h^{-1} at a mean wind speed for the world ocean of 7.5 m s^{-1}. Wanninkhof (1992) highlighted one possible reason for this discrepancy; the ^{14}C determination is a long-term average over a wide variation in wind speeds. If K_v increases non-linearly with wind speed, the average exchange coefficient would lie above the value of the curve at the average wind. Assuming a quadratic relation between gas exchange and wind speed, Wanninkhof estimated that this effect accounted for a factor of 1.26 between the two values. (One objection to this argument however, is that the available field data do not show such a steep non-linearity.)

Is the discrepancy between the ^{14}C data and inert tracer gas exchange values explainable by known factors? A definite answer cannot be given, because of the indication that variables other than wind speed can influence gas exchange. On the basis of our own dual tracer data from the North Sea however, the answer would be no: reductions of order 25 % in the ^{14}C data would be necessary to bring the two close to agreement. Similarly, statistical analysis of the data shown in figure 1 suggests that the discrepancy is significant: if the standard deviation around the best fit line is taken as an estimator of the uncertainty of a single point, a chi-squared test gives $p < 1\,\%$ that the data are related by a linear regression constrained to pass through the ^{14}C point.

Recently, Wanninkhof *et al.* (1993) published some tracer-based measurements which superficially suggest exchange rates comparable to or greater than that of $^{14}CO_2$. Below, we present evidence that the method favoured by Wanninkhof *et al.* to reduce their data is of doubtful validity in the ocean, and in figure 1 we have plotted their data as reduced by the more straightforward method which we used previously (Watson *et al.* 1991*b*). If their analysis *is* correct however, one consequence is that inert tracer experiments greatly overestimate CO_2 exchange in the ocean.

(*b*) *Interpretation of the dual tracer data: new evidence using bacterial spores as a tracer*

The dual tracer method employs two volatile tracers having different diffusivities (Watson *et al.* 1991*b*; Wanninkhof *et al.* 1993). The quantity measured is the ratio of the two tracers as a function of time, from which only the difference in exchange rate between the two tracers can be derived. To derive absolute values, it is necessary to assume a Schmidt number dependency for K_v so as to obtain a second equation relating the two tracers. Watson *et al.* (1991*b*) assumed a $Sc^{-1/2}$ dependency, whereas Wanninkhof *et al.* (1993) preferred a variable dependency derived from measurements by Asher *et al.* (1992) in a small laboratory 'foam tank'. These different Schmidt number dependencies give results higher by > 20 % at wind speeds (measured at 10 m height) greater than 10 ms^{-1}. Figure 2 plots the data of Wanninkhof *et al.* (1993) using both calculation schemes; but it is difficult to know which gives the more correct results.

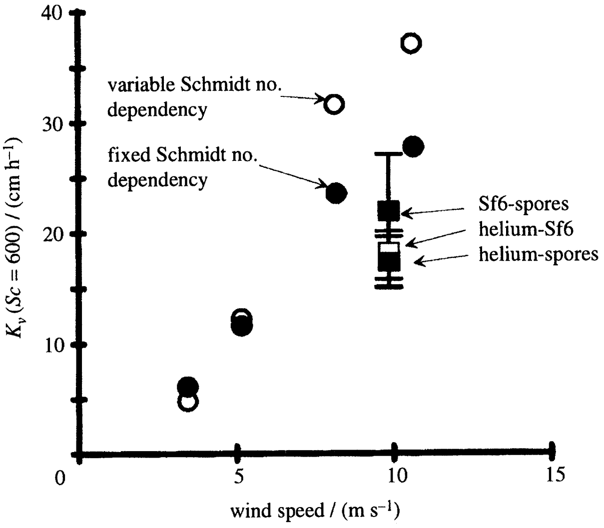

Figure 2. The dual tracer data of Wanninkhof *et al.* (1993) reduced by the variable-power Schmidt number method (their preferred method) and using $Sc^{-1/2}$. At values of K of 20–25 cm h^{-1}, the difference is of order 20 %. Also shown are values for gas exchange obtained using a conservative and non-volatile tracer, bacterial spores, compared to simultaneous dual-tracer experiment. The gas exchange rates obtained by ratioing against the spores agree with values obtained assuming a $Sc^{-1/2}$ reduction of the data. Circles refer to Wanninkhof data; squares refer to Nightingale data.

Recently, we circumvented this problem using a new technique in which bacterial spores are used as a third tracer (Nightingale *et al.* 1993). Because the spores are conservative, their gas exchange rate is zero, and gas transfer rates derived by ratioing against them should be absolute; the results of a 'spores plus tracer' release experiment in the North Sea are superimposed on figure 2. The data lie below those of Wanninkhof *et al.* even when the $Sc^{-1/2}$ scheme is applied to their numbers (this is generally true for our North Sea data compared to their measurements on Georges Bank). More importantly, the values obtained with the spores give within measurement error, essentially the same values as the fixed exponent reduction scheme. Currently, therefore, we believe that the evidence favours the lower gas exchange rates we have obtained, at least for winds up to 10 m s^{-1}.

(*c*) *Interpretation of dual-tracer data: theoretical considerations*

Although the particular version of variable Schmidt number exponent used by Wanninkhof *et al.* (1993) is not supported by our field data, we do expect that at high wind speeds where bubbles are important, poorly soluble gases will depart from a $K_v \alpha Sc^{-1/2}$ rule, and correct interpretation of dual tracer data requires that this be taken into account. Under these same conditions however, the more soluble CO_2 will be much less affected, as it is less efficiently transported by bubbles. It therefore follows that under these conditions, the gas exchange rates for these tracers will provide only an upper limit to the rate for CO_2. In fact, calculations recently reported by Merlivat *et al.* (1993) suggest that under these conditions, even the artificially low estimates of K_v obtained assuming a constant Schmidt number exponent provide upper bounds to the true value for CO_2.

3. MODEL CALCULATIONS OF THE UPTAKE OF CARBON DIOXIDE FROM THE ATMOSPHERE BY THE NORTH ATLANTIC.

(*a*) *Correspondence between CO_2 uptake and heat release*

The North Atlantic is probably the ocean region for which the most comprehensive set of data on surface pCO_2 are available. At least for the summer season, a relatively good picture of the distribution of surface pCO_2 can therefore be obtained. Unfortunately, continuing uncertainty over the value of the gas exchange rate which is appropriate for CO_2, plus important gaps in the data for the winter months in particular, make it difficult to obtain an accurate answer for the uptake of atmospheric CO_2 by integrating the gas exchange equation. However, there are other ways to calculate the budget based on the fact that the North Atlantic together with its marginal seas, forms a basin which is nearly enclosed to the north, with a ventilation from the south which has been the object of much study because of its importance in global climate.

It is helpful to break the CO_2 uptake into two components, one anthropogenic and the other natural. The anthropogenic flux is due to the steady rise in atmospheric CO_2, which drives a flux into the ocean. However, it is now appreciated (Broecker & Peng 1992) that the North Atlantic was a sink for CO_2 even before the industrial revolution. This pre-industrial sink arises because the thermohaline circulation draws surface water into the North Atlantic from the south. It has become warm and salty during its long residence in the subtropical and equatorial regions, and also has come almost to equilibrium with atmospheric CO_2. North of about 15–20° N, this water begins to cool as it is moved north and east by the Gulf Stream and North Atlantic drift. During this cooling it tends to take up CO_2 from the atmosphere. Much of this water recirculates at or near the surface, in the subtropical gyre. If it remains at the surface it may be re-heated and desorb some CO_2 as it travels southward in the eastern limb. Alternatively, it may be subducted into the thermocline, in which case, on isolation from the atmosphere, it has taken up net CO_2 and given out net heat. Finally, in the northern North Atlantic, Greenland and Labrador seas, water becomes sufficiently dense to sink, and begin a subsurface journey back to the south, as the lower limb of the conveyor circulation. The net effect both of the conveyor circulation and the thermocline ventilation is to take up CO_2 and give out heat. By contrast, in the Pacific, water moving northward in the Kuroshio current may cool and take up CO_2 but because little subsurface water is formed, most of it returns south still near the surface so that there is little net uptake of CO_2 or release of heat.

A correspondence therefore exists between uptake and release of CO_2 due to heating or cooling, and the amount of heat released to the atmosphere. The correspondence need not be exact, because in general the two processes do not have exactly matched timescales; in general, the CO_2 uptake must lag the cooling, so that it is possible for heat to be released but the corresponding CO_2 uptake not to reach equilibrium. However, in the next section we make the approximation that the 'thermodynamic' component of the uptake can be exactly calculated from the heat budget.

(*b*) *A calculation of the steady-state uptake, constrained by the heat budget*

We write for the flux of CO_2 (defined as positive into the water)

$$F = V\Delta\Sigma CO_2$$

where volume of water entering the North Atlantic at the surface and leaving subsurface. Formally, this includes both the 'ocean conveyor' transport and water subducted into the thermocline. We define $\Delta\Sigma CO_2$ (as in the work of Broecker & Peng 1992) as the amount of CO_2 picked up from the atmosphere. Our approach is to assume that the surface water remains at equilibrium with a constant atmospheric burden, so that we obtain the non-anthropogenic portion of the CO_2 uptake of the region. We consider the following processes which tend to change the amount of CO_2 in the sample: (i) cooling due to loss of heat to the atmosphere; (ii) reduction in efficiency of the biological pump the further north one goes, evidenced by the appearance of non-zero nutrient concentrations at the surface; (iii) addition of alkalinity due to the same processes as in (ii); and (iv) addition of fresh water. We write:

$$\begin{aligned} F = \{&\Delta T[(\partial\Sigma CO_2)/\partial T]_{pco_2} \\ &+\Delta PO_4[(\partial\Sigma CO_2)/\partial PO_4]_{pco_2} \\ &+\Delta Alk[(\partial\Sigma CO_2)/\partial Alk]_{pco_2} \\ &+\Delta S[(\partial\Sigma CO_2/\partial S]_{pco_2}\}, \qquad (1) \end{aligned}$$

where the four terms in brackets correspond to the four processes listed above. All the partial derivatives are to be evaluated at a constant pCO_2; i.e., the changes are while remaining in equilibrium with the atmosphere.

It is straightforward to calculate the values of the derivatives for all the above processes. Though in general the results are dependent on what temperature, salinity, alkalinity and TCO_2 we start from, fortunately they do not vary too much over the range of conditions encountered in the North Atlantic.

The first term within the brackets is the uptake of carbon due to heating or cooling of the water by ΔT degrees. This term, which is the largest in the expression, is directly related to the net heat transport into the region. The heat transport across 24° N is estimated by Isemer, Willebrand & Hasse (1989) to be 1×10^{15}W. For consistency this heat flux must equal to $Q = V.\Delta T\ \mathrm{C_p}$, where c_p is the heat capacity of water. In reality of course, no single temperature difference will do, and we should be integrating these quantities across the range of different waters subducted in the North Atlantic, but by substituting in terms of Q we avoid this difficulty for the first term. $[(\partial \Sigma CO_2)/\partial T]_{p\mathrm{CO_2}}$ can be written in terms of the Revelle buffer factor β:

$$\beta = [\partial \ln (p\mathrm{CO_2})]/[\partial \ln (\Sigma \mathrm{CO_2})],$$

and the factor

$$\tau = [\partial \ln (p\mathrm{CO_2})]/\partial T \approx 0.0423\ {}^{\circ}\mathrm{C}^{-1}$$

(Takahashi *et al.* 1993):

$$[(\partial \Sigma \mathrm{CO_2})/\partial T]_{p\mathrm{CO_2}} = -\Sigma \mathrm{CO_2}\{[\partial \ln (\Sigma \mathrm{CO_2})]/\partial T\} = [(\Sigma \mathrm{CO_2}\cdot\tau)/\beta].$$

Thus the first term of the expression is equal to $(-Q\Sigma \mathrm{CO_2}\cdot\tau)/C_p\beta$, where the negative sign expresses the fact that the heat and carbon dioxide fluxes are in opposite directions, with Q negative for a cooling. The chief advantage of expressing the term in this way is that we do not need to specify in detail how much water is being transported and by how much it is being cooled. For $Q = -10^{15}$W, $\Sigma \mathrm{CO_2} = 2000$ mmol kg^{-1}, $\beta = 10$ and τ as given above, this term equals 0.75 Gt C a^{-1}.

The second term in the expression is easily evaluated. $[(\partial \Sigma \mathrm{CO_2})/\partial \mathrm{PO_4}]_{p\mathrm{CO_2}}$ is equal to the negative of the Redfield ratio for phosphate, $R = 106$. (It is negative because, for a positive input of phosphate and carbon from below, exactly the same quantity of carbon must leave the water to restore equilibrium with the atmosphere.) Using the same logic, and solving the carbonate equilibria (we used the constants due to Goyet & Poisson 1989), we investigated how the quantities $[(\partial \Sigma \mathrm{CO_2}/\partial S]_{p\mathrm{CO_2}}\cdot[(\partial \Sigma \mathrm{CO_2})/\partial \mathrm{Alk}]_{p\mathrm{CO_2}}$ change for conditions appropriate to the surface North Atlantic, from temperatures of 25 °C to 0 °C. The first varies by about 20 %, with a mean around −9.3 μM per salinity unit, while the second varied only 10 %, with a mean of about 0.84 (dimensionless). Equation (1) can therefore be approximated by

$$F = \{-[(Q\Sigma \mathrm{CO_2}\cdot)/C_p\beta] + (Q/C_p\Delta T)\}\ (-106\Delta \mathrm{PO_4} + 0.84\Delta \mathrm{Alk} - 9.3\Delta S). \quad (2)$$

Where we have substituted $Q/c_p\Delta T$ for the volume transport V.

To make progress evaluating the other terms, we must specify more about the circulation. For a sample calculation, we used data from TTO stations 36 and 123 to represent water before and after the journey north. The TTO expedition was during the summer, and so extreme surface values at the northern station (123) would not represent water ready to be subducted, being considerably too warm, and too depleted in nutrients and CO_2 as a result of the seasonal net productivity. We used averages of the top 300 m from the northern station therefore. Clearly, this is highly approximate, because we are trying to use a single water type to represent both water being subducted into the thermocline and water about to join the lower limb of the 'conveyor' circulation, so this can only be regarded as a preliminary calculation. Table 1 gives the relevant data.

Using values from the last row of table 1 in equation (2), we find corrections to the uptake CO_2 as follows; −89 μM for the net increase CO_2 due to a lessening in the efficiency of the 'biological pump': +16.7 μM due to a freshening of the water as it travels north, which allows it to take up more CO_2, and +12.6 μM due to a net increase in alkalinity. The dominant effect is the first one, but the other two are large enough to be significant. Putting in values for Q of 10^{15}W and ΔT of −18.7, the net flux comes to 0.48 Gt C a^{-1}.

One objection to the argument of the calculation above is that the water may not stay at equilibrium with the atmosphere, but drop below it. Certainly. summertime data for the North Atlantic show a substantial under-saturation. However, it is the wintertime values which are more relevant, and these, while much less numerous, indicate that much of the northern North Atlantic is reasonably close to saturation (Takahashi *et al.* 1993). Because of the sensitivity of $p\mathrm{CO_2}$ to small changes in $\Sigma \mathrm{CO_2}$, departures from equilibrium of order of 10–20 μatm do not in fact greatly influence the result.

Table 1. *Parameters for representative 'northern' and 'southern' surface waters in the North Atlantic.*

TTO station	position	temperature °C	salinity	PO_4 μM	alkalinity μM
123 (north)	53° N 33° W	6.8	34.8	0.85	2297
36 (south)	21° N 54° W	25.5	36.6	0.01	2282[a]
difference		−18.7	−1.8	0.84	15

[a] Normalized to station 123 salinity.

Table 2. *Unptake of atmospheric CO_2 by the North Atlantic, north of 15° N.*

			flux
	data		$\mathrm{Gt\ C\ a^{-1}}$
preindustrial:	Brewer *et al.* (1989) modified as in UNE*Sc*O, (1991)	0.41	
	Broecker & Peng (1992)	0.6	
	heat budget estimate (this work)	0.48	
	best estimate:		0.5 ± 0.1
	correction for riverine flux		-0.05 ± 0.02
anthropogenic	Sarmiento *et al.* (1992)		0.25 ± 0.1
	total		0.7 ± 0.15

(*c*) *Earlier estimates*

Two calculations of the uptake, based on budgeting CO_2 flowing north and south in the N Atlantic, already exist in the literature. To date, such calculations have assumed that the system is in steady state which means that correctly done, they calculate the pre-industrial situation rather than that at the present time, and are thus comparable with our calculation. The first of these was attempted by Brewer *et al.* (1989), using CO_2 data and estimates of the currents on a section at 25° N across the basin. They obtained a value of 0.26 Gt C a^{-1} for the net southward transport, but they did not correct for the fossil-fuel component carried northwards by the surface waters, so this estimate was a lower limit only. The value, corrected for fossil fuel transport, was reported by Brewer (UNE*Sc*O 1991) to be 0.41 Gt C a^{-1}.

Like us, Broecker & Peng (1992) calculated $\Delta\Sigma CO_2$, the change in inorganic carbon content of a sample due to exchange with the atmosphere. They derived this as the difference between measured and expected ΣCO_2, where the expected value was calculated (to within an arbitrary constant) by accounting for changes due to salinity variation and *in situ* uptake/regeneration of organic and inorganic carbon using alkalinity, phosphate and nitrate as tracers of these processes. They made a first-order correction for the fossil fuel component of measured ΣCO_2. Assuming a volume transport for the 'conveyor belt' circulation of 20 Sv, they estimated the pre-industrial uptake to be 0.6 Gt C a^{-1}. The 'overturn' rate implied by our calculation ($V = Q/c_p \Delta T$) is 12.8 Sv, considerably lower than the value they use. The transport value that Broecker & Peng used is based on estimates of the deep water 'conveyor belt' return flow but the northward flowing water which makes up the upper limb of the conveyor need not be entirely at the surface, and indeed cannot be for consistency with the heat budget so their estimate may be high on that account. However, they do not explicitly account for water subduced into the North Atlantic thermocline and subsequently upwelled at, or south of, the equator. It may be expected then that their figure is low. Our own estimate is also only a first effort, being based on an approximate use of two stations to represent all subducting water.

(*d*) *The anthropogenic uptake*

The transient uptake of the global ocean due to rising atmospheric CO_2 has been the object of intense study, and the accepted value (IPCC 1990) is 2.0 ± 0.8 Gt C a^{-1}. To zero order we may estimate the uptake due to any region to be this number times the area fraction of the world ocean represented by the region. The North Atlantic north of 15° N is 10% of the global ocean, thus we obtain 0.2 Gt C a^{-1}. In fact, as shown by the three-dimensional simulations of the uptake (Maier-Reimer & Hasselman 1987; Sarmiento *et al.* 1992), the anthropogenic signal does not enter the ocean uniformly everywhere but preferentially in regions of upwelling and convective overturn. The North Atlantic takes up rather more than its share because of the deep convection which occurs there in regions north of about 35° N. Using the figures given by Sarmiento *et al.*, we calculate an uptake of 0.25 Gt C a^{-1}. An error of ± 0.1 would give this the same confidence as the global figure assigned by IPCC.

There is a further small addition to the budget which could be made: it is now appreciated (Sarmiento & Sundquist 1992) that in the steady-state the oceans must have been a small net source of CO_2 to the atmosphere, of order 0.5 Gt C a^{-1}, to balance the export of carbon from the land biosphere to the ocean in rivers. Lacking further information, if we assign this flux evenly over the whole ocean this would suggest that the pre-industrial North Atlantic uptake should be reduced by approximately 0.05 Gt C a^{-1}.

Table 2 summarizes our calculation for the current rate of uptake of atmospheric CO_2 by the North Atlantic, north of 15° N. For the steady-state uptake, we simply took a mean and 1-σ standard deviation of the three estimates discussed above. Our best estimate is 0.7 Gt C a^{-1}, with an uncertainty approximately 0.15 Gt C a^{-1}.

3. CONCLUSIONS

There still remains a problem in reconciling the gas exchange coefficient derived from the ^{14}C inventory in the oceans to the otherwise coherent body of gas exchange measurements using inert tracer gases; the ^{14}C value seems too high by about 25% after averaging effects are taken into account. While we search for a resolution of this discrepancy, non-gas exchange methods of calculating the sink in the North Atlantic are easier to apply, and give a reasonably precise value for the uptake by this ocean of 0.7 ± 0.15 Gt C a^{-1}. Tans *et al.* (1990) obtained 0.53 Gt C a^{-1} for the same area by the gas exchange method, using a ^{14}C-calibrated gas exchange relation. Bearing in mind various corrections to their figure which have been explored in the literature, such as the the thermal skin effect (particularly large in the North Atlantic, Robertson & Watson 1992), and the 'riverine' flux, these two estimates seem reasonably consistent. The remaining difference might be explained by as-yet-inadequate data coverage for pCO_2. Tans *et al.* (1990) found it necessary to postulate a northern hemisphere terrestrial sink of order 2 Gt C a^{-1} to obtain the correct hemispheric gradient for atmospheric CO_2 in their transport model. Subsequently Sarmiento & Sundquist (1992) pointed out that some of this must be a pre-existing, steady state sink required to balance the present export of carbon down rivers, (approximately 0.6 Gt C a^{-1} globally). Although it seems likely that the Tans *et al.* (1990) figure for the North Atlantic is a little low, by 0.1–0.2 Gt C a^{-1}, and their estimate for the terrestrial sink thereby high by the same amount, these are rather small corrections. Their basic conclusion, that a sizeable terrestrial sink is implied in northern temperate latitudes, remains valid.

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Discussion

H. Leach. (*University of Liverpool, U.K.*). I suspect that the riverine input to the N. Atlantic is greater than 10% of the world total, as the majority of the world's river systems flow into the Atlantic (albeit partly in equatorial reqions).

A. J. Watson. It is true that the *input* is greater than 10%, but it is the *output* which matters: how much of that carbon (much of it organic) is balanced by an outgoing sea-to-air flux in the N. Atlantic. That depends on how labile the riverine input is. If it breaks down quickly the efflux would occur close to where the riverine inputs are, but if it is long-lived, then it would be more evenly distributed over the world oceans.

M. Follows (*MIT, Cambridge, U.S.A.*), Regarding the 'solubility pump', estimated at ~ 0.75 Gt C a^{-1}. This estimate relies on the assumption that the subducted surface waters have had sufficient time, following any heat exchange, to equilibriate for ambient conditions. This may not be so everywhere in the basin. Rapid cooling in the Gulf Stream supplies waters to the subtropical gyre which are subducted shortly afterwards (within a few years). This may not be sufficient time for equilibriation, and reduces the efficiency of the sulubility pump. Does Dr Watson think this may be a significant effect?

A. J. Watson. It is true that the assumption that the CO_2 comes back to equilibrium with respect to the atmosphere represents an upper limit: the uptake could be less if subduction occurs within a short period of cooling. Overall, the net 'conveyor belt' transport of a few tens of Sverdrups suggests that residence times in the surface N. Atlantic are measured in decades, which is long enough for the CO_2 to come most of the way to equilibrium, but the fact that the pCO_2 data, even for winter, shows some undersaturation, indicates that it does not quite make it to equilibrium.