The change in oceanic O_2 inventory associated with recent global warming

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Oceans general circulation models predict that global warming may cause a decrease in the oceanic O_2 inventory and an associated O_2 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_2 flux/heat flux ratios are shown to occur in a range of 2 to 10 nmol of O_2 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_2 solubility, indicating that most of the O_2 exchange is biologically mediated through links between heating and stratification. The change in oceanic O_2 inventory through the 1990s is estimated to be $0.3 \pm 0.4 \times 10^{14}$ mol of O_2 per year based on scaling the observed anomalous long-term ocean warming by natural O_2 flux/heating ratios and allowing for uncertainty due to decadal variability. Implications are discussed for carbon budgets based on observed changes in atmospheric O_2/N_2 ratio and based on observed changes in ocean dissolved inorganic carbon.

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 (3–5).

Repeated hydrographic surveys also indicate that small detectable changes have occurred in oceanic dissolved O_2 concentrations. As summarized in Table 1, detectable decreases in O_2 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_2 changes is unclear, and different mechanisms, including changes in ocean circulation rates (6–9), changes in preformed values (10), 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_2 changes, found at intermediate depths, are in the direction of decreasing O_2 concentrations. A global reduction in dissolved O_2 is predicted by ocean general circulation models (OGCMs) driven by increasing greenhouse gases (12–15). In the model simulations, most of the O_2 decrease is attributed to enhanced stratification.

Stratification has two competing effects on subsurface oxygen concentrations. First, it reduces the upwelling of nutrients from deeper waters into surface waters, 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_2 concentrations by reducing subsurface O_2 utilization rates. Second, stratification limits the downward transport from O_2 from well-oxygenated surface waters into the ocean interior, which serves to reduce subsurface O_2 concentrations.

In the modeling studies cited above, the effect of stratification on O_2 transport exceeds the effect on subsurface O_2 utilization, leading to a net O_2 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 nonpreformed nutrients—i.e., those that 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, mol) and sea-to-air O_2 flux (Z, mol yr^{-1}) are linked according to

$$dI/dt = -Z + \alpha \, dC_{org}/dt, \qquad [1]$$

where C_{org} is the oceanic inventory of organic carbon, including both particulate and dissolved forms, and α 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 $\alpha dC_{org}/dt$ 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 organic carbon (see also ref. 14). On these time scales, we therefore expect that changes in the oceanic O_2 inventory, due to stratification or other causes, should be roughly balanced by O_2 exchanges with the atmosphere ($dI/dt \approx -Z$).

Estimates based on OGCMs for oceanic O_2 outgassing due to global warming lie in the range of 0.2 to 0.7×10^{14} mol yr^{-1} for the past few decades, with predictions of 1.0 to 1.6×10^{14} mol yr^{-1} for late 21st century (12–15). According to these estimates, roughly a quarter of the predicted outgassing is attributable to the direct effect of warming on the O_2 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_2 concentrations over a 20-year time frame of between 1 and 5 μmol kg^{-1} if the changes are confined to the top 1,000 m of the oceans. Larger changes are predicted for the Southern Oceans due to reductions in deep convection (12, 13).

Table 1. Significant recent changes in dissolved O_2 concentrations

Study	Location	Time span	Depth range, m	O_2 change, $\mu mol\ kg^{-1}$
Garcia *et al.* (10)	Atlantic 24°N section, averaged over full section	1981–1992	800–1,900	−3 to −7
Pahlow and Riebesell (11)	North Pacific, basin average	1950s–1990s	Unreported	~−5
Keller *et al.* (9)*	North Pacific, basin average	1970s–1990s	300–500	−1 to −2
			1,000–1,600	+2 to +3
Shaffer *et al.* (7)	Pacific, 28°S section, averaged from 52°–88°W	1967–1995	800–1,200	−5 to −8
Bindoff and McDougal (6)	Indian Ocean, 32°S section, averaged from 30°–117°E	1962–1997	300–800	−7 to −8
			2,500–4,000	+3
Matear *et al.* (13)	Southern Ocean, 110°–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 $O_2 - O_2^o$, rather than O_2 concentration, where O_2^o is the solubility.

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_2 inventory could be important. Dissolved O_2 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_2 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_2 are diagnostic of changes in the efficiency of the marine biological pump, which may influence the rate at which the oceans absorb anthropogenic CO_2 (12). Finally, at least two approaches for estimating sinks of anthropogenic carbon dioxide require corrections for changes in oceanic O_2 inventory. The purpose of this paper is to provide an independent estimate of the plausible O_2 inventory changes associated with recent global warming and to discuss the implications for global carbon budgeting.

## Natural Warming and O_2 Outgassing

It is easily established that a close association exists between ocean warming and O_2 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_2 to the atmosphere, while in the fall and winter, when the upper ocean is cooled, the oceans are a sink of O_2 from the atmosphere. These seasonal air–sea O_2 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_2 solubility (20).

We have estimated the ratio of seasonal O_2 outgassing to seasonal heating from global archived measurements of dissolved O_2 in surface waters, climatological winds, and climatological air–sea heat fluxes (21). The O_2 flux/heating ratio varies between 1.5 nmol of O_2 per joule at lower latitudes to 4 or 5 nmol of O_2 per joule in the 40° to 60° latitude bands, as shown in Fig. 1. Consistent with Najjar and Keeling (20), we find ratios that are larger than expected from the effect of warming on the O_2 solubility by factors between 1.5 and 2.5. We further have shown, based on comparisons with atmospheric O_2/N_2 data (21), that the component of the O_2 flux that correlates with heating dominates large-scale seasonal O_2 exchange. These results indicate that seasonal heating, through its effect on stratification, biological productivity, and O_2 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 (Θ), as shown in Fig. 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 the processes controlling the efficiency of the biological pump. Assuming rapid air–sea solubility equilibration, the solubility component is simply given by the O_2 solubility (O_2^o), so that the remaining biological pump component is proportional to the (apparent) preformed phosphate content ($PO_4 - (O_2^o - O_2)/175$) of the water (26).

A prominent feature in Fig. 2 is the strong association between O_2^* and Θ in waters of the main thermocline 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. Outside the North Atlantic, the O_2^*/Θ slope of ~22 $\mu mol\ kg^{-1}\ °C^{-1}$ in waters between 6° and 18°C, is equivalent to ~5 nmol of O_2 per joule of warming, as derived
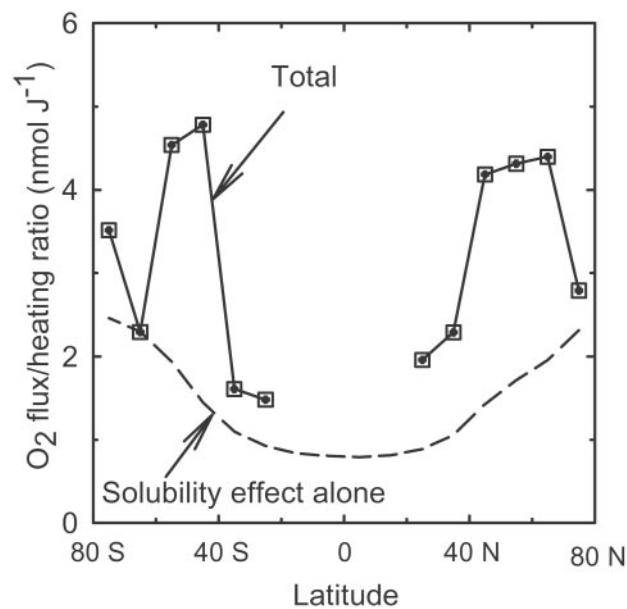
Fig. 1. Ratio of the seasonal O_2 outgassing to the seasonal upper ocean warming by 10° latitude bands. Dashed line indicates the ratios expected based on changes in O_2 solubility alone. Ratios from 20°N to 20°S are poorly defined due to weak seasonal forcing. The seasonal O_2 outgassing here accounts for the anomalous flux after the mean annual outgassing or ingassing is subtracted.
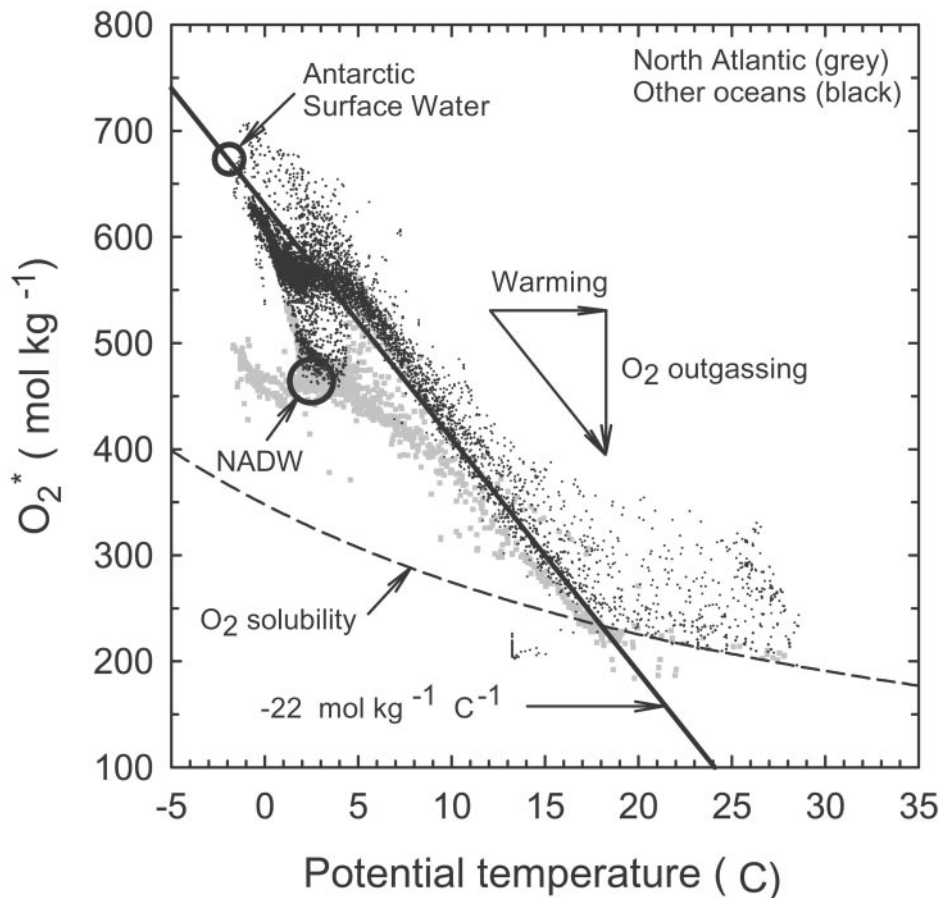
Fig. 2. Scatter plot of the tracer $O_2^* = O_2 + 175PO_4$ versus potential temperature for data collected on the Geochemical Ocean Section Study (22–24). The data through the main thermocline of the Indian and Pacific oceans are seen to scatter around a line with a slope of approximately $-22 \ \mu$mol kg^{-1} °C^{-1}. Changes in O_2^* are generally larger than expected from changes in the O_2 solubility (dashed line). Antarctic surface water data are from ref. 25. NADW, North Atlantic deep water.

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/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^*/Θ trend is seen in Fig. 2 for the thermocline of the North Atlantic Ocean compared with other oceans, possibly owing to the lower nutrient content of the North Atlantic. The North Atlantic trend of ~13 μmol kg^{-1} °C^{-1} (equivalent to ~3 nmol J^{-1}) connects low-latitude surface waters in the Atlantic with North Atlantic Deep Water (NADW), which lies below the O_2^*/Θ trend of the other oceans. A steeper O_2^*/Θ ratio of around 30 to 40 μmol kg^{-1} °C^{-1} (equivalent to 7.5–10 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 O_2 by deeper waters, while the breakdown of stratification induced by wintertime cooling and brine rejection from sea ice enhances O_2 uptake and deepwater formation (27). The air–sea exchanges and water-mass-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 O_2.

Due to sparse coverage, Fig. 2 does not resolve well water masses in the Equatorial Pacific. Here, however a very different relationship between heating and O_2 flux is known to exist. Equatorial upwelling raises cool, oxygen-deficient waters to the surface, where a net uptake of O_2 from the atmosphere (20) and a net heating of the water occurs. The 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 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 O_2 release to the atmosphere (20, 28). Integrated over a wider latitude band, the net effect of Equatorial upwelling on heat and O_2 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_2 response of the ocean to warming and stratification, the O_2 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_2 flux/heating ratios generally lie in the range of 2 to 10 nmol J^{-1}. 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 with time

Table 2. Estimated oceanic O_2 outgassing 1990–2000 due to changing radiative forcing

Ocean region	Heating		O_2/heat ratio, nmol J^{-1}	O_2 outgassing	
	10^{22} J yr^{-1}	%		10^{14} mol yr^{-1}	%
North Atlantic	0.18 ± 0.08	30	3 ± 1.5	0.05 ± 0.04	18
Deep Southern Ocean	0.06 ± 0.03	10	10 ± 5.0	0.06 ± 0.04	20
Other oceans	0.36 ± 0.16	60	5 ± 2.5	0.18 ± 0.12	61
Global total	0.6 ± 0.18	100	4.9	0.29 ± 0.13	100

Heating rates are based on observed warming in each region from 1955 to 1995 (1), scaled to yield total of 0.6×10^{22} J yr^{-1}, the warming attributable to increasing radiative forcing from 1990 to 2000 (4, 5). Error analysis assumes 45% uncertainty in individual heating rates and 50% uncertainty in O_2/heat ratios, with all errors uncorrelated.

scales of months (seasonal exchanges). Some differences exist from ocean to ocean, with the North Atlantic having smaller O_2 response per unit heating or cooling than other high-latitude regions. This analysis does not resolve the O_2 response of the oceans to heating and cooling on thousand-year and longer time scales.

Anthropogenic Warming and O_2 Outgassing

In Table 2 we use the O_2 flux/heating relationships found above to formulate an estimate of the global air–sea O_2 flux from 1990 to 2000. We consider three ocean regions: (*i*) North Atlantic (at all depths), (*ii*) the deep Southern Ocean (>1,000 m), and (*iii*) the remaining oceans (at all depths). Warming in each region is assumed to produce O_2 outgassing proportional to observed steady-state O_2^*/Θ relationships in these regions. The approach is motivated by the rough universality of O_2/heat ratios for processes ranging from warming and cooling on seasonal time scales to steady-state warming/cooling over decades 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 300-m depth, we rely on model simulations (4, 5) as a means of extrapolating the observed long-term (1950s–1990s) 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 0.29×10^{14} mol of 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 nmol J^{-1}.

The uncertainty around our central estimate attributable to uncertainties in regional O_2^*/Θ ratios and long-term warming rates is $\pm 0.13 \times 10^{14}$ mol of 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 nmol of 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 of O_2 variability on a decadal basis. Here we adopt a slightly higher estimate of $\pm 4 \times 10^{14}$ mol of 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 of O_2 yr^{-1} for the total oceanic O_2 outgassing from 1990 to 2000.

From 1990 to 1998, the global upper ocean (<300 m) heat content increased at a rate of $\sim 0.5 \times 10^{22}$ J yr^{-1} (1), which is faster than the rate of $\sim 0.2 \times 10^{22}$ J yr^{-1} that we would estimate

from projecting long-term warming rates. If we assume that the additional warming of $\sim 0.3 \times 10^{22}$ J yr^{-1} persisted through year 2000, and we add the difference to our outgassing estimate, then our central estimate increases from 0.29×10^{14} mol yr^{-1} to 0.44×10^{14} mol yr^{-1}, assuming a scaling of 5 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 1997–1998 El Niño event (1). In any case, the correction would be within our allowed uncertainties for decadal variability of $\pm 0.4 \times 10^{14}$ 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 O_2 outgassing for carbon budgeting? A correction for oceanic O_2 outgassing is needed to estimate land and ocean carbon sinks based on the global budgets of atmospheric O_2 and CO_2 (31, 32). These can be written

$$\Delta CO_2 = F - O - B \qquad [2]$$

and

$$\Delta O_2 = -\alpha_F F + \alpha_B B + Z, \qquad [3]$$

where F is the CO_2 source from fossil-fuel burning, O and B are, respectively, the ocean and land sinks, α_F and α_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. Eqs. **2** and **3** are solved to yield estimates of O and B, using ΔO_2 and ΔCO_2 derived, respectively, from observed changes in atmospheric O_2/N_2 ratio and CO_2 mole fraction, F and α_F derived from industrial records, and $\alpha_B \approx 1.1$ (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 Intergovernmental Panel on Climate Change (34) report, based on our above estimate of $Z = 0.29 \pm 0.4$ mol of O_2 per 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 Pg of 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

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Table 3. O₂-based global carbon budget 1990–2000

Budget item	Pg of C yr⁻¹	
	Manning (33)	Revised budget
Fossil-fuel burning	6.33 ± 0.4	6.33 ± 0.4
Atmospheric CO_2 increase	3.21 ± 0.1	3.21 ± 0.1
Total ocean CO_2 sink	1.68 ± 0.5	1.86 ± 0.6
Total land CO_2 sink	1.44 ± 0.7	1.26 ± 0.8

Budgets are based on the decadal trend in atmospheric O_2/N_2 ratio at two northern hemisphere stations in the Scripps O_2/N_2 network. Manning (33) assumes $Z = 0.16 \pm 0.16 \times 10^{14}$ mol of O_2 yr⁻¹; revised budget assumes $0.29 \pm 0.4 \times 10^{14}$ mol of O_2 yr⁻¹ (see text). Budgets differ in assumed ocean warming rate, and in assumed oceanic O_2 outgassing per unit warming. Both budgets allow for outgassing of N_2 (which affects the observed O_2/N_2 ratio) at a rate based on N_2 solubility of 2.2 nmol of N_2 per J of warming.

biology (36–40). In effect, what is reported is not the change DIC, but rather the change in the quantity DIC + O_2/α, where $\alpha \approx 1.3$ (36, 37). 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 $(dI/dt)/\alpha$, 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 1950s and 1990s (1), and assuming the O_2 inventory decreases by 5 nmol of O_2 J⁻¹, yields an upwards correction of ~ 9 Pg of C (1 Pg = 10^{15} g) over the 1955–1995 period. In comparison, the total oceanic uptake from preindustrial times through 1990 is estimated to be 107 ± 27 Pg of C yr⁻¹ (34).

Recent estimates of change in oceanic inventories of DIC (38–40) 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 are additionally normalized based on regressions against Θ 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 0.29×10^{14} mol of O_2 yr⁻¹ for recent oceanic O_2 outgassing caused by changing radiative forcing lies within the range estimated based on recent OGCMs (12–15). 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 on the basis of 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^*/Θ relationships—or equivalently, preformed phosphate/Θ 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/Θ 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 with the study Broecker et al. (41), who used PO_4^*, ^{14}C, and chlorofluorocarbon (CFC) data to support the argument that the ventilation rate of deep waters around Antarctica slowed substantially in the 20th 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 10×10^6 m³ s⁻¹ yields a required outgassing rate of 0.3×10^{14} mol of O_2 yr⁻¹, which is 5 times larger than our estimate of 0.06×10^{14} mol of O_2 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 $\sim 0.4 \times 10^{22}$ J yr⁻¹, based on the $\sim 3°C$ 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 3,000 m, the maximum depth considered by Levitus et al. (1). Second, recent work (42) suggests that a large 20th-century slow-down is not necessary to explain the CFC and PO_4^* data.

A reliable assessment of the global air–sea 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 O_2 can be expected at the level of 0.4×10^{14} mol of O_2 yr⁻¹ or larger, which corresponds to a change of 0.7 μmol of O_2 kg⁻¹ per decade, if spread uniformly over 2,000 m. 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 O_2/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 O_2 and organic carbon, along with inorganic carbon and nutrients, should be given some priority in future ocean observing systems.

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