

THE CHANGE IN OCEANIC O<sub>2</sub> INVENTORY ASSOCIATED  
WITH RECENT GLOBAL WARMING

Ralph Keeling  
Hernan Garcia<sup>1</sup>

Scripps Institution of Oceanography  
University of California, San Diego  
La Jolla, CA 92093-0244  
rkeeling@ucsd.edu

<sup>1</sup>Now at  
National Oceanographic and Atmospheric Administration, OCL-NODC  
1315 East-West Highway  
Silver Spring, MD 20910

Submitted to the Proceedings of the National Academy of Sciences: 18 Sept. 2001

Revised: 19 Dec. 2001  
Revised: 17 Jan. 2002  
Accepted: April, 2002

## ABSTRACT

Oceans general circulation models predict that global warming may cause a decrease in the oceanic O<sub>2</sub> inventory and an associated O<sub>2</sub> outgassing. An independent argument is presented here in support of this prediction based on observational evidence of the ocean's biogeochemical response to natural warming. On time scales from seasonal to centennial, natural O<sub>2</sub> flux/heat flux ratios are shown to occur in a range of 2 to 10 nmol O<sub>2</sub> per Joule of warming, with larger ratios typically occurring at higher latitudes and over longer time scales. The ratios are several times larger than would be expected solely from the effect of heating on the O<sub>2</sub> solubility, indicating that most of the O<sub>2</sub> exchange is biologically mediated through links between heating and stratification. The change in oceanic O<sub>2</sub> inventory through the 1990's is estimated to be  $0.3 \times 10^{14}$  to  $0.4 \times 10^{14}$  mol O<sub>2</sub> per year based on scaling the observed anomalous long-term ocean warming by natural O<sub>2</sub> flux/heating ratios and allowing for uncertainty due to decadal variability. Implications are discussed for carbon budgets based on observed changes in atmospheric O<sub>2</sub>/N<sub>2</sub> ratio and based on observed changes in ocean dissolved inorganic carbon.

## INTRODUCTION

Repeated hydrographic surveys indicate that the upper 3 km of the oceans have warmed (1) and intermediate waters of high-latitude origin have freshened (2) over the past few decades. Model studies indicate that upper-ocean warming, high-latitude freshening, and an associated increase in the density stratification of the upper ocean are expected consequences of the changes in atmospheric radiative forcing caused by fossil-fuel burning and other human activities (3,4,5).

Repeated hydrographic surveys also indicate that small detectible changes have occurred in oceanic dissolved O<sub>2</sub> concentrations. As summarized in Table 1, detectible decreases in O<sub>2</sub>

have been found in intermediate waters in the North Pacific, North Atlantic, South Pacific, and South Indian oceans, while small increases have possibly been found in deeper waters in the North Pacific and South Indian Oceans. What caused these O<sub>2</sub> changes is unclear, and different mechanisms, including changes in ocean circulation rates (6,7,8,9), changes in preformed values (10), and changing Redfield ratios (11), and changes in biological production (8) have been offered as possible explanations in different regions. While the changes may partly reflect natural decadal variability, the clearest O<sub>2</sub> changes, found at intermediate depths, are in the direction of decreasing O<sub>2</sub> concentrations. A global reduction in dissolved O<sub>2</sub> is predicted by ocean general circulation models (OGCMs) driven by increasing greenhouse gases (12,13,14,15). In the model simulations, most of the O<sub>2</sub> decrease is attributed to enhanced stratification.

Stratification has two competing effects on subsurface oxygen concentrations. First, it reduces the transport of nutrients from deeper waters into the upper ocean, thus decreasing photosynthetic production and the associated flux of organic detritus into the ocean interior. This flux is often referred to as the “biological pump” (16), and reducing the rate of this pump increases subsurface O<sub>2</sub> concentrations by reducing subsurface O<sub>2</sub> utilization rates. Second, stratification limits the downward transport from O<sub>2</sub> from well-oxygenated surface waters into the ocean interior, which serves to reduce subsurface O<sub>2</sub> concentrations.

In the modeling studies cited above, the effect of stratification on O<sub>2</sub> transport exceeds the effect on subsurface O<sub>2</sub> utilization, leading to a net O<sub>2</sub> decrease. This result is expected considering that stratification allows for more complete biological utilization of nutrients in surface waters, thus lowering the “preformed” (i.e. initial) nitrate and phosphate content of waters sinking into the oceans interior. To conserve the total ocean nutrient inventory, an

increase must occur in the inventory of non-preformed nutrients, i.e. those which accumulate in subsurface waters from oxidative decomposition of organic detritus. Since  $O_2$  is consumed by organic decomposition in proportion to the amount of nitrate or phosphate released (17), subsurface  $O_2$  inventories can be expected to decrease in response to increased stratification. In general, the competing effects of the biological pump and vertical mixing on  $O_2$  concentrations can be assessed based on their net impact on the vertical nutrient distributions. This net impact we refer to as the “efficiency” (as opposed to “rate”) of the biological pump.

Stratification can also be expected to induce a net release of  $O_2$  from the ocean to the atmosphere. The oceanic  $O_2$  inventory ( $I$ , moles) and sea-to-air  $O_2$  flux ( $Z$ , moles/yr) are linked according to

$$dI/dt = -Z + \lambda dC_{org}/dt \quad (1)$$

where  $C_{org}$  is the oceanic inventory of organic carbon, including both particulate and dissolved forms, and  $\lambda$  is the  $O_2:C$  oxidative ratio for destruction or production of marine organic matter, and where small terms related to river and sediment transports have been neglected. The term  $\lambda dC_{org}/dt$  effectively accounts for the column-integrated net production of  $O_2$  by marine photosynthesis and respiration. This term is presumably small, although not necessarily negligible (18), because the main effect of marine photosynthesis and respiration on time scales of years to centuries is to redistribute inorganic materials within the ocean, rather than to cause accumulation or destruction of the organic carbon (see also ref. 14). If stratification reduces subsurface  $O_2$  inventories via changes in the efficiency of the biological pump, a roughly equal outgassing of  $O_2$  from the ocean to the atmosphere is therefore expected.

Estimates based on OGCMs for oceanic  $O_2$  outgassing due to global warming lie in the

range of  $0.2$  to  $0.7 \times 10^{14}$  mol yr<sup>-1</sup> for the past few decades, with predictions of  $1.0$  to  $1.6 \times 10^{14}$  mol yr<sup>-1</sup> for late 21<sup>st</sup> century (12,13,14,15). According to these estimates, roughly a quarter of the predicted outgassing is attributable to the direct effect of warming on the O<sub>2</sub> solubility, while the remainder is due to increased stratification. The predicted changes for the past few decades amount to an average decrease in oceanic O<sub>2</sub> concentrations over a 20-year time frame of between  $1$  and  $5 \mu\text{mol kg}^{-1}$  if the changes are confined to the top 1000m of the oceans. Larger changes are predicted for the Southern Oceans due to reductions in deep convection (12,13). It is hard to test these predictions with existing hydrographic data given the sparse coverage and the lack of comprehensive syntheses.

There are several reasons why changes in the oceanic O<sub>2</sub> inventory could be important. Dissolved O<sub>2</sub> concentration is a useful diagnostic of ocean circulation and biological activity which can provide constraints on models of physical and biogeochemical response to climate change (13). Small changes in O<sub>2</sub> content could influence extent of hypoxic regions in coastal seas, in sediments, or in the open ocean, with consequences for the cycling of nitrogen and other redox-sensitive elements and for the distribution of many marine organisms (19). Changes in O<sub>2</sub> are diagnostic of changes in the efficiency of the marine biological pump, which may influence the rate at which the oceans absorb anthropogenic CO<sub>2</sub> (12). Finally, at least two approaches for estimating sinks of anthropogenic carbon dioxide require corrections for changes in oceanic O<sub>2</sub> inventory. The purpose of this paper is to provide an independent estimate of the plausible O<sub>2</sub> inventory changes associated with recent global warming and to discuss the implications for global carbon budgeting.

## NATURAL WARMING AND O<sub>2</sub> OUTGASSING

It is easily established that a close association exists between ocean warming and O<sub>2</sub> outgassing over a range of space and time scales in the open ocean. At middle and high latitudes during the spring and summer, when the upper ocean is heated by the atmosphere, the oceans are a source of O<sub>2</sub> to the atmosphere, while in the fall and winter, when the upper ocean is cooled, the oceans are a sink of O<sub>2</sub> from the atmosphere. These seasonal air-sea O<sub>2</sub> exchanges are driven partly by biological exchanges, linked to seasonal stratification, nutrient supply, and irradiance, and partly by effects of heating and cooling on O<sub>2</sub> solubility (20).

We have estimated the ratio of seasonal O<sub>2</sub> outgassing to seasonal heating from global archived measurements of dissolved O<sub>2</sub> in surface waters, climatological winds, and climatological air-sea heat fluxes (21). The O<sub>2</sub> flux/heating ratio varies between 1.5 nmol O<sub>2</sub> per Joule at lower latitudes to 4 or 5 nmol O<sub>2</sub> per Joule in the 40° to 60° latitude bands, as shown in Figure 1. Consistent with Najjar and Keeling (20), we find ratios that are larger than expected from the effect of warming on the O<sub>2</sub> solubility by factors between 1.5 to 2.5. We further have shown, based on comparisons with atmospheric O<sub>2</sub>/N<sub>2</sub> data (21), that the component of the O<sub>2</sub> flux that correlates with heating dominates large-scale seasonal O<sub>2</sub> exchange. These results indicate that seasonal heating, through its effect on stratification, biological productivity, and O<sub>2</sub> solubility, is a major driver of the exchange, and not just coincidentally correlated with the exchange.

Linkages between heat fluxes and oxygen fluxes are also evident on longer time scales, as revealed from a plot of the tracer  $O_2^* = O_2 + 175PO_4$  versus potential temperature ( $\theta$ ), as shown in Figure 2. The tracer  $O_2^*$ , which is identical to Broecker's tracer  $PO_4^*$  (25) but

expressed in  $O_2$  rather than  $PO_4$  units, is a measure of the  $O_2$  gained or lost by a water parcel through air-sea gas exchange (26).  $O_2^*$  is largely conserved below the sea surface, where photosynthesis and respiration produce compensating effects on  $O_2$  and  $PO_4$ .  $O_2^*$  keeps track of air-sea  $O_2$  exchanges driven by both solubility changes and by the processes controlling the efficiency of the biological pump. Assuming rapid air-sea equilibration, the solubility component is simply given by the  $O_2$  solubility ( $O_2^0$ ), so that the remaining biological pump component is proportional to the (apparent) preformed phosphate content ( $PO_4 - (O_2^0 - O_2)/175$ ) content of the water (26).

A prominent feature in Figure 2 is the strong association between  $O_2^*$  and  $\Delta T$  in waters of the main thermocline waters between 6 and 18°C. Waters around 18°C consistently have lower  $O_2^*$  than waters around 6°C, indicating that conversion of cooler water to warmer water, which occurs mostly at low latitudes, leads to outgassing of  $O_2$ , while the conversion of warmer water back to cooler water, which occurs mostly at higher latitudes, leads to uptake of  $O_2$ . In the Indian and Pacific ocean, the  $O_2^*/\Delta T$  slope of  $\sim 22 \mu\text{mole kg}^{-1} \text{ } ^\circ\text{C}^{-1}$  in waters between 6°C and 18°C, is equivalent to  $\sim 5 \text{ nmol of } O_2 \text{ per Joule of warming}$ , as derived by multiplying by seawater density and dividing by heat capacity. The slope is several times larger than expected from solubility changes alone, indicating that the  $O_2$  exchanges are mainly controlled by variations in the efficiency of the marine biological pump. A generally weaker and but more variable  $O_2/\text{heat}$  relationship is indicated for waters warmer than about 18°C, which is consistent with the lower nutrient content of these waters and a reduction of influence of biological relative to solubility effects.

A less steep  $O_2^*/\Delta T$  trend is seen in Figure 2 for the thermocline of the North Atlantic

ocean compared to other oceans, possibly owing to the lower nutrient content of the North Atlantic. The North Atlantic trend of  $\sim 13 \mu\text{mole kg}^{-1} \text{ } ^\circ\text{C}^{-1}$  (equivalent to  $\sim 3 \text{ nmole J}^{-1}$ ) connects low-latitude surface waters in the Atlantic with North Atlantic Deep Water (NADW), which lies below the  $\text{O}_2^*$  trend of the other oceans. A steeper  $\text{O}_2^*$  ratio of around 30 to 40  $\mu\text{mole kg}^{-1} \text{ } ^\circ\text{C}^{-1}$  (equivalent to 7.5 to 10  $\text{nmol J}^{-1}$ ) is found for the deep Antarctic sequence (25), which is driven by ventilation of deep waters around Antarctica. Here stratification induced by warming and freshening in the summer months inhibits the uptake of  $\text{O}_2$  by deeper waters, while the breakdown of stratification induced by winter-time cooling and brine rejection from sea ice enhances  $\text{O}_2$  uptake and deepwater formation (27). The air-sea exchanges and watermass-mixing around Antarctica effectively convert circumpolar deep water, which derives largely from NADW, into colder Antarctic surface waters. By this conversion, the oceans around Antarctica release heat to the atmosphere and take up  $\text{O}_2$ .

Due to sparse coverage, Figure 2 doesn't resolve well water masses in the Equatorial Pacific. Here, however a very different relationship between heating and  $\text{O}_2$  flux is known to exist. Equatorial upwelling raises cool, oxygen-deficient waters to the surface, where a net uptake of  $\text{O}_2$  from the atmosphere (20) and a net heating of the water occurs. The  $\text{O}_2$  flux/heating ratio in the Equatorial Pacific is thus opposite in sign to the cases considered above. This feature is a result of the upwelled waters having been exposed to the surface for a very brief period of weeks or days, which is insufficient to allow  $\text{O}_2$  to equilibrate with the atmosphere and for biological production to remove the nutrients. As the upwelled waters spread laterally away from the Equator, the net effect of warming and nutrient withdrawal leads to an overall  $\text{O}_2$  release to the atmosphere (20,28). Integrated over a wider latitude band, the net effect of



Equatorial upwelling on heat and O<sub>2</sub> exchange is therefore more concordant with the main thermocline trend.

The patterns noted above suggest the following generalizations: Although the changing efficiency of the biological pump dominates the O<sub>2</sub> response of the ocean to warming and stratification, the O<sub>2</sub> response is nevertheless strongly tied, over a range of space and time scales, to the net air-sea heat flux. For time scales of months to centuries, the O<sub>2</sub> flux/heating ratios generally lie in the range of 2 to 10 nmol J<sup>-1</sup>. Larger ratios are found at higher latitudes, particularly in the Southern Hemisphere and for processes occurring over time scales of decades to centuries (e.g. thermocline ventilation) compared to time scales of months (seasonal exchanges). Some differences exist from ocean to ocean, with the North Atlantic having smaller O<sub>2</sub> response per unit heating or cooling than other high latitude regions. This analysis does not resolve the O<sub>2</sub> response of the oceans to heating and cooling on thousand-year and longer time scales.

#### ANTHROPOGENIC WARMING AND O<sub>2</sub> OUTGASSING

In Table 2 we use the O<sub>2</sub> flux/heating relationships found above to formulate an estimate of the global air-sea O<sub>2</sub> flux from 1990 to 2000. We consider three ocean regions: (1) North Atlantic (at all depths), (2) the deep Southern Ocean (>1000m), and (3) the remaining oceans (at all depths). Warming in each region is assumed to produce O<sub>2</sub> outgassing proportional to observed steady-state O<sub>2</sub>\*/heat relationships in these regions. The approach is motivated by the observation that similar O<sub>2</sub>/heat ratios are found for both transient warming on seasonal time scales and for steady-state warming/cooling over time scales from years to centuries. The

approach effectively adopts the “null hypothesis” that the ocean’s response to transient warming on decadal time scales is governed by similar ratios.

Because compilations of ocean warming (1) have been completed only through year 1998, and because these compilations do not resolve warming on a yearly basis below 300m depth, we rely on the model simulations (4,5) as a means of extrapolating the observed long-term (1950's-1990's) warming in each region through the 1990-2000 period. The approach effectively accounts for the warming caused by anthropogenic radiative forcing but not natural variability. The latter we treat as a source of noise. We derive a central estimate of the global  $O_2$  outgassing of  $0.29 \pm 0.10 \times 10^{14}$  moles  $O_2$   $yr^{-1}$  for 1990-2000, where 18% of the total  $O_2$  outgassing is attributable to warming in the North Atlantic, 20% in the deep Southern Ocean, and 61% in the remainder of the upper ocean. Our estimate corresponds to a global average  $O_2$  flux heating ratio of  $5 \text{ nmol } J^{-1}$ .

The uncertainty around our central estimate attributable to uncertainties in regional  $O_2$ /heat ratios and long-term warming rates is  $\pm 0.13 \times 10^{14}$  moles  $O_2$   $yr^{-1}$ . A much larger uncertainty must be allowed for decadal variability (15,29,30). One estimate of this can be derived by multiplying the global  $O_2$ /heat ratio of  $5 \text{ nmol } O_2 J^{-1}$  by the decadal variability in global ocean heat storage, which we estimate from heat storage data (1), after removing the long-term trend, to be  $\pm 5 \times 10^{22}$  J, which yields  $\pm 2.5 \times 10^{14}$  mol  $O_2$  variability on a decadal basis. Here we adopt a slightly higher estimate of  $\pm 4 \times 10^{14}$  mol  $O_2$ , on the grounds that the heat storage data (1) may underestimate true variability due to spatial and temporal averaging, and given uncertainties in the appropriate  $O_2$ /heat ratio. Treating the decadal variability as a source of random noise, we derive an estimate of  $0.29 \pm 0.4 \times 10^{14}$  mol  $O_2$   $yr^{-1}$  for the total oceanic  $O_2$

outgassing from 1990 to 2000.

From 1990 to 1998, the global upper ocean (< 300m) heat content increased at a rate of  $\sim 0.5 \times 10^{22} \text{ J yr}^{-1}$  (1), which is faster than the rate of  $\sim 0.2 \times 10^{22} \text{ J yr}^{-1}$  which we would estimate from projecting long-term warming rates. If we assume that the additional warming of  $\sim 0.3 \times 10^{22} \text{ J yr}^{-1}$  persisted through year 2000, and we add the difference to our outgassing estimate, then our central estimate increases from  $0.29 \times 10^{14} \text{ mol yr}^{-1}$  to  $0.44 \times 10^{14} \text{ mol yr}^{-1}$ , assuming a scaling of  $5 \text{ nmol J}^{-1}$ . To apply such a correction is premature, however, because the global 1990-1998 heating trend is heavily influenced by a large anomaly in the North Atlantic in 1998, which was possibly a transient associated with the 1997/98 El Nino event (1). In any case, the correction would be within our allowed uncertainties for decadal variability of  $\pm 0.4 \times 10^{14} \text{ mol yr}^{-1}$ . Once heat storage data are compiled through 2000, it may be possible to refine the decadal outgassing estimate and reduce the allowed uncertainties.

## CARBON BUDGETING

What are the implications of oceanic  $\text{O}_2$  outgassing for carbon budgeting? A correction for oceanic  $\text{O}_2$  outgassing is needed to estimate land and ocean carbon sinks based on the global budgets of atmospheric  $\text{O}_2$  and  $\text{CO}_2$  (31,32). These can be written,

$$\text{CO}_2 = F - O - B \quad (2)$$

$$\text{O}_2 = -\alpha_F F + \alpha_B B + Z \quad (3)$$

where  $F$  is the  $\text{CO}_2$  source from fossil-fuel burning,  $O$  and  $B$  are respectively the ocean and land

sinks,  $\lambda_F$  and  $\lambda_B$  are global-average  $O_2:C$  exchange ratios for fossil-fuel and land biota, and  $Z$  is the net source of  $O_2$  from the oceans. Equation (1) and (2) are solved to yield estimates of  $O$  and  $B$ , using  $\Delta O_2$  and  $\Delta CO_2$  derived respectively from observed changes in atmospheric  $O_2/N_2$  ratio and  $CO_2$  mole fraction,  $F$  and  $\lambda_F$  derived from industrial records, and  $\lambda_B \approx 1.1$  (31,32).

Previously it has been assumed that the ocean outgassing term  $Z$  is zero to within the uncertainties (31,32), or allowance has alternately been made for  $O_2$  outgassing based on the solubility effect alone (33). In Table 3, we correct the estimate of Manning (33), as cited in the recent IPCC (34) report, based on our above estimate of  $Z = 0.29 \pm 0.4 \text{ mol } O_2/\text{yr}$ , where this estimate implicitly allows for the effect of anthropogenic warming on both solubility and stratification. The correction increases the oceanic sink by  $0.18 \text{ Pg C yr}^{-1}$  and decreases the land sink by the same amount relative to the Manning (33) estimate. Although the change is small relative to other uncertainties, it nevertheless helps to reconcile the estimated oceanic sink with recent model estimates (35).

A correction for oceanic  $O_2$  is also needed for carbon budgets based on direct measurement of changes in dissolved inorganic carbon (DIC) in the ocean. Detecting the input of anthropogenic  $CO_2$  into the oceans is difficult due to large natural variability in DIC caused by ocean biology. This difficulty is commonly overcome by normalizing to a constant  $O_2$  concentration to filter out the variability due to ocean biology (36,37,38,39,40). In effect, what is reported is not the change DIC, but rather the change in the quantity  $DIC + O_2/\lambda$ , where  $\lambda \approx 1.3$  (35,36). By design, this approach neglects changes in DIC caused by variations in the efficiency of the biological pump. If the dissolved  $O_2$  inventory decreases globally due to stratification, the approach will underestimate oceanic  $CO_2$  uptake by an amount given

approximately by  $(dI/dt)/\lambda$ , where  $dI/dt$  is the change in oceanic  $O_2$  inventory. The correction is the same sign and a similar magnitude to that required based on atmospheric  $O_2$  and  $CO_2$  budgets. Taking the observed ocean warming of  $\sim 2 \times 10^{23}$  J between the middle 1950's and 1990's (1), and assuming the  $O_2$  inventory decreases by  $5 \text{ nmol } O_2 \text{ J}^{-1}$ , yields an upwards correction of  $\sim 9 \text{ Pg C}$  over 1955-1995 period. In comparison, the total oceanic uptake from preindustrial times through 1990 is estimated to be  $107 \pm 27 \text{ Pg C yr}^{-1}$  (34).

Recent estimates of change in oceanic inventories of DIC (38,39,40) have not allowed for changing  $O_2$  inventory, and therefore are presumably biased low, although more work is needed to establish reliable corrections in the individual ocean basins and globally. If the DIC data is additionally normalized based on regressions against  $\Delta T$  and alkalinity, then additional corrections may be needed for changing ocean heat content (independent of the effect on  $O_2$ ) and alkalinity inventory.

## DISCUSSION

Our estimate of  $0.29 \times 10^{14} \text{ mol } O_2 \text{ yr}^{-1}$  for recent oceanic  $O_2$  outgassing caused by changing radiative forcing lies within the range estimated based on recent OGCMs (12,13,14,15). The relatively good agreement between these independent estimates strengthens the case that a long-term ocean outgassing of this magnitude may actually be occurring. Nevertheless, the similarity in these estimates undoubtedly results partly from similar assumptions. For example, the estimates commonly assume that Redfield P/ $O_2$  ratios are constant with time and space, and that phosphate is the ultimate limiting nutrient. Also, while our estimate assumes that the  $O_2$  response to transient warming is similar to the  $O_2$  response to steady-state warming and cooling,

the OGCMs similarly assume that the response of the ocean biology to transient warming can be understood based on parameters adjusted to duplicate steady-state behavior. It is unclear if these assumptions form a realistic basis for projection.

Our estimate effectively assumes that  $O_2^*/\square$  relationships remain relatively constant during transient warming, or equivalently that preformed phosphate/ $\square$  relationships remain constant during transient warming. For example, the  $O_2$  flux/heating ratio we adopt for warming of the main thermocline would be obtained if the main effect of warming was to deepen the thermocline without altering the preformed phosphate/ $\square$  relationship across the thermocline, or if the surface isotherms progress polewards during the transient at the same rate as the isolines of surface phosphate. The  $O_2$  flux/heating ratio we adopt for the deep Southern Ocean would be obtained if warming caused a reduction in deepwater formation around Antarctica, thus increasing the influence of other source waters on the chemistry of the deep ocean.

Our estimate of the effect of Southern Ocean warming on  $O_2$  exchange can be compared to the study Broecker et al. (41), who used  $PO_4^*$ ,  $^{14}C$ , and chloro-fluorocarbon (CFC) data to support the argument that the ventilation rate of deep waters around Antarctica slowed substantially in the 20<sup>th</sup> century. According to their scenario, the  $PO_4^*$  content of the deep ocean should now be decreasing with time, in which case a net  $O_2$  outgassing should also be occurring, as required by the links between  $PO_4^*$  (i.e.  $O_2^*$ ) and the air-sea  $O_2$  flux. Taking their estimate of the difference in  $PO_4^*$  content of southern source waters relative to average deep waters and their estimate that the input rate has slowed by  $10^7 10^6 \text{ m}^3 \text{ s}^{-1}$ , yields a required outgassing rate of  $0.3^7 10^{14} \text{ mol } O_2 \text{ yr}^{-1}$ , which is five times larger than our estimate of  $0.06^7 10^{14} \text{ mol } O_2 \text{ yr}^{-1}$  for the deep Southern Ocean (Table 2). We defend our smaller estimate on the following grounds:

First, the Broecker et al scenario implies that the deepwater heat content should be increasing by  $\sim 0.4 \times 10^{22} \text{ J yr}^{-1}$ , based on the  $\sim 3^\circ\text{C}$  difference in temperature between southern surface waters and average deep waters. A warming rate of this magnitude is inconsistent with the observed temperature trends (1), unless the warming is mostly confined below 3000m, the maximum depth considered by Levitus et al. (1). Second, recent work (42) suggests that a large 20<sup>th</sup> century slow-down is not necessary to explain the CFC and  $\text{PO}_4^*$  data.

A reliable assessment of the global air-sea  $\text{O}_2$  flux will ultimately require an approach based on direct observations rather than model studies. Over the next few decades, global systematic decreases in dissolved  $\text{O}_2$  can be expected at the level of  $0.4 \times 10^{14} \text{ mol O}_2 \text{ yr}^{-1}$  or larger, which corresponds to a change of  $0.7 \mu\text{mol O}_2 \text{ kg}^{-1}$  per decade, if spread uniformly over 2000m. Resolving these changes against natural variability will require a high measurement density, but this may be feasible with appropriate sensor and platform development and with a concerted long-term observing program. Resolving these changes is needed for carbon budgeting, as a complement to lower-density DIC measurements and atmospheric  $\text{O}_2/\text{N}_2$  measurements, and would help to assess the overall impact of climate change on the biogeochemistry and biodiversity of the oceans. Another source of uncertainty in carbon budgets involves change in oceanic organic carbon (18), which we have assumed is small, but is not well constrained. We suggest that a program to directly monitor oceanic inventories of  $\text{O}_2$  and organic carbon, along with inorganic carbon and nutrients, should be given some priority in future ocean observing systems.

## ACKNOWLEDGEMENTS

We thank Scott Doney, Ray Najjar, and Corinne LeQuere for helpful comments. This work was supported by the National Science Foundation under ATM-0000923, National Oceanic and Atmospheric Administration under NA77RJ0453A, and the National Aeronautics and Space Administration under NAG5-6668, and was completed in part while one of us (R.K.) was hosted at the Max Planck Institute for Biogeochemistry in Jena, Germany.



## REFERENCES

1. Levitus, S., Antonov, J.I., Boyer, T.P. & Stephens, C. (2000) *Science* **287**, 2225-2229.
2. Wong, A.P.S., Bindoff, N.L. & Church, J.A. (1999) *Nature (London)* **400**, 440-443.
3. Manabe, S., Stouffer, R.J., Spelman, M.J. & Bryan K. (1991) *Journal of Climate* **4**, 785-818.
4. Levitus, S., Antonov, J.I., Wang, J., Delworth, T.L., Dixon, K.W. & Broccoli, A.J. (2001) *Science* **292**, 267-270.
5. Barnett, T.P., Pierce, D.W. & Schnur, R. (2001) *Science* **292**, 270-274.
6. Bindoff, N.L. & McDougall, T.J. (2000) *Journal of Physical Oceanography* **30**, 1207-1222.
7. Shaffer, G., Leth, O., Ulloa, O., Bendtsen, J., Daneri, G., Dellarossa, V., Hormazabal, S. & Sehlstedt, P.-I. (2000) *Geophysical Research Letters* **27**, 1247-1250.
8. Emerson, S., Mecking, S., Abell, J. (2001) *Global Biogeochemical Cycles* **15**, 535-554.
9. Keller, K., Slater, R.D., Bender, M. & Key, R.M. (2002) *Deep-Sea Research II* **49**, 345-362.
10. Garcia, H., Cruzado, A., Gordon, L. & Escanez, J. (1998) *Journal of Geophysical Research*

103, 2817-2830.

11. Pahlow, M. & Riebesell, U., (2000) *Science* **287**, 831-833.
12. Sarmiento, J.L., Hughes, T.M.C, Stouffer, R.J. & Manabe, S. (1998) *Nature (London)* **393**, 245-249.
13. Matear, R.J., Hirst, A.C. & McNeil, B.I. (2000) *Geochemistry, Geophysics, Geosystems*, American Geophysical Union paper number 2000G000086.
14. Plattner, G.-K., Joos, F., Stocker, T.F. & Marchal, O. (2001) *Tellus Series B* **53**, 564-592.
15. Bopp, L., Le Quere, C., Heimann, M., Manning, A.C., Monfray, P. (2002) *Biogeochemical cycles*, in press.
16. Volk, T. & Hoffert, M.I. (1985) in *The carbon cycle and atmospheric CO<sub>2</sub>, Archean to Present; AGU Geophysical Monograph 32*, eds. Sundquist, E.T., Broecker, W.S. (American Geophysical Union, Washington DC), pp. 99-110.
17. Redfield, A.C., Ketchum, B.H. & Richards, F.A. (1962) in *The Sea, Vol. 2*, ed. Hill, M.N. (Interscience, New York), pp. 26-77.
18. Hansell, D.A. & Carlson, C.A. (2001) *Deep-Sea Research II* **48**, 1649-1667.

19. Rogers, A.D. (2000) *Deep Sea Research II* **47**, 119-148.
20. Najjar, R.G. & Keeling, R.F. (2000) *Global Biogeochemical Cycles* **14**, 573-584.
21. Garcia, H.E. & Keeling, R.F. (2002) *Journal of Geophysical Research*, in press.
22. Bainbridge, A.E. (1981) *GEOSECS Atlantic Expedition Vol. 1 hydrographic data 1972-1973* (National Science Foundation, Washington, D.C.).
23. Broecker, W.S., Spenser, D.W. & Craig, H. (1982) *GEOSECS Pacific Expedition Volume 3 hydrographic data 1973-1974* (National Science Foundation, Washington, D.C.).
24. Weiss, R.F., Broecker, W.S., Craig H. & Spenser, D.W. (1983) *GEOSECS Indian Ocean Expedition Volume 5 hydrographic data 1977-1978* (National Science Foundation, Washington, D.C.).
25. Broecker, W.S. et al. (1998) *Journal of Geophysical Research* **203**, 15833-15843.
26. Keeling, R.F. & Peng, T.-H. (1995) *Philosophical Transactions of the Royal Society London, Series B* **348**, 133-142.
27. Gordon, A.L. & Huber, B.A. (1990) *Journal of Geophysical Research* **95**, 11655-11672.

28. Stephens, B.B., Keeling, R.F., Heimann, M., Six, K.D., Murnane, R. & Caldeira, K. (1998) *Global Biogeochemical Cycles* **12**, 213-230.
29. Bender, M., Ellis, T., Tans, P., Francey, R., & Lowe, D. (1996) *Global Biogeochemical Cycles* **10**, 9-21.
30. McKinley, G.A., Follows & M.J., Marshall J. (2000) *Geophysical Research Letters* **27**, 2933-2936.
31. Keeling, R.F. & Shertz, S.R. (1992) *Nature (London)* **358**, 723-727.
32. Battle, M., Bender, M.L., Tans, P.P., White, J.W.C., Ellis, J.T., Conway, T., Francey & R.J. (2000) *Science* **287**, 2467-2470.
33. Manning, A.C. (2001) *Temporal Variability of atmospheric oxygen from both continuous measurements and a flask sampling network: tools for studying the global carbon cycle*, Ph.D. Thesis, (University of California, San Diego).
34. Prentice I.C. et al. (2001) in *Climate Change 2001, Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change* (Cambridge University Press, Cambridge, U.K.) 183-237.
35. Orr, J.C. et al. (2001) *Global Biogeochemical Cycles* **15**, 43-60.

36. Brewer, P.G. (1978) *Geophysical Research Letters* **5**, 997-1000.
37. Chen, C.-T.A. & Millero, F.J. (1979) *Nature (London)* **277**, 205-206.
38. Gruber, N. (1998) *Global Biogeochemical Cycles* **12**, 165-191.
39. Sabine, C.L., Key, R.M., Johnson, K.M., Millero, F.J., Poisson, A., Sarmiento, J.L., Wallace, D.W.R. & Winn, C.D. (1999) *Global Biogeochemical Cycles* **13**, 179-198.
40. Peng, T.-H., Wanninkhof, R., Bullister, J.L., Feely, R.A. & Takahashi, T. (1998) *Nature (London)* **396**, 560-563.
41. Broecker, W.S., Sutherland, S. & Peng, T.-H. (1999) *Science* **286**, 1132-1135.
42. Orsi, A.H., Jacobs, S.S., Gordon, A.L. & Visbeck, M. (2001) *Geophysical Research Letters* **28**, 2923-2926.

## FIGURE CAPTIONS

Figure 1. Ratio of the seasonal  $O_2$  outgassing to the seasonal upper ocean warming by  $10^{-6}$  latitude bands. Dashed line indicates the ratios expected based on changes in  $O_2$  solubility alone. Ratios from  $20^{\circ}N$  to  $20^{\circ}S$  are poorly defined due to weak seasonal forcing. The seasonal  $O_2$  outgassing here accounts for the anomalous flux after subtracting the mean annual outgassing.

Figure 2. Scatter plot of the tracer  $O_2^* = O_2 + 175 PO_4$  versus potential temperature for data collected on the Geochemical Ocean Section Study (22, 23, 24). The data through the main thermocline of the Indian and Pacific oceans are seen to scatter around a line with a slope of approximately  $22 \mu\text{mol kg}^{-1} \text{ } ^\circ\text{C}^{-1}$ . Changes in  $O_2^*$  are generally larger than expected from changes in the  $O_2$  solubility (dashed line). Antarctic Surface Water from ref. 25. NADW: North Atlantic Deep Water.

Table 1. Significant recent changes in dissolved O<sub>2</sub> concentrations.

| Study                     | Location   | Time Span     | Depth Range, m | O <sub>2</sub> change $\frac{\Delta}{\text{yr}}$ mol kg <sup>-1</sup> |
|---------------------------|--|---------------|----------------|---|
| Garcia et al. (10)        | Atlantic 24°N section, averaged over full section    | 1981-1992     | 800-1900       | -3 to -7  |
| Pahlow and Riebesell (11) | North Pacific, basin average                         | 1950's-1990's | unreported     | ~-5   |
| Keller et al. (9)*        | North Pacific, basin average                         | 1970's-1990's | 300-500        | -1 to -2  |
|                           |  |               | 1000-1600      | +2 to +3  |
| Shaffer et al. (7)        | Pacific, 28°S section, averaged from 52°-88°W        | 1967-1995     | 800-1200       | -5 to -8  |
| Bindoff and McDougal (6)  | Indian Ocean, 32°S section, averaged from 30°-117°E  | 1962-1997     | 300-800        | -7 to -8  |
|                           |  |               | 2500-4000      | +3  |
| Matear et al. (13)        | Southern Ocean, 110°E-170°E, 50°-60°S                | 1965-1995     | >400           | -5 to -15   |
| Emerson et al. (8)*       | North Pacific, 154°W section, averaged from 22°-44°N | 1980-1997     | 100-600        | -9 to -20   |

\*Report change in O<sub>2</sub>-O<sub>2</sub><sup>0</sup>, rather than O<sub>2</sub> concentration, where O<sub>2</sub><sup>0</sup> is the solubility.

Table 2. Estimated oceanic O<sub>2</sub> outgassing 1990-2000 based on changing radiative forcing\*.

| Ocean Region        | Heating, 10 <sup>22</sup> J yr <sup>-1</sup> | Heating, percent | O <sub>2</sub> /heat ratio, nmol J <sup>-1</sup> | O <sub>2</sub> outgassing, 10 <sup>14</sup> mol yr <sup>-1</sup> | Outgassing, percent |
|---------------------|--|------------------|--|--|---------------------|
| North Atlantic      | 0.18 $\times$ 0.08                           | 30%              | 3 $\times$ 1.5                                   | 0.05 $\times$ 0.04   | 18%                 |
| Deep Southern Ocean | 0.06 $\times$ 0.03                           | 10%              | 10 $\times$ 5.0                                  | 0.06 $\times$ 0.04   | 20%                 |
| Other Oceans        | 0.36 $\times$ 0.16                           | 60%              | 5 $\times$ 2.5                                   | 0.18 $\times$ 0.12   | 61%                 |
| Global Total        | 0.6 $\times$ 0.18                            | 100%             | 4.9  | 0.29 $\times$ 0.13   | 100%                |

\*Heating rates based on observed warming in each region from 1955-1995 (1), scaled to yield total of  $0.6 \times 10^{22} \text{ J yr}^{-1}$ , the warming attributable to increasing radiative forcing from 1990-2000 (4, 5). Error analysis assumes 45% uncertainty in individual heating rates and 50% uncertainty in  $\text{O}_2/\text{heat}$  ratios, with all errors uncorrelated.



Table 3. O<sub>2</sub>-based global carbon budget 1990-2000 (Pg C yr<sup>-1</sup>)\*.

|                                      | Manning (33) | Revised budget |
|--------------------------------------|--------------|----------------|
| Fossil-fuel burning                  | 6.33 ± 0.4   | 6.33 ± 0.4     |
| Atmospheric CO <sub>2</sub> increase | 3.21 ± 0.1   | 3.21 ± 0.1     |
| Total Ocean CO <sub>2</sub> sink     | 1.68 ± 0.5   | 1.86 ± 0.6     |
| Total Land CO <sub>2</sub> sink      | 1.44 ± 0.7   | 1.26 ± 0.8     |

\*Budgets based on the decadal trend in atmospheric O<sub>2</sub>/N<sub>2</sub> ratio at two northern hemisphere stations in the Scripps O<sub>2</sub>/N<sub>2</sub> network. Manning (33) assumes  $Z = 0.16 \pm 0.16 \times 10^{14}$  mol O<sub>2</sub> yr<sup>-1</sup>; revised budget assumes  $0.29 \pm 0.4 \times 10^{14}$  mol O<sub>2</sub> yr<sup>-1</sup> (see text). Budgets differ in assumed ocean warming rate, and in assumed oceanic O<sub>2</sub> outgassing per unit warming. Both budgets allow for outgassing of N<sub>2</sub> (which impacts the observed O<sub>2</sub>/N<sub>2</sub> ratio) at a rate based on N<sub>2</sub> solubility of 2.2 nmol N<sub>2</sub> per J of warming.

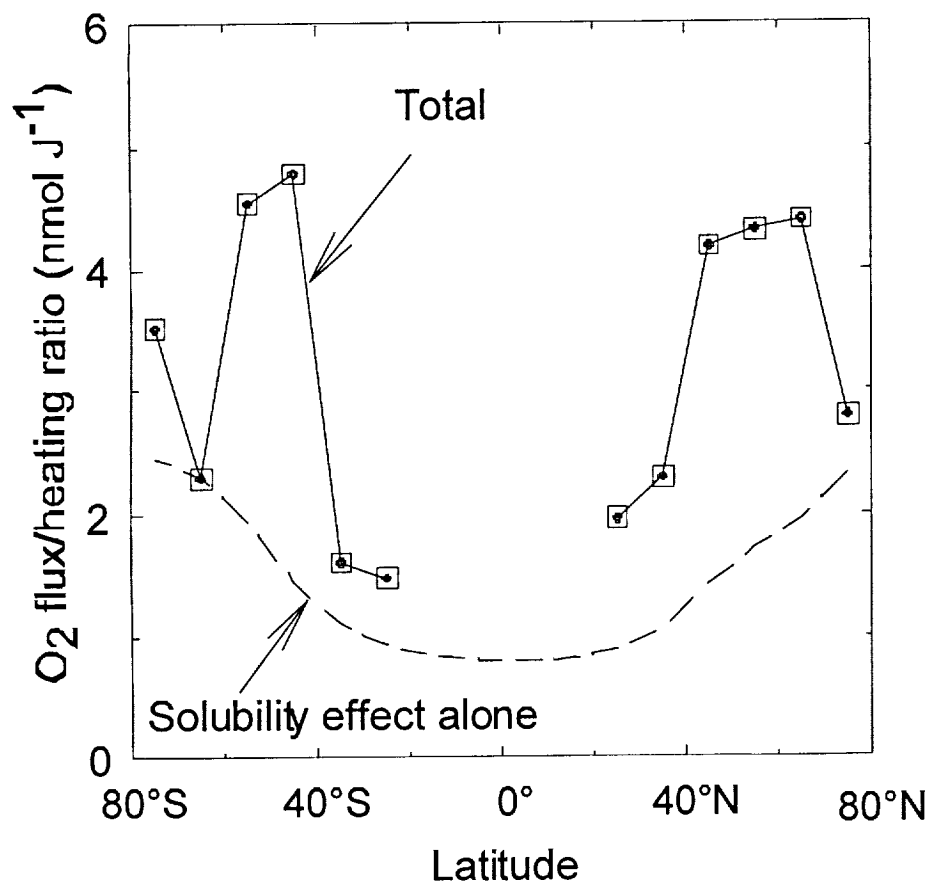


Figure 1.

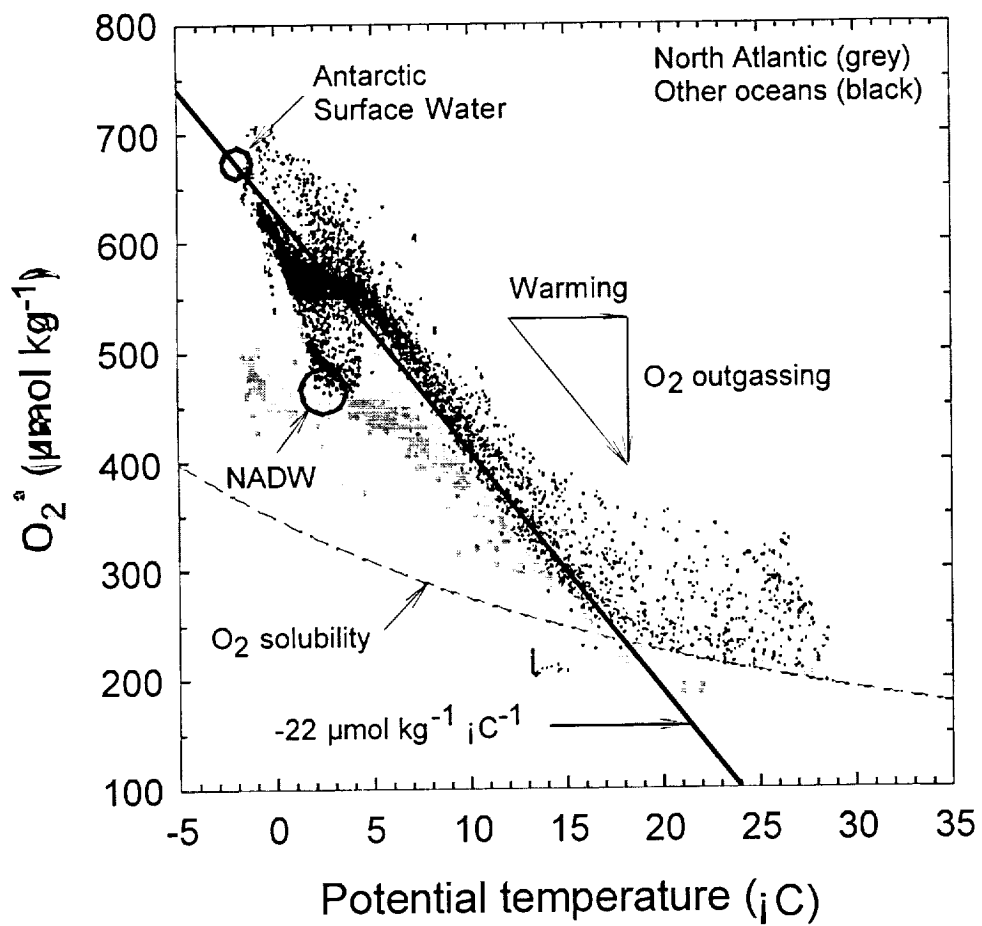


Figure 2.