

# Global oceanic and land biotic carbon sinks from the Scripps atmospheric oxygen flask sampling network

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## ABSTRACT

Measurements of atmospheric O<sub>2</sub>/N<sub>2</sub> ratio and CO<sub>2</sub> concentration are presented over the period 1989–2003 from the Scripps Institution of Oceanography global flask sampling network. A formal framework is described for making optimal use of these data to estimate global oceanic and land biotic carbon sinks. For the 10-yr period from 1990 to 2000, the oceanic and land biotic sinks are estimated to be  $1.9 \pm 0.6$  and  $1.2 \pm 0.8$  Pg C yr<sup>-1</sup>, respectively, while for the 10-yr period from 1993 to 2003, the sinks are estimated to be  $2.2 \pm 0.6$  and  $0.5 \pm 0.7$  Pg C yr<sup>-1</sup>, respectively. These estimates, which are also compared with earlier results, make allowance for oceanic O<sub>2</sub> and N<sub>2</sub> outgassing based on observed changes in ocean heat content and estimates of the relative outgassing per unit warming. For example, for the 1993–2003 period we estimate outgassing of  $0.45 \times 10^{14}$  mol O<sub>2</sub> yr<sup>-1</sup> and  $0.20 \times 10^{14}$  mol N<sub>2</sub> yr<sup>-1</sup>, which results in a correction of 0.5 Pg C yr<sup>-1</sup> on the oceanic and land biotic carbon sinks. The basis for this oceanic outgassing correction is reviewed in the context of recent model estimates. The main contributions to the uncertainty in the global sinks averages are from the estimates for oceanic outgassing and the estimates for fossil fuel combustion. The oceanic sink of 2.2 Pg C yr<sup>-1</sup> for 1993–2003 is consistent, within the uncertainties, with the integrated accumulation of anthropogenic CO<sub>2</sub> in the ocean since 1800 as recently estimated from oceanic observations, assuming the oceanic sink varied over time as predicted by a box-diffusion model.

## 1. Introduction

Evidence continues to grow supporting significant anthropogenic-induced changes in the Earth's climate system (e.g. Tans et al., 1996; Moberg et al., 2005). One of the major players causing such changes is changes in atmospheric CO<sub>2</sub> concentrations, owing to the ability of CO<sub>2</sub> to close a portion of the otherwise open absorption window in the radiation spectrum, at 12–17 μm (Peixoto and Oort, 1992), preventing infrared radiation from escaping back into space, thus warming the Earth (Arrhenius, 1896). As anthropogenic CO<sub>2</sub> production continues to accelerate from the combustion of fossil fuels it becomes increasingly important to understand the partitioning of CO<sub>2</sub> into the atmospheric, oceanic, and terrestrial reservoirs so that reliable future projections of climate and climate change can be made.

Careful measurements of background atmospheric CO<sub>2</sub> concentrations from a large number of monitoring stations around the world provide us with spatial and temporal data on the

increase of CO<sub>2</sub> in the atmospheric reservoir (e.g. GLOBALVIEW-CO<sub>2</sub>, 2004). But quantifying the partitioning of CO<sub>2</sub> uptake in the oceanic and terrestrial reservoirs is very difficult because these reservoirs are so heterogeneous. In addition to using atmospheric oxygen (O<sub>2</sub>) measurements as described and utilized in this paper, several other methods have been employed to estimate oceanic and land biotic carbon sinks. These include: use of surface ocean pCO<sub>2</sub> data (Tans et al., 1990; Takahashi et al., 1999); use of subsurface dissolved inorganic carbon data (Peng et al., 1998; Sabine and Feely, 2001; Sabine et al., 2004); combined use of atmospheric and oceanic <sup>13</sup>C/<sup>12</sup>C data (Quay et al., 1992; Tans et al., 1993; Bacastow et al., 1996; Heimann and Maier-Reimer, 1996; Gruber and Keeling, 1999); use of inverse atmospheric transport models (Keeling et al., 1989b; Tans et al., 1990; Enting et al., 1995); and use of ocean carbon models (several models are compared in Orr, 1997).

Each of these methods has inherent strengths and weaknesses. The oceanic pCO<sub>2</sub> method suffers from a sparsity of data, particularly in the Southern Hemisphere, and from uncertainties in gas transfer velocities (Liss and Merlivat, 1986). <sup>13</sup>CO<sub>2</sub>/<sup>12</sup>CO<sub>2</sub> methods make use of the fact that during terrestrial photosynthesis uptake of carbon favours the lighter <sup>12</sup>C isotope whereas discrimination between the two isotopes in oceanic carbon

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uptake is very small (Ciais et al., 1995). Interpreting  $^{13}\text{C}/^{12}\text{C}$  data is complicated, however, by a disequilibrium effect, arising because land biotic respiration occurs from carbon stocks that were assimilated up to several decades earlier. In addition,  $\text{C}_3$  and  $\text{C}_4$  plants discriminate against  $^{13}\text{C}$  to differing degrees and the global relative distributions of  $\text{C}_3$  and  $\text{C}_4$  plants, especially in the tropics, is not well known and changes with time. Heimann and Maier-Reimer (1996) suggested that even with a factor of 2 reduction in the largest uncertainties in these  $^{13}\text{C}$  methods, the uncertainty in the oceanic carbon sink would still be  $0.8 \text{ Pg C yr}^{-1}$  or greater.

Atmospheric  $\text{O}_2$  measurements provide an additional ocean/land carbon sink partitioning method as first discussed by Machta (1980) and expanded upon by Keeling (1988b), Keeling et al. (1993) and Bender et al. (1996). The atmospheric  $\text{O}_2$  method also involves assumptions and simplifications which we discuss in this paper, however, much additional information can be gained because it is an independent technique, with assumptions unrelated to other techniques such as those employing  $^{13}\text{C}$  data.  $\text{O}_2$  and  $\text{CO}_2$  are inversely linked by the processes of photosynthesis, respiration and combustion. For example, photosynthesis of land biota produces atmospheric  $\text{O}_2$  and consumes atmospheric  $\text{CO}_2$ , whereas combustion of fossil fuel or biomass burning consumes  $\text{O}_2$  and produces  $\text{CO}_2$ . However, several characteristics, all related to oceanic processes, result in decoupled changes in the atmospheric concentrations of  $\text{O}_2$  and  $\text{CO}_2$ . While rising atmospheric levels of  $\text{CO}_2$  induce a  $\text{CO}_2$  flux into the oceans, the corresponding fossil fuel-derived atmospheric  $\text{O}_2$  decrease is not offset by an  $\text{O}_2$  flux from the oceans. This is because in the ocean–atmosphere system, 99% of the  $\text{O}_2$  is in the atmosphere because  $\text{O}_2$  is relatively insoluble in seawater (e.g. Keeling, 1988b), hence the relative changes in atmospheric  $\text{O}_2$  concentrations caused by fossil fuel combustion are very small and result in no appreciable change in the equilibrium position with respect to the ocean. In contrast, only 2% of the carbon in the ocean–atmosphere system is in the atmosphere (e.g. Bender and Battle, 1999), thus changes in atmospheric  $\text{CO}_2$  are relatively significant and perturb the atmosphere–ocean equilibrium, driving a flux of  $\text{CO}_2$  across the air–sea interface into the oceans.

A second decoupling between  $\text{O}_2$  and  $\text{CO}_2$  arises at the air–sea interface. The buffering chemistry of the  $\text{CO}_2$  system in seawater causes surface waters to equilibrate with the atmosphere at least 10 times slower for  $\text{CO}_2$  than  $\text{O}_2$ . Air–sea exchanges of  $\text{CO}_2$  driven by marine photosynthesis are thus suppressed relative to those of  $\text{O}_2$ , and the same applies to air–sea exchanges driven by the ventilation of thermocline and deeper waters. These differences in equilibration rates influence air–sea  $\text{O}_2/\text{CO}_2$  exchange ratios and the relative phasing of  $\text{O}_2$  and  $\text{CO}_2$  exchanges both seasonally and interannually (Keeling and Shertz, 1992; Keeling and Severinghaus, 2000). Further suppression of  $\text{CO}_2$  exchange relative to  $\text{O}_2$  arises from thermally driven fluxes related to solubility changes, which typically have a reinforcing effect on  $\text{O}_2$  exchange and a counteracting effect on  $\text{CO}_2$  exchange driven by

photosynthesis or ventilation (Keeling and Shertz, 1992; Keeling and Garcia, 2002).

In addition, for processes on land, although  $\text{O}_2$  and  $\text{CO}_2$  are always inversely coupled, different processes have different  $\text{O}_2:\text{CO}_2$  molar exchange ratios and thus can be distinguished from each other. Fossil fuel combustion (and cement manufacture) has a global average  $\text{O}_2:\text{CO}_2$  exchange ratio of about 1.39 moles of  $\text{O}_2$  consumed per mole of  $\text{CO}_2$  produced (Keeling, 1988a), whereas land biotic photosynthesis and respiration has an average ratio of about 1.1 (Severinghaus, 1995). These ratios can vary over spatial and temporal scales, for example, in regions with high natural gas usage such as The Netherlands values greater than 1.5 have been observed (H. Meijer, personal communication), whereas a study at the WLEF tower in Wisconsin, USA, has shown ratios as low as 0.97 (B. Stephens, personal communication). Interpretation of these ratios when derived from atmospheric air samples, however, is problematic, because it is difficult to isolate the different contributing processes.

For a more in-depth discussion of the physical, chemical and biological controls and influences on atmospheric  $\text{O}_2$  concentrations, the reader is referred to Keeling et al. (1993), Bender et al. (1998) and Bender and Battle (1999).

Keeling and Shertz (1992) presented the first time series of precise atmospheric  $\text{O}_2$  measurements, showing data from 3 yr of sampling at three different locations. From these data they calculated the first estimates of oceanic and land biotic carbon sinks from atmospheric  $\text{O}_2$  measurements. Keeling et al. (1996) updated this first estimate with three more years of data, and also interpreted the latitudinal gradient of atmospheric  $\text{O}_2$  concentrations to estimate the hemispheric distribution of the land biotic sink. Bender et al. (1996) established an independent sampling program and from their data they calculated independent estimates of the oceanic and land biotic  $\text{CO}_2$  sinks. In a continuation of the same sampling program, Battle et al. (2000) updated the oceanic and land biotic sinks estimate to mid-1997 and compared these results with sinks derived from an analysis of  $^{13}\text{CO}_2$  data.

In order to estimate oceanic and land biotic  $\text{CO}_2$  sinks prior to 1989 when atmospheric  $\text{O}_2$  measurement flask programs first began, Bender et al. (1994) and Battle et al. (1996) studied air in the firm of Antarctic ice sheets at Vostok and South Pole, respectively. Another analysis of old air was carried out by Langenfelds et al. (1999) using the Cape Grim Air Archive, a suite of tanks filled with air samples between 1978 and 1997. Unfortunately, unsuitable sampling techniques meant that most of the samples contained artefacts in  $\text{O}_2$  concentration, but despite this Langenfelds et al. (1999) were able to give an estimate of the oceanic and land biotic sinks for this time period.

The remainder of this paper will update and expand on the results of Keeling and Shertz (1992) and Keeling et al. (1996), showing eight additional years of data and a larger network of sampling stations. We calculate global oceanic and land

biotic carbon sinks over different time periods during 1990–2003 and we compare these results with other published results. We present a review of different estimates attempting to account for oceanic O<sub>2</sub> outgassing caused by warming oceans, which impact global carbon sink budgets. We also demonstrate the effects of the chosen time period on global carbon sink calculations, and the effects of incorporating data from one or more additional monitoring stations. Finally we discuss the future potential for reducing uncertainties in global carbon sink estimates when derived from atmospheric O<sub>2</sub> measurements.

## 2. Definitions and formal relations

In this section we bring together formal definitions of several terms now commonly used in atmospheric O<sub>2</sub> work. A key term is the unit used for reporting O<sub>2</sub> concentrations. Typically, gas concentrations are reported in mole fraction (or ppm) units. However, for O<sub>2</sub>, because of its high abundance in the atmosphere, there is a problem using these units because of non-negligible interferences caused by dilution effects. For example, adding 1 μmol of CO<sub>2</sub> to 1 mol of air causes the O<sub>2</sub> mole fraction to decrease by 0.2 μmol, because the total number of moles has increased while the amount of O<sub>2</sub> is unchanged. Such effects could result in erroneously attributing a change in O<sub>2</sub> mole fraction to a flux of O<sub>2</sub> into or out of the atmosphere. This problem is reduced by reporting changes in O<sub>2</sub> as changes in the O<sub>2</sub>/N<sub>2</sub> ratio, which is sensitive to changes in only one interfering species, namely N<sub>2</sub>. Thus, following Keeling and Shertz (1992), we define

$$\delta(O_2/N_2) = \frac{(O_2/N_2)_{\text{sam}} - (O_2/N_2)_{\text{ref}}}{(O_2/N_2)_{\text{ref}}} \times 10^6, \quad (1)$$

where  $\delta(O_2/N_2)$  is the observed O<sub>2</sub>/N<sub>2</sub> concentration in ‘per meg’ units,  $(O_2/N_2)_{\text{sam}}$  is the ratio of O<sub>2</sub> to N<sub>2</sub> in the sample air and  $(O_2/N_2)_{\text{ref}}$  is the ratio of O<sub>2</sub> to N<sub>2</sub> in an arbitrary reference gas cylinder. The value 1 per meg is equivalent to 0.001 per mil, the unit typically used in stable isotope work.

In a given air parcel, changes in the  $\delta(O_2/N_2)$  ratio can be induced either by changes in O<sub>2</sub> or N<sub>2</sub> according to

$$\Delta(\delta(O_2/N_2)) = \left( \frac{\Delta O_2}{X_{O_2}} - \frac{\Delta N_2}{X_{N_2}} \right) \times \frac{1}{M_{\text{air}}}, \quad (2)$$

where  $\Delta O_2$  and  $\Delta N_2$  are the changes in moles of atmospheric O<sub>2</sub> and N<sub>2</sub>, respectively,  $X_{O_2}$  and  $X_{N_2}$  are the standard mole fractions in air of O<sub>2</sub> and N<sub>2</sub>, respectively, and  $M_{\text{air}}$  is the total number of moles of dry air in the air parcel. This equation is a linearization, valid when  $\Delta O_2$  and  $\Delta N_2$  are small. We use  $X_{O_2} = 0.20946$  from Machta and Hughes (1970) and  $X_{N_2} = 0.78084$  (Weast and Astle, 1982). It follows from eq. 2 that the addition of 1 μmole of O<sub>2</sub> to a mole of dry air will increase  $\Delta(\delta(O_2/N_2))$  by 4.8 per meg, while the addition of 1 μmole of N<sub>2</sub> would reduce  $\Delta(\delta(O_2/N_2))$  by 1.3 per meg. N<sub>2</sub> contributions to  $\Delta(\delta(O_2/N_2))$  are generally much smaller than O<sub>2</sub> contributions because N<sub>2</sub> is approximately four times more abundant in the atmosphere than

O<sub>2</sub>, and because N<sub>2</sub> fluxes are typically several orders of magnitude smaller than O<sub>2</sub> fluxes. In practice, the only corrections we apply for N<sub>2</sub> involve air–sea gas exchange fluxes caused by temperature-induced ocean solubility changes.

CO<sub>2</sub> concentrations are expressed as a mole fraction in dry air and thus for a given air parcel, a change in CO<sub>2</sub> concentration can be represented by

$$\Delta X_{\text{CO}_2} = \frac{\Delta \text{CO}_2}{M_{\text{air}}}, \quad (3)$$

where  $\Delta X_{\text{CO}_2}$  is the observed change in atmospheric CO<sub>2</sub> mole fraction in the air parcel, typically given in ppm units, and  $\Delta \text{CO}_2$  is the change in moles of atmospheric CO<sub>2</sub> in the air parcel.

We also frequently refer to the quantity atmospheric potential oxygen (APO) (see Stephens et al. (1998)) which reflects a weighted sum of O<sub>2</sub> and CO<sub>2</sub> in an air parcel, where the weighting is adjusted so that the sum is essentially invariant with respect to O<sub>2</sub> and CO<sub>2</sub> exchanges in land biota. A change in APO in an air parcel (in moles) is thus defined as

$$\Delta \text{APO} = \Delta O_2 + \alpha_B \Delta \text{CO}_2, \quad (4)$$

where  $\alpha_B$  represents the average O<sub>2</sub>:CO<sub>2</sub> molar exchange ratio for land biotic photosynthesis and respiration and  $\Delta O_2$  and  $\Delta \text{CO}_2$  are as defined above. We use  $\alpha_B = 1.10$  based on measurements in Severinghaus (1995), that is, 1.10 moles of atmospheric O<sub>2</sub> are produced for every mole of atmospheric CO<sub>2</sub> consumed by land biota and vice versa. We assume that this value is representative of the O<sub>2</sub>:CO<sub>2</sub> exchange ratio of all land biota. This definition of APO is a simplified version of the formula presented in Stephens et al. (1998) since here we have neglected influences from CH<sub>4</sub> and CO oxidation which have a minor influence on the APO interhemispheric gradient (the focus of Stephens et al. (1998)) but negligible influence on long-term trends in APO (the focus of this paper).

It is also useful to define an APO tracer concentration according to

$$\delta \text{APO} = \delta(O_2/N_2) + \frac{\alpha_B}{X_{O_2}} (X_{\text{CO}_2} - 350), \quad (5)$$

where  $\delta \text{APO}$  is the APO concentration in per meg in a given air parcel, and  $X_{\text{CO}_2}$  is the absolute CO<sub>2</sub> concentration in the air parcel in μmol mol<sup>-1</sup>, and where 350 is an arbitrary reference. By considering a change in APO concentration in an air parcel,  $\Delta(\delta \text{APO})$ , we can then relate this to the change in APO abundance in moles,  $\Delta \text{APO}$ , by substituting eqs. 2–4 into eq. 5 to give

$$\Delta(\delta \text{APO}) = \left( \frac{\Delta \text{APO}}{X_{O_2}} - \frac{\Delta N_2}{X_{N_2}} \right) \times \frac{1}{M_{\text{air}}}. \quad (6)$$

As an atmospheric tracer,  $\delta \text{APO}$  is sensitive to changes in O<sub>2</sub> and CO<sub>2</sub>, via eq. 4, as well as to changes in N<sub>2</sub>, via eq. 6. The tracer has the important property that it is largely conserved with respect to land biotic processes, which produce compensating effects on O<sub>2</sub> and CO<sub>2</sub>. The dominant influences on  $\delta \text{APO}$

are air–sea exchanges of  $O_2$ ,  $N_2$ ,  $CO_2$ , and combustion of fossil fuels, which alters  $O_2$  and  $CO_2$  abundances in different proportions than land biotic exchanges (Keeling et al., 1998b; Stephens et al., 1998).

The global budgets for atmospheric  $CO_2$  and  $O_2$  can be, respectively, represented by

$$\Delta CO_2 = F - O - B, \text{ and} \quad (7)$$

$$\Delta O_2 = -\alpha_F F + \alpha_B B + Z, \quad (8)$$

where  $\Delta CO_2$  and  $\Delta O_2$  are as defined above, the changes in an air parcel of atmospheric  $CO_2$  and  $O_2$ , respectively (in moles), where here the ‘air parcel’ is taken to be the global atmospheric inventory.  $F$  is the atmospheric source of  $CO_2$  emitted from fossil fuel combustion and cement manufacture,  $O$  is the oceanic  $CO_2$  sink,  $B$  is the net land biotic  $CO_2$  sink (including biomass burning, land use changes and land biotic uptake),  $\alpha_F$  and  $\alpha_B$  are the global average  $O_2:CO_2$  molar exchange ratios for fossil fuels and land biota, respectively, and  $Z$  is the net exchange of atmospheric  $O_2$  with the oceans, incorporating effects from both the solubility and biological pumps (including ocean circulation processes which may affect the efficiencies of these pumps). All quantities, except for the dimensionless exchange ratios,  $\alpha_F$  and  $\alpha_B$ , are expressed in units of moles per year. Typical values for  $\alpha_F$  and  $\alpha_B$  are 1.39 and 1.1, respectively.

The early estimates of global carbon sinks derived from atmospheric  $O_2$  and  $CO_2$  budgets assumed that there was no systematic long-term oceanic effect on atmospheric  $O_2$ .  $Z$  was thus taken to be zero to within the rather poorly constrained uncertainties (Keeling and Shertz, 1992; Keeling et al., 1996; Battle et al., 2000). This assumption appeared reasonable on the grounds that the change in atmospheric  $O_2$  abundance was too small to drive a significant disequilibrium flux. More recently it has been realized that long-term ocean warming (Levitus et al., 2000) may induce  $O_2$  outgassing due to changes in both the solubility and biological pumps (Sarmiento et al., 1998), offsetting the observed atmospheric  $O_2$  decrease. Thus recent estimates, reviewed and discussed in Section 4.3, have applied an oceanic  $O_2$  outgassing correction based on observed ocean warming (Manning, 2001; Bopp et al., 2002; Keeling and Garcia, 2002; Plattner et al., 2002; Le Quéré et al., 2003).

Previously, to solve for the oceanic and land biotic carbon sinks, eq. 8 above has been used to obtain the land biotic sink and then eq. 7 has been applied to obtain the oceanic sink (Keeling and Shertz, 1992; Keeling et al., 1996). In this paper we use a different methodology. We substitute eqs. 7 and 8 into eq. 4 to give

$$\Delta APO = (-\alpha_F + \alpha_B)F - \alpha_B O + Z, \quad (9)$$

where  $\Delta APO$  is the globally averaged change in APO in moles per year. We then solve eq. 9 for  $O$  and relate directly to the observed quantity,  $\Delta(\delta APO)$  in per meg, (using eqs. 4 and

6–8 above) to yield

$$O = \left[ (-\Delta(\delta APO) \times M_{\text{air}} \times X_{O_2}) + (-\alpha_F + \alpha_B)F + \left( \frac{Z_{\text{eff}}}{M_C} \right) \right] \frac{1}{\alpha_B}, \quad (10)$$

where

$$Z_{\text{eff}} = \left( Z - \Delta N_2 \frac{X_{O_2}}{X_{N_2}} \right) \times M_C \quad (11)$$

and where  $Z_{\text{eff}}$ , in units of  $\text{Pg C yr}^{-1}$ , represents the net effect of oceanic  $O_2$  outgassing on the oceanic and land biotic carbon sinks, taking also into consideration the offset caused by concurrent  $N_2$  outgassing.  $M_C$  is the molar mass of carbon, taken as 12.01 g/mol. In all cases, the oceanic carbon sink will increase by the amount  $Z_{\text{eff}}$  and the land biotic carbon sink will decrease by the same amount.

Using the value for  $O$  from eq. 10, we then compute the land biotic sink according to

$$B = F - O - \Delta X_{CO_2} \times M_{\text{air}} \quad (12)$$

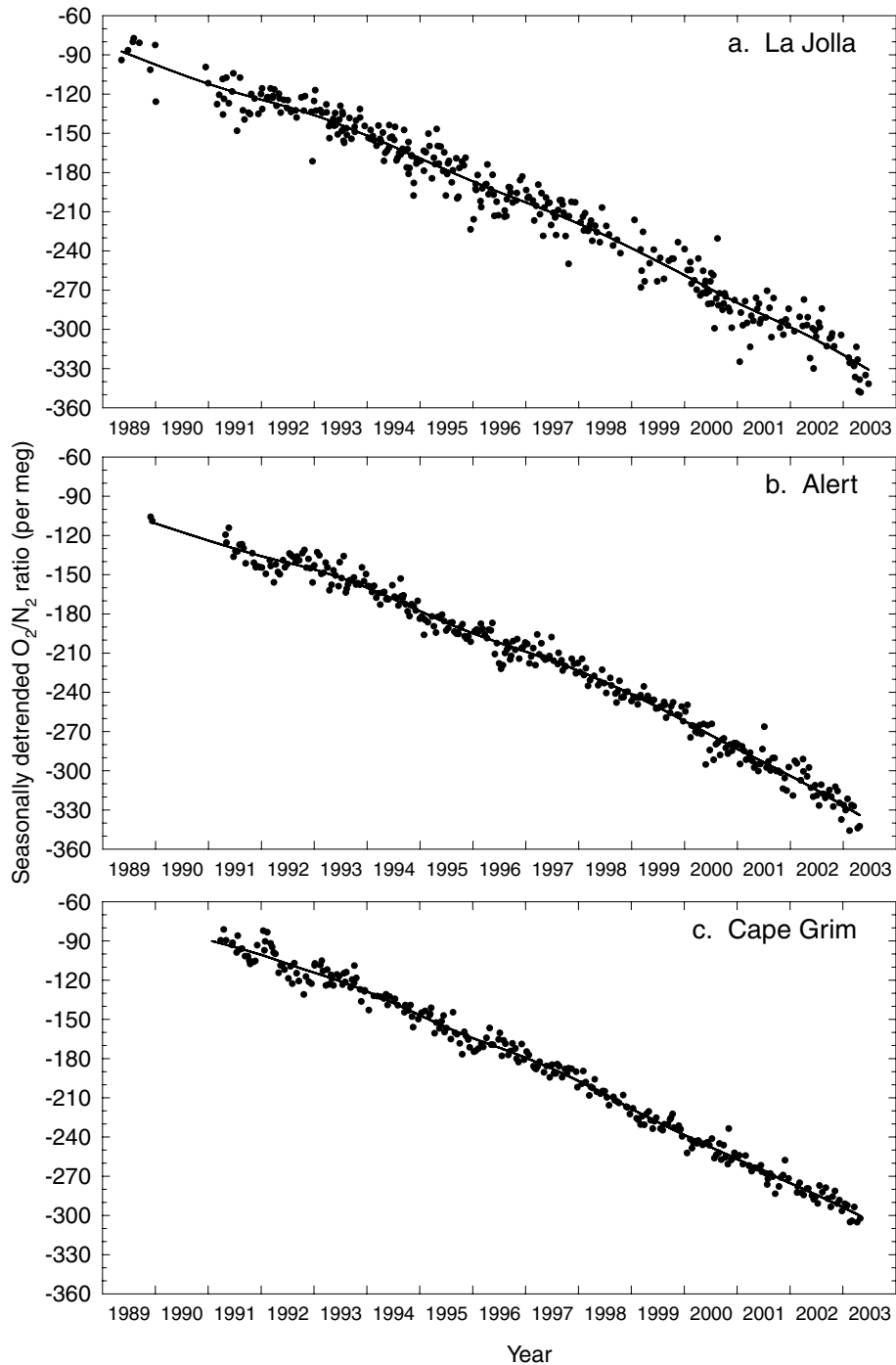
by solving eq. 7 for  $B$ , and substituting for  $\Delta CO_2$  in eq. 3.

This approach has several advantages. First, uncertainty is reduced because short-term (daily to seasonal) atmospheric variability is less in APO than in  $O_2/N_2$  ratios. This can be seen by contrasting the scatter in the data of Fig. 1 with Fig. 2 (figures discussed in Section 3 below; y-axis ranges are equivalent to aid the eye). Second, with this methodology, we have the option of using global atmospheric  $CO_2$  data sets from other sources to derive  $\Delta X_{CO_2}$ , in particular the NOAA/CMDL network, which has a much denser global coverage than our own network, thus giving a more robust estimate of the land biotic sink. And third, we expect longer term interannual variability in APO to be reduced compared to  $O_2/N_2$  ratios because the APO signal is not affected by interannual variability in the land biotic sink (assuming that possible temporal changes in the land biotic  $O_2:CO_2$  ratio have negligible influence). This approach of using APO data to solve for the oceanic carbon sink is essentially the same approach as used by Battle et al. (2000), except Battle et al. (2000) did not have  $Z$  or  $\Delta N_2$  terms.

### 3. Observed long-term atmospheric trends

Figures 1 and 2 show  $O_2/N_2$  ratios and APO, respectively, for La Jolla, California (LJO), Alert, Canada (ALT) and Cape Grim, Australia (CGO), the three stations with the longest records in our network. The data have been filtered to remove a four-harmonic fit representing the average seasonal cycle. Each data point reflects the seasonally adjusted average of flask replicates sampled on a given date. Also shown is a stiff Reinsch (1967) spline to account for the interannual trend and other non-seasonal variability.

The data show consistent downward trends at all stations reflecting the global decreases in  $O_2/N_2$  ratio and APO. Although



*Fig. 1.* O<sub>2</sub>/N<sub>2</sub> ratio data in per meg from La Jolla, California, U.S.A. (LJO; 32°52'N, 117°15'W, 15 m a.s.l. (above sea level)), Alert, Canada (ALT; 82°27'N, 62°31'W, 210 m a.s.l.) and Cape Grim, Tasmania, Australia (CGO; 40°41'S, 144°41'E, 94 m a.s.l.). The four harmonic component of the least-squares curve fit to the data has been removed, resulting in the seasonally adjusted data shown. Each point is the average of replicate flask samples collected on a given date.

there is some interannual variability to the trends as well as variations between the three stations, overall the station trends are highly concordant. In this paper we are principally interested in quantifying overall long-term trends; the gradients between

stations and interannual variability will be discussed in more detail elsewhere. As outlined in the Appendix, we estimate uncertainties in our long-term trends of  $\pm 6$  per meg and  $\pm 4$  per meg for the periods 1990–2000 and 1993–2003, respectively.

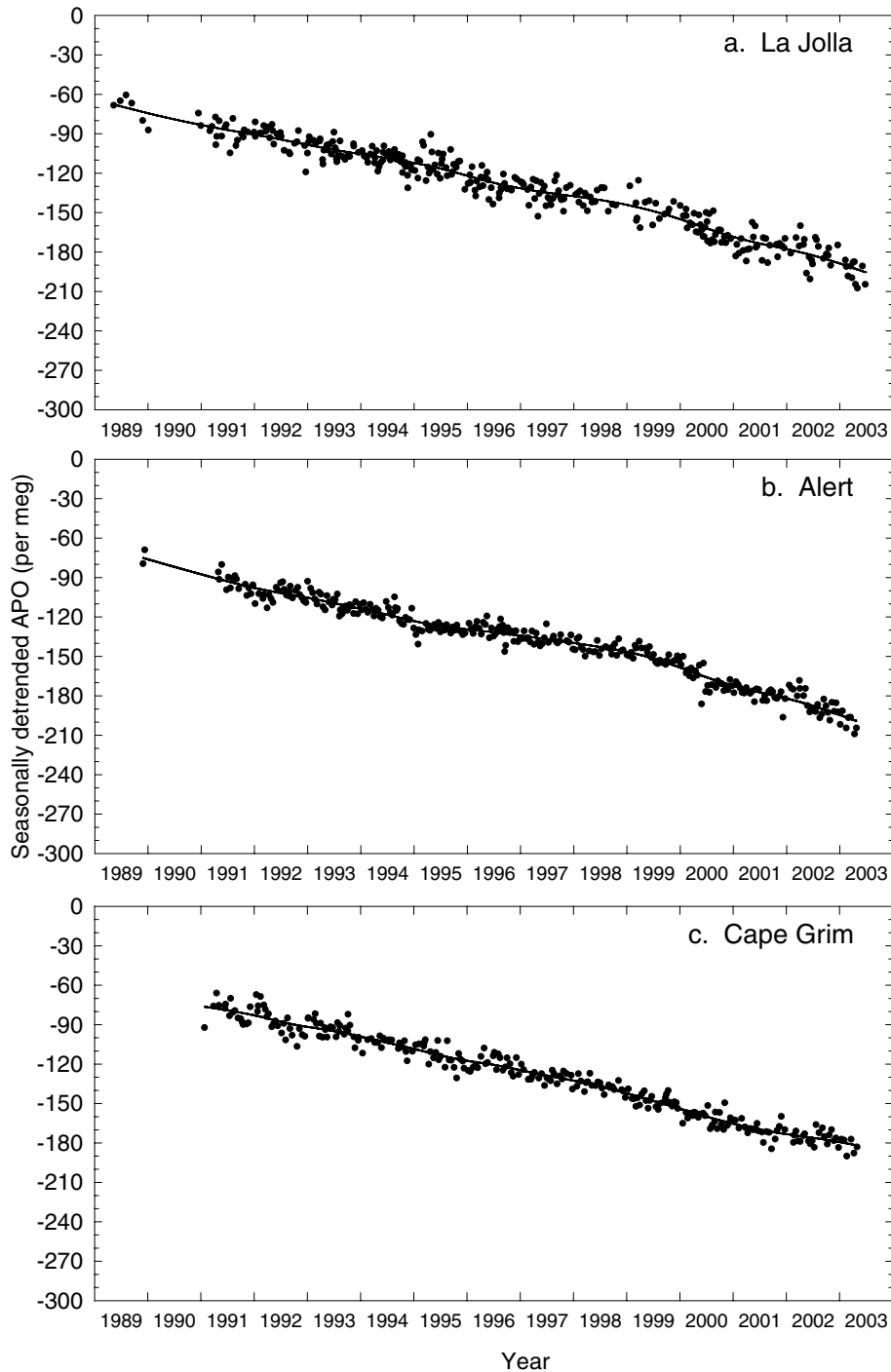


Fig. 2. As for Figure 1, but showing APO in per meg. y-axis ranges are the same as in Figure 1, therefore, scatter in the data can be directly compared between  $O_2/N_2$  ratios and APO. The figures shows that variability is less in APO than in  $O_2/N_2$  ratios.

#### 4. Global oceanic and land biotic carbon sinks

##### 4.1. Calculation for the decade from 1993 to 2003

Using eqs. 10 and 12, we calculate what we believe is our best estimate for global carbon sinks over a 10-yr period, shown in

Table 1, Part 1. This covers the period from 1993–2003, that is, after we improved our gas handling procedures in 1992 (Keeling et al., 2005), and when we have full records from both Southern Hemisphere and Northern Hemisphere stations. We use our atmospheric data from Alert, La Jolla and Cape Grim to calculate

Table 1. Different estimates of oceanic and land biotic carbon sinks

Time Period	Stations	$\Delta$ APO (per meg yr <sup>-1</sup> )	$\Delta$ CO <sub>2</sub> (ppm yr <sup>-1</sup> )	Z <sub>eff</sub> (Pg C/y)	Fossil Fuel (F) (Pg C yr <sup>-1</sup> )	Ocean sink (O) <sup>d</sup> (Pg C yr <sup>-1</sup> )	Land sink (B) <sup>a</sup> (Pg C yr <sup>-1</sup> )
Part 1 Our most recent decadal results							
1993–2003 <sup>b</sup>	ALT, LJO, CGO	-8.78	1.76	0.48	6.48	2.24	0.51
Part 2 Effects of different oceanic O <sub>2</sub> outgassing estimates							
1990–2000	IPCC (2001), Manning (2001)	-8.17	1.51	0.10	6.33	1.71 <sup>c</sup>	1.41 <sup>c</sup>
1990–2000	Keeling and Garcia (2002)	-8.17 <sup>d</sup>	1.51 <sup>d</sup>	0.28	6.33 <sup>d</sup>	1.89 <sup>e</sup>	1.23 <sup>e</sup>
1990–2000	Plattner et al. (2002)	-8.17 <sup>d</sup>	1.51 <sup>d</sup>	0.78	6.33 <sup>d</sup>	2.4	0.7
1990–2000	Le Quéré et al. (2003)	-8.17 <sup>d</sup>	1.51 <sup>d</sup>	0.33	6.33 <sup>d</sup>	1.9	1.2
Part 3 <sup>f</sup> Isolating discrepancies with Battle et al. (2000)							
1991.5–1997.5	Battle et al. (2000)	-8.79 <sup>g</sup>	1.34 <sup>g</sup>	0	6.39 <sup>h</sup>	2.0 <sup>h</sup>	1.4 <sup>h</sup>
1991.5–1997.5	SIO data set: ALT, CGO	-7.78	1.28	0	6.39 <sup>i</sup>	1.4	2.2
1992–1997.5	Princeton data set: CGO only	-8.75	1.46	0			
1992–1997.5	SIO data set: CGO only	-8.65	1.41	0			
Part 4 <sup>j</sup> Effects from stations used in constructing global averages							
1991.5–2002.5	ALT, LJO, CGO	-8.46	1.57	0.48	6.44	2.13	0.98
	ALT, LJO	-8.23	1.57	0.48	6.44	2.03	1.07
1994–2002.5	ALT, LJO, CGO	-8.70	1.78	0.48	6.53	2.19	0.55
	ALT, LJO, KUM, SMO, CGO	-8.74	1.78	0.48	6.53	2.21	0.53
1997.5–2002.5	ALT, LJO, CGO	-9.24	1.93	0.48	6.60	2.38	0.11
	ALT, LJO, KUM, SMO, CGO	-9.12	1.93	0.48	6.60	2.33	0.16
	ALT, CBA, LJO, KUM, SMO, CGO, PSA	-9.04	1.93	0.48	6.60	2.30	0.20
Part 5 Effects from decadal time period used							
1991.5–2001.5	ALT, LJO, CGO	-8.80	1.52	0.48	6.42	2.27	0.92
1992–2002	ALT, LJO, CGO	-8.77	1.58	0.48	6.44	2.25	0.83
1992.5–2002.5	ALT, LJO, CGO	-8.48	1.65	0.48	6.47	2.13	0.83
1993–2003	ALT, LJO, CGO	-8.78	1.76	0.48	6.48	2.24	0.51
1993.5–2003.5	ALT, LJO, CGO	-9.24	1.84	0.48	6.52	2.41	0.21

<sup>a</sup>All calculations in this table of the oceanic and land biotic carbon sinks (except those which report results from prior literature) used eqs. 10 and 12, and used  $\alpha_B = 1.1$ ,  $X_{O_2} = 0.2095$ ,  $X_{N_2} = 0.7808$ ,  $Z = 0.45 \times 10^{14}$  mol yr<sup>-1</sup>,  $\Delta N_2 = 0.20 \times 10^{14}$  mol yr<sup>-1</sup> and  $M_{air} = 1.769 \times 10^{20}$  mol. All calculations of land biotic sinks, except those in Part 3, used global CO<sub>2</sub> data from the CMDL/NOAA network (P. Tans, personal communication).

<sup>b</sup>A time period of, for example, 1993–2003 represents a 10-yr period, with annual average endpoints centred on January 1993 and January 2003.

<sup>c</sup>As explained in the Appendix, the numbers reported here are actually adjusted by 0.03 Pg C yr<sup>-1</sup> from those reported in Manning (2001).

<sup>d</sup>These prior studies used the same values as given in the IPCC assessment.

<sup>e</sup>These values have also been adjusted by 0.03 Pg C yr<sup>-1</sup> from the values presented in the Keeling and Garcia (2002) paper, since they applied their correction directly to the values given in Manning (2001).

<sup>f</sup>In this Part we calculated CO<sub>2</sub> trends only from the stations indicated in the ‘stations’ column from the network indicated (Scripps or Princeton), following the methodology of Battle et al. (2000).

<sup>g</sup>Calculated with our methodology using the original Battle et al. (2000) data set.

<sup>h</sup>Taken directly from Battle et al. (2000).

<sup>i</sup>We used the same value for fossil fuel emissions as Battle et al. (2000), to better assess the cause of differences in the oceanic and land biotic sinks. Using our own data would have resulted in a fossil fuel emissions value of 6.30 Pg C yr<sup>-1</sup>.

<sup>j</sup>In all analyses in this Part, Northern Hemisphere stations were averaged to give a Northern Hemisphere proxy for APO, Southern Hemisphere stations were averaged to give a Southern Hemisphere proxy, and global average trends were then computed as the average of these two proxies. We used a fixed oceanic outgassing term so as to assess the effect only from the number of stations.

the global atmospheric trend in APO in a similar manner to Keeling et al. (1996). We calculate the global atmospheric trend in CO<sub>2</sub> from data provided by the more dense CMDL/NOAA flask sampling network (P. Tans, personal communication). We use fossil fuel emission data from Marland et al. (2002) up to 2000. For years 2001–2003 we approximate fossil fuel emissions as

being the same as in year 2000. A sensitivity analysis showed that increasing the estimate for each of these last 3 years by 0.3 Pg C has an impact of less than 0.1 Pg C yr<sup>-1</sup> on the derived global sinks. We take the ocean heat content anomaly over this period as 0.29 PW from Willis et al. (2004) (corresponding to  $0.92 \times 10^{22}$  J yr<sup>-1</sup>) and use Keeling and Garcia’s (2002) values

of 4.9 nmol/J and 2.2 nmol/J for the relationship between outgassing per unit heat content of O<sub>2</sub> and N<sub>2</sub>, respectively, giving outgassing of  $0.45 \times 10^{14}$  mol O<sub>2</sub> yr<sup>-1</sup> and  $0.20 \times 10^{14}$  mol N<sub>2</sub> yr<sup>-1</sup>. These outgassing terms result in a correction of Z<sub>eff</sub> = 0.48 Pg C yr<sup>-1</sup> in the global carbon sinks. Thus we find:

oceanic carbon sink =  $2.24 \pm 0.61$  Pg C/yr, and

land biotic carbon sink =  $0.51 \pm 0.74$  Pg C/yr.

(Uncertainties given are 1σ standard deviations, as for all other uncertainties given in this paper).

#### 4.2. Calculation for the decade from 1990 to 2000

The data and results presented in this section and shown in Table 1, Part 2, first row, were already used in the IPCC (Intergovernmental Panel for Climate Change) Third Assessment

Report (Prentice et al., 2001), in their presentation of the oceanic and land biotic sinks for the 10-yr period from 1990 to 2000 (referencing Manning (2001)). Our calculation technique subtracts an APO global annual average centred on 1 January 2000 from an annual average centred on 1 January 1990, and therefore, requires atmospheric measurements spanning the period from 1 July 1989 to 1 July 2000, that is, 11 full years of data. La Jolla is the only station for which we have an uninterrupted data set over this time period. The Alert record comes close, with samples collected on two dates in 1989, in November and December. Our strategy used both the La Jolla and Alert records to define a global average, with a slightly different method of calculating the beginning point of the Alert record. In the Appendix this difference is described, along with our uncertainty estimates.

Global averages of APO were calculated in a similar manner to Keeling et al. (1996). That is, for each of La Jolla and Alert we

Table 2. Globally and annually averaged trends from 1990 to 2000<sup>a</sup>

Year	O <sub>2</sub> /N <sub>2</sub> (per meg)			APO <sup>b</sup> (per meg)		
	Alert	La Jolla	Average	Alert	La Jolla	Average
1990.0	-111.1	-95.7	-103.4	-75.6	-74.7	-75.1
1990.5	-117.7	-107.3	-112.5	-81.5	-79.9	-80.7
1991.0	-123.3	-113.8	-118.6	-87.2	-83.5	-85.4
1991.5	-131.4	-125.1	-128.2	-93.2	-89.3	-91.3
1992.0	-140.8	-127.9	-134.4	-100.2	-90.7	-95.4
1992.5	-141.6	-129.0	-135.3	-102.6	-94.1	-98.3
1993.0	-142.1	-134.7	-138.4	-103.3	-98.9	-101.1
1993.5	-149.3	-140.6	-144.9	-109.0	-101.6	-105.3
1994.0	-158.4	-150.4	-154.4	-113.6	-106.5	-110.1
1994.5	-168.3	-162.4	-165.3	-117.2	-110.1	-113.7
1995.0	-180.2	-169.3	-174.8	-125.3	-112.5	-118.9
1995.5	-191.5	-178.5	-185.0	-131.2	-115.7	-123.4
1996.0	-197.0	-192.3	-194.6	-130.9	-123.8	-127.4
1996.5	-204.7	-196.9	-200.8	-132.9	-129.8	-131.3
1997.0	-211.2	-201.8	-206.5	-136.7	-132.9	-134.8
1997.5	-216.1	-209.9	-213.0	-139.1	-136.1	-137.6
1998.0	-225.4	-217.8	-221.6	-143.4	-139.1	-141.2
1998.5	-236.2	-229.4	-232.8	-146.7	-143.0	-144.9
1999.0	-244.6	-239.9	-242.2	-147.1	-145.1	-146.1
1999.5	-250.8	-245.3	-248.0	-150.8	-147.2	-149.0
2000.0	-262.5	-255.7	-259.1	-159.3	-154.4	-156.8
Trend <sup>c</sup>	-151.4	-160.0	-155.7	-83.72	-79.73	-81.73
Trend (10 <sup>14</sup> mol) <sup>d</sup>	-56.13	-59.31	-57.72	-31.03	-29.55	-30.29

<sup>a</sup>All data are annual averages, calculated every 6 months, centered on 1 January and 1 July of each year, as described in the text (section 4.2). The 'average' columns are the averages of Alert and La Jolla.

<sup>b</sup>APO, Atmospheric Potential Oxygen, is defined in section 2, and is essentially the O<sub>2</sub>/N<sub>2</sub> ratio added to 1.1 times the concurrent CO<sub>2</sub> concentration value. APO is an approximately conservative tracer with respect to the land biota.

<sup>c</sup>Global trends for the decade from 1990 to 2000 are calculated simply as the 1990.0 annual averages subtracted from the 2000.0 averages.

<sup>d</sup>Uses total moles of dry air equal to  $1.769 \times 10^{20}$ , and an atmospheric O<sub>2</sub> mole fraction of 0.2095 (Machta and Hughes, 1970).



used the curve fits described in Section 3 to adjust all flask data to the 15th of each month, then monthly means were calculated. For the few months with no flask data, monthly means were obtained from the curve fits. Twelve consecutive monthly means were averaged to compute annual means for APO, with this calculation repeated at 6-month time steps centred on 1 January and 1 July of each year.

Table 2 shows annual averages of both  $O_2/N_2$  ratio data and calculated APO data for La Jolla, Alert and the average of these two stations. These APO annual averages are shown graphically as solid circles in Fig. 3, which also shows calculated annual averages of  $CO_2$  from these two stations. These data points show the expected trends of decreasing APO over time and increasing  $CO_2$  concentrations. Thus the observed atmospheric change at Alert and La Jolla over the 10-yr period from 1990 to 2000 was an APO decrease of  $81.7 \pm 8.2$  per meg. For  $\Delta X_{CO_2}$  (eq. 12), as proposed above, NOAA/CMDL data were used (Conway et al., 1994), thus yielding a land biotic carbon sink that is compatible with the more globally representative atmospheric  $CO_2$  increase as determined by the more extensive NOAA/CMDL network.

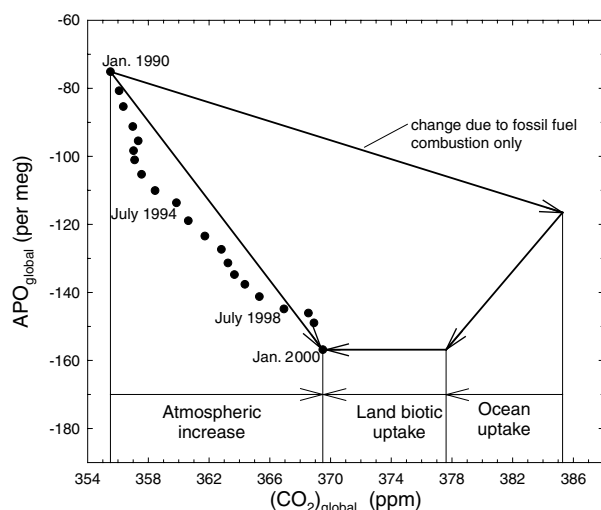


Fig. 3. Vector diagram showing the calculation of the global oceanic and land biotic carbon sinks. Solid circles are annual averages of the observed APO and  $CO_2$  concentrations, calculated by averaging data from Alert and La Jolla. Also shown is a fossil fuel combustion line, representing the change in APO and atmospheric  $CO_2$  concentrations that would have occurred if all  $CO_2$  emitted remained in the atmosphere. The slope for the oceanic sink is fixed to an APO: $CO_2$  molar ratio of 1.1 (i.e.  $\alpha_B$ , see eq. 4), whereas the land biotic sink is a horizontal line, having no affect on APO, as explained in the text (Section 2). Note that in this figure,  $CO_2$  data shown are from our own measurements made at La Jolla and Alert, not from the NOAA/CMDL network used in the IPCC calculations of Section 4.2. This is because the NOAA/CMDL data were not in a format that allowed conversion to this graphical format. However, the purpose of this figure is descriptive only. For simplification purposes, this figure does not show the oceanic  $O_2$  outgassing term,  $Z_{eff}$ .

Table 3. Global fossil fuel combustion data for the 1990s

Year	$CO_2$ produced <sup>a</sup> (Pg C) <sup>b</sup>	$O_2$ consumed <sup>c</sup> (Pg $O_2$ )	APO consumed (Pg $O_2$ )	$O_2:C$ molar ratio
1990	6.126	22.648	1.799	1.388
1991	6.214	23.091	1.825	1.395
1992	6.088	22.605	1.788	1.394
1993	6.093	22.657	1.789	1.396
1994	6.253	23.214	1.836	1.393
1995	6.401	23.715	1.880	1.391
1996	6.553	24.330	1.925	1.394
1997	6.654	24.662	1.954	1.391
1998	6.649	24.747	1.953	1.397
1999	6.492	24.217	1.907	1.400
Total	63.523	235.886	18.656	1.394 <sup>d</sup>
Total ( $10^{14}$ mol)	52.89	73.71	15.53	
Total (ppm, per meg)	29.92	198.90	41.91	

<sup>a</sup>Data are from Marland et al. (2002), and include  $CO_2$  produced from solid, liquid and gas fuel, as well as from flared gas and cement manufacture.

<sup>b</sup>1 Pg is  $10^{15}$  g, equivalent to 1 Gt.

<sup>c</sup> $O_2$  consumed is calculated assuming full combustion of all fossil fuel types, and using  $O_2:CO_2$  molar ratios for each fuel type from Keeling (1988). That is,  $O_2:CO_2$  is 1.17 for solid fuel; 1.44 for liquid fuel; 1.95 for gas fuel; and 1.98 for flared gas. (Cement manufacture does not consume  $O_2$ ).

<sup>d</sup>Average  $O_2:CO_2$  molar ratio.

The global value for  $\Delta X_{CO_2}$  was determined to be 15.1 ppm  $CO_2$  (equivalent to 32.1 Pg C) using a 2-D atmospheric transport model described in Tans et al. (1989).

The amount of  $CO_2$  produced from global fossil fuel combustion and cement manufacture was calculated from data in Marland et al. (2002). The corresponding amount of  $O_2$  (and thus APO) consumed was calculated from a knowledge of the relative fraction of the different fossil fuel types combusted each year (Marland et al., 2002) and the average  $O_2:CO_2$  oxidative ratios for each fuel type given in Keeling (1988a), assuming full combustion of fossil fuel carbon to  $CO_2$ . These data are shown in Table 3. For the 10-yr period from January 1990 to January 2000 these global fossil fuel emissions resulted in  $63.5 \pm 3.8$  Pg C of  $CO_2$  being released to the atmosphere (or  $52.9 \times 10^{14}$  mol  $CO_2$ , F in eq. 10; see also bottom of Table 3), and, if no other processes were involved, would have resulted in a total APO decrease of  $41.9 \pm 2.5$  per meg and an atmospheric  $CO_2$  increase of  $29.9 \pm 1.8$  ppm (see bottom of Table 3). These hypothetical APO and  $CO_2$  changes are shown in Fig. 3 as a straight line labelled 'change due to fossil fuel combustion only'.

The oceanic  $O_2$  outgassing term, Z in eqs. 8, 9 and 11, should incorporate effects due to both the solubility and biological pumps, but in the IPCC calculations repeated here only a solubility correction was applied. A  $1 W/m^2$  warming rate was

assumed over the global oceans from 1990 to 2000 ( $0.71 \text{ W/m}^2$  over the entire surface of the Earth), corresponding to a total of  $1.14 \times 10^{23} \text{ J}$  of energy being absorbed by the oceans over this time period. A 100% uncertainty was assigned to this warming rate. We use an  $\text{O}_2$  solubility temperature dependence of  $5.818 \times 10^{-6} \text{ mol/kg/K}$  (Weiss, 1970), calculated assuming a linear relationship between waters at  $0^\circ\text{C}$  and  $24^\circ\text{C}$ , resulting in a total of  $1.59 \times 10^{14} \text{ mol O}_2$  outgassed from the oceans from 1990 to 2000 ( $Z$  in eq. 11). Net  $\text{N}_2$  outgassing from the oceans will also occur, offsetting the  $\text{O}_2$  outgassing as observed in the atmospheric  $\text{O}_2/\text{N}_2$  ratio (or APO) according to eqs. 2, 6 and 10. Using an  $\text{N}_2$  solubility temperature dependence of  $9.468 \times 10^{-6} \text{ mol/kg/K}$  (Weiss, 1970), this results in a total of  $2.58 \times 10^{14} \text{ mol N}_2$  outgassed from the oceans from 1990 to 2000 ( $\Delta\text{N}_2$  in eq. 11).

Inserting the above data into eqs. 10 and 12 results in average oceanic and land biotic carbon sinks for the 10-yr period from 1990 to 2000 of:

oceanic carbon sink =  $1.71 \pm 0.52 \text{ Pg C/yr}$ , and

land biotic carbon sink =  $1.41 \pm 0.66 \text{ Pg C/yr}$ .

(Note that Manning (2001) reported oceanic and land biotic sinks of  $1.68$  and  $1.44 \text{ Pg C yr}^{-1}$ , respectively. The reason for these small differences is given in the Appendix). These results show that the global oceanic and land biotic carbon sinks are of approximately comparable magnitude and importance in the global carbon budget. However, it should be kept in mind that this value for the land biotic carbon sink is the net effect of all processes which have an impact on the land biota. The gross land biotic sink is much larger, since the net sink takes into account carbon sources such as biomass burning, deforestation and other land-use changes. These results are also shown graphically in Fig. 3. Here the land biotic carbon sink can be represented by a horizontal line, since it has no influence on APO, whereas the oceanic carbon sink has a slope of  $\alpha_B$ .

In summary, we emphasize that in the approach used here, the global oceanic carbon sink was determined from atmospheric data in the Northern Hemisphere only, and then using this result, the land biotic carbon sink was calculated from globally averaged  $\text{CO}_2$  data. This approach provides a more robust estimate of the land biotic sink, advantageous since the land sink exhibits much greater natural variability than the oceanic sink (Battle et al., 2000; Manning, 2001). We also emphasize that our approach accounts only for the effect of ocean warming on  $\text{O}_2$  and  $\text{N}_2$  solubility, neglecting any warming effects on the biological pump. We expect that this resulted in a small underestimation of the oceanic sink and overestimation of the land biotic sink.

#### 4.3. Oceanic outgassing

Since our calculations for the IPCC report were completed, four studies (Bopp et al., 2002; Keeling and Garcia, 2002; Plattner

et al., 2002; Le Quéré et al., 2003) have produced independent estimates for  $Z$  and  $Z_{\text{eff}}$  based on ocean warming effects. All of these included estimates of the biological pump effect, based on the hypothesis that this effect might also be closely related to global ocean heat fluxes (Keeling and Garcia, 2002). This relationship is only an approximation, however, and may change over time. The range of values found for  $Z_{\text{eff}}$  in the literature can be seen in the final column of Table 4. Despite the fact that these estimates agree to within their uncertainties ( $\sim \pm 0.5 \text{ Pg C yr}^{-1}$ ), some differences are still comparatively large when considered in the context of the net global carbon sinks. Here we examine some of the assumptions applied and data used in deriving these different estimates.

All estimates essentially involve establishing a linear relationship between the oceanic  $\text{O}_2$  outgassed and the ocean heat flux (column 3 of Table 4), then multiplying this relationship by an estimate of the ocean heat flux (column 4 of Table 4), resulting in the oceanic  $\text{O}_2$  outgassed in moles (column 5 of Table 4,  $Z$ ). Finally moles of  $\text{O}_2$  outgassed is converted into the effect on the oceanic and land biotic carbon sinks, that is,  $Z_{\text{eff}}$ , using eq. 11.

Keeling and Garcia (2002) derived an  $\text{O}_2$  flux/heat flux relationship by considering the relationship between the tracer  $\text{O}_2^*$  and potential temperature ( $\Theta$ ) from GEOSECS data.  $\text{O}_2^* = \text{O}_2 + 175\text{PO}_4$  is mostly conserved below the sea surface, where photosynthesis and respiration produce compensating effects on  $\text{O}_2$  and  $\text{PO}_4$ . Hence  $\text{O}_2^*$  is a conservative tracer with respect to oceanic biotic activity and thus is a measure of  $\text{O}_2$  gained or lost through air-sea gas exchange (Keeling and Peng, 1995; Gruber et al., 2001). It is then straightforward to convert  $\text{O}_2^*/\Theta$  in  $\mu\text{mol kg}^{-1} \text{ }^\circ\text{C}^{-1}$  to moles of  $\text{O}_2$  outgassed per Joule of warming using the density and heat capacity of seawater. Thus Keeling and Garcia (2002) calculated a global  $\text{O}_2$  flux/heat flux value from a weighted average of  $\text{O}_2^*/\Theta$  data from several ocean basins. This approach assumes that steady-state  $\text{O}_2$  flux/heat flux relationships also apply to transient warming. Bopp et al. (2002) used an ocean biogeochemistry model nested in a coupled climate model and Plattner et al. (2002) used a physical-biogeochemical model in deriving their  $\text{O}_2$  flux/heat flux relationships. Le Quéré et al. (2003) simply used the Bopp et al. (2002) estimate. The three studies produced strikingly similar results of  $\sim 5\text{--}6 \text{ nmol}$  of  $\text{O}_2$  outgassed per Joule of warming, when all studies considered the global ocean at all depths. Plattner et al. (2002) also calculated  $8.3 \text{ nmol/J}$  when they considered only the top 300 m of the surface ocean.

In estimating the global heat flux anomaly, the four studies differed markedly. Bopp et al. (2002) used ocean heat flux data from Levitus et al. (2000), deriving an average value of  $1.0 \times 10^{22} \text{ Joules}$  of warming per year for the period from 1990 to 1997. Bopp et al. (2002) then estimated oceanic and land biotic carbon sinks for this 7-yr period. Plattner et al. (2002) also used the Levitus et al. (2000) heat flux data, but calculated an average value of  $1.24 \times 10^{22} \text{ J yr}^{-1}$  from 1990 to 1995. Plattner et al. (2002) then extrapolated their result to the year 2000 by

Table 4. Estimates of oceanic O<sub>2</sub> outgassing

Study	Time period	O <sub>2</sub> flux/ heat flux (nmol/J)	heat flux (10 <sup>22</sup> J yr <sup>-1</sup> )	atmospheric increase, Z (10 <sup>14</sup> mol O <sub>2</sub> yr <sup>-1</sup> )	effect on carbon sinks, Z <sub>eff</sub> (Pg C yr <sup>-1</sup> )
IPCC (2001), Manning (2001)	1990–2000	1.4 <sup>a</sup>	1.14	0.16 ± 0.16	0.10
Keeling and Garcia (2002)	1990–2000	4.9 ± 1.6	0.6 ± 0.18	0.29 ± 0.4	0.28
Bopp et al. (2002) model	1990–2000	6.1 ± 0.6	0.55	0.34	0.3
Bopp et al. (2002) with Levitus et al. (2000)	1990–1997	6.1 ± 0.6	1.0	0.61	0.66 ± 0.5 <sup>b</sup>
Plattner et al. (2002) model	1990–2000	5.9	0.71	0.42	0.46 <sup>c</sup>
Plattner et al. (2002) with Levitus et al. (2000)	1990–2000	5.9	1.24	0.73	0.78 ± 0.5
Plattner et al. (2002) with Levitus et al. (2000) 0–300 m	1990–2000	8.3	0.67	0.56	0.60
Le Quéré et al. (2003)	1990–2000	6.1 <sup>d</sup>	0.55	0.34	0.33
This work	1993–2003	4.9 <sup>e</sup>	0.92 <sup>e</sup>	0.45	0.48

<sup>a</sup>The IPCC result considered only O<sub>2</sub> outgassing caused by the O<sub>2</sub> solubility dependence on temperature, thus, this value is much lower than the other studies.

<sup>b</sup>Bopp et al. (2002) give a value of 0.5 Pg C yr<sup>-1</sup> in their paper. However, this value had erroneously subtracted the temperature solubility component of O<sub>2</sub> outgassing (L. Bopp, personal communication).

<sup>c</sup>Plattner et al. (2002) did not give this value, therefore, we calculated it using our eq. 11 and their given values of 0.42 × 10<sup>14</sup> mol O<sub>2</sub> yr<sup>-1</sup> and 2.1 nmol N<sub>2</sub>/J.

<sup>d</sup>This study used the O<sub>2</sub> flux/heat flux relationship derived in Bopp et al. (2002).

<sup>e</sup>We used the O<sub>2</sub> flux/heat flux relationship derived in Keeling and Garcia (2002), and the heat flux value from Willis et al. (2004).

assuming the same linear trend of  $1.24 \times 10^{22}$  J yr<sup>-1</sup> for the second half of the decade, a procedure which does not appear to be supported by subsequently available data. Keeling and Garcia (2002) used a value of  $0.6 \times 10^{22}$  J yr<sup>-1</sup> for the decade of the 1990s, calculated from both the Levitus et al. (2000) data set and using model simulations (Barnett et al., 2001; Levitus et al., 2001) to extrapolate up to 2000.

In order to update the global heat flux estimates to include the last few years, Le Quéré et al. (2003) used global mean sea surface height anomaly (SSHa) data (Cabanès et al., 2001) as a proxy for ocean heat content, deriving a value of  $0.55 \times 10^{22}$  J yr<sup>-1</sup> for the 1990s. Recently, however, Miller and Douglas (2004) have suggested that non-steric effects are the dominant contribution to SSHa, calling into question the approach of Le Quéré et al. (2003). The most recent estimate for ocean heat content was calculated by Willis et al. (2004) finding a value of  $0.92 \times 10^{22}$  J yr<sup>-1</sup> for the period 1993–2003 for the upper 750 m of the water column. This result was found by combining satellite altimetric height data with *in situ* temperature profiles.

The number of moles of O<sub>2</sub> outgassed, Z, varies between the recent studies from  $0.29 \times 10^{14}$  to  $0.73 \times 10^{14}$  mol yr<sup>-1</sup>, not including the IPCC result. The effect on the oceanic and land biotic carbon sinks was then calculated after subtracting an N<sub>2</sub> outgassing term, where all studies used similar N<sub>2</sub> flux/heat

flux relationships, ranging from 2.1 nmol J<sup>-1</sup> to 2.3 nmol J<sup>-1</sup>. However, because widely different heat fluxes were used, the N<sub>2</sub> correction was of differing magnitude between the studies. The final results of the different studies for the oceanic and land biotic carbon sinks are summarized in Part 2 of Table 1 (for those studies which spanned the entire 1990s decade).

In summary, although it is reassuring that three independent studies produced very similar relationships between oceanic O<sub>2</sub> outgassing and heat flux, this relationship remains poorly established observationally. Also, all three studies share certain assumptions such as assuming that phosphate is the ultimate limiting nutrient, and that O<sub>2</sub>/PO<sub>4</sub> ratios have the same constant value (Keeling and Garcia, 2002). For example, Plattner et al. (2002) found that using an O<sub>2</sub>/PO<sub>4</sub> ratio of -138 (Redfield et al., 1963) (instead of -170) resulted in a 15% reduction in the amount of O<sub>2</sub> outgassed. The main reason for discrepancies in different Z<sub>eff</sub> estimates lies in the estimates of total ocean heat flux as shown in Table 4, and, as more heat flux data become available, these discrepancies will be significantly reduced. Finally, it should be kept in mind that even when discrepancies between the existing studies can be reconciled, all studies had large uncertainties for their estimates of O<sub>2</sub> outgassing corrections to the carbon sinks, of up to ±0.5 Pg C yr<sup>-1</sup>.

It has been suggested that ocean warming could also result in CO<sub>2</sub> outgassing (Siegenthaler and Oeschger, 1978;

Keeling et al., 1989a; Sarmiento and Le Quéré, 1996). This affects the ocean uptake of  $\text{CO}_2$  driven by rising atmospheric  $\text{CO}_2$  concentration. However, it will have no effect on the oceanic carbon sink as calculated from atmospheric  $\text{O}_2/\text{N}_2$  and  $\text{CO}_2$  data, which accounts for oceanic uptake by all processes (once the  $\text{O}_2$  budget is correctly balanced with the outgassing term,  $Z$ , as described above). Care must, therefore, be taken in comparing our results of oceanic carbon uptake to other methods which neglect warming effects, as discussed below in Section 4.6.

#### 4.4. Comparisons with Battle et al. (2000)

Battle et al. (2000) reported oceanic and land biotic carbon sinks for the 6-yr period from July 1991 to July 1997. They constructed global trends in a similar manner as presented here. As a Northern Hemisphere proxy they used our  $\text{O}_2/\text{N}_2$  data from Alert in 1991 and 1992 which they ‘spliced’ together with their own data from Point Barrow, Alaska ( $71^\circ 19' \text{N}$ ,  $156^\circ 36' \text{W}$ ) from 1993 onward. As a Southern Hemisphere proxy they used Cape Grim data averaged from both their own independent flask collection program as well as our Cape Grim data. They combined these data with  $\text{CO}_2$  data from the NOAA/CMDL (Boulder, Colorado) program, to estimate oceanic and land biotic sinks of  $2.0 \pm 0.6 \text{ Pg C yr}^{-1}$  and  $1.4 \pm 0.8 \text{ Pg C yr}^{-1}$ , respectively. This estimate did not make allowance for any oceanic outgassing of  $\text{O}_2$  and  $\text{N}_2$ .

Because of the different time period used, it is not possible to directly compare these results with our calculations above. Therefore, we recalculate oceanic and land biotic carbon sinks with the Scripps data, as described above, but using the same time period as the Battle et al. (2000) study, and assuming  $Z = \Delta \text{N}_2 = 0$  (in eq. 11), and using our own Alert and Cape Grim data as Northern and Southern Hemisphere proxies, respectively. This yields  $1.4 \pm 0.4 \text{ Pg C yr}^{-1}$  and  $2.2 \pm 0.6 \text{ Pg C yr}^{-1}$  for the oceanic and land biotic sinks, respectively (see also Table 1, Part 3). This oceanic sink is unusually low, however, this is most likely due to a combination of not accounting for ocean warming, and the relatively short time period considered of 6 yr. We have examined our APO trends, and found them to exhibit more than twice as much interannual variability on 6-yr averaged periods when compared to 10-yr averaged periods. This is most likely explained by variability in air–sea exchanges of  $\text{O}_2$ , and not by variability in the oceanic carbon sink.

Although our oceanic and land biotic sink estimates agree with the Battle et al. (2000) estimates within their uncertainties, the magnitude of the differences is nevertheless larger than expected from the uncertainties attributed to the atmospheric trends in  $\text{O}_2/\text{N}_2$  ratios and  $\text{CO}_2$  concentrations. We find that for the 6-yr period, the Battle et al. (2000) data set, when processed with our methodology for calculating atmospheric trends, gives a 6.1 per meg greater APO decrease than our own data set (Table 1, Part 3).

To isolate the origin of this discrepancy, we first compare Cape Grim-only data from the two independent networks, for which we have overlapping records from 1992 to 1997.5. Here the Battle et al. (2000) data exhibit only a 0.5 per meg greater APO decrease (Table 1, Part 3). This shows that the discrepancy between the Battle et al. (2000) result and our result over the same period is not caused primarily by the Cape Grim data, and that the two different sampling networks have excellent agreement. For  $\text{CO}_2$  however, for the 6-yr period, Battle et al. (2000) have a 0.35 ppm greater  $\text{CO}_2$  increase than our results, whereas for the Cape Grim-only data, they have a 0.27 ppm greater  $\text{CO}_2$  increase over the 5.5-yr period. We believe that a large part of these discrepancies arise from differences in  $\text{CO}_2$  calibration scales (Battle et al. (2000) flask samples are analysed by CMDL/NOAA, U.S.A.).

In the case of  $\text{O}_2/\text{N}_2$  data, a more significant discrepancy is found in the Northern Hemisphere data. Here, in hindsight, the Battle et al. (2000) technique of splicing together the early Alert data with Point Barrow data appears to be problematic. From several more years of overlapping data (which were not available to Battle et al. (2000)), it is now clear that, on average,  $\text{O}_2/\text{N}_2$  ratios are lower and  $\text{CO}_2$  concentrations are higher at Point Barrow than at Alert. Furthermore, over the relevant time period,  $\text{O}_2/\text{N}_2$  ratios decreased more rapidly and  $\text{CO}_2$  concentrations increased more rapidly at Point Barrow than at Alert. In the face of these apparently real concentration differences between the stations, the Battle et al. (2000) technique of splicing data from the two stations would have the effect of overestimating both the  $\text{O}_2/\text{N}_2$  decrease and the  $\text{CO}_2$  increase.

Differences in calculation techniques employed by Battle et al. (2000) also contribute to the discrepancy in our global oceanic and land biotic sink estimates. Using the Battle et al. (2000) data set with our calculation methodology, results in a change of between 0.1 and 0.2  $\text{Pg C yr}^{-1}$  in both oceanic and land biotic carbon sinks. This discrepancy can partly be traced to Battle et al. (2000) having effectively used APO data to calculate the oceanic sink (as we do), but then using the  $\text{O}_2$  budget instead of the  $\text{CO}_2$  budget to calculate the land biotic sink (effectively eq. 8 instead of eq. 7). Other calculation differences with Battle et al. (2000) concern the manner in which trends were obtained from the data. First, when calculating the global atmospheric trends in  $\text{O}_2/\text{N}_2$  ratio and  $\text{CO}_2$  concentration, Battle et al. (2000) used not only annual averages (as we use), but also actual data values at the time of year when  $\text{O}_2/\text{N}_2$  ratios are at their seasonal minimum (in winter), and fitting a straight line through these points. They state that their reason for doing so is because the oceanic mixed layer is deeper at this time, making it more likely that the ocean will be in equilibrium with the atmosphere and that the effect of ventilation imbalances will be minimized. Battle et al. (2000) then used the average from these two methods when reporting global trends. Second, in their calculation of global trends, Battle et al. (2000) fit a linear least-squares fit to all data from the measurement period. By contrast, our method computes

the global atmospheric trends by drawing a line through the first and last annual means for the time period of interest (see e.g. Fig. 3).

#### 4.5. Site and time period effects on global carbon sinks

In Part 4 of Table 1, we examine the effect of site selection on calculations of global carbon sinks. This is particularly pertinent in assessing the IPCC calculation in Section 4.2, where no Southern Hemisphere data were used in the oceanic carbon sink calculation. Such analyses must necessarily be carried out on different time periods than the IPCC calculation owing to the constraint of the time periods for which data from different stations are available.

We show comparisons over three different time periods, based on when new stations were added to our global network. The first comparison, over an 11-yr period from 1991.5 to 2002.5, directly demonstrates the effect of adding a Southern Hemisphere station. We have calculated the oceanic carbon sinks using only Alert and La Jolla APO data, as in the IPCC assessment, and then with Alert, La Jolla and Cape Grim, Tasmania APO data. Then, as with the IPCC calculations and our 'best estimate' over 1993–2003, we used CMDL/NOAA global CO<sub>2</sub> data to calculate the land biotic carbon sink. Addition of the Cape Grim APO data resulted in a bigger global oceanic sink and a smaller land biotic sink by about 0.10 Pg C yr<sup>-1</sup>. These results suggest that the IPCC calculations for the 1990s (after additional corrections for ocean warming, as given above) may have been biased towards a larger land biotic sink by about 0.1 Pg C yr<sup>-1</sup>.

The second comparison is over an 8.5-yr period when we had additional APO data from two tropical sites, Cape Kumukahi, Hawaii (KUM; 19.5°N, 154.8°W) and American Samoa (SMO; 14.3°S, 170.6°W). We compare an analysis using only Alert, La Jolla and Cape Grim, with an analysis using all five sites. We find that the land biotic sink decreases and the oceanic sink increases by 0.02 Pg C yr<sup>-1</sup> when we include the two tropical sites. Finally, over a 5-yr period, we added two high latitude sites, Cold Bay, Alaska (CBA; 55.2°N, 162.7°W) and Palmer Station, Antarctica (PSA; 64.9°S, 64.0°W). We calculated global sinks using three, five and seven stations. The maximum differences found were 0.08 and 0.09 Pg C yr<sup>-1</sup> in oceanic and land biotic sinks, respectively.

In summary, when at least one site from each hemisphere is used, we find maximum differences of 0.20 per meg yr<sup>-1</sup> in the APO trend, resulting in differences all smaller than 0.1 Pg C yr<sup>-1</sup> in the oceanic and land biotic sinks. These results also imply that atmospheric measurements from other laboratories with different sampling sites should be comparable to, and able to be merged with ours, provided intercalibration procedures are adequate. These results also re-emphasize the fact that the discrepancy with the Battle et al. (2000) results are not explained by the choice of different stations in computing the global atmospheric trends.

In Part 5 of Table 1, we examine the effect of the time period used in determining 10-yr (decadal) average global carbon sinks. We calculated 10-yr averages over five different 10-yr periods, where each period is offset from the previous by 6 months. We used Alert, La Jolla and Cape Grim data to calculate APO trends, and CMDL/NOAA data for CO<sub>2</sub> trends. We find differences in consecutive decadal averages of up to 0.17 Pg C yr<sup>-1</sup> and 0.32 Pg C yr<sup>-1</sup> in the oceanic and land biotic sinks, respectively. These results demonstrate that care must be taken when drawing conclusions from decadal averaged global carbon sinks (e.g. in comparing changes between the 1980s and 1990s as discussed in Schimel et al. (2001), Prentice et al. (2001) and Le Quééré et al. (2003)), since interannual variability can cause these average sinks to change by as much as 0.3 Pg C yr<sup>-1</sup> from only a 6-month shift in the 10-yr average. In the case of the land biotic carbon sink, the 1990s decadal average was about 1 Pg C yr<sup>-1</sup> greater than in the 1980s, therefore, even with our findings here, it can be confidently concluded that there was indeed a significant change in the global land biotic sink over these two decades (as also found previously by Schimel et al. (2001), Prentice et al. (2001) and Le Quééré et al. (2003)).

The variations in the oceanic and land biotic carbon sinks for different time periods and station combinations shown in Table 1 result mostly from differences in the estimated APO and CO<sub>2</sub> trends. While the experimental uncertainties in these trends are small enough that the variations are mostly statistically significant, uncertainties in the interannual variations in the air–sea exchange of O<sub>2</sub> prevents us from interpreting these variations reliably in terms of variations in the oceanic and land biotic sinks. It is for this reason that we focus here primarily on trends integrated over periods of many years, thus reducing the impact of the variable air–sea O<sub>2</sub> exchanges on our results.

In spite of this difficulty of interpreting shorter-term variations, we do find that the land biotic sink shows more variability than the oceanic sink (compare results in Table 1), and this agrees with several recent studies suggesting that land carbon exchanges are globally more variable than oceanic exchanges (Nakazawa et al., 1993; Bousquet et al., 2000). In fact it is likely that the oceanic carbon sink is even more stable than implied by our results. This follows because interannual variations in ocean ventilation or biological production will tend to drive larger changes in atmospheric O<sub>2</sub> than CO<sub>2</sub> (Keeling and Severinghaus, 2000). Fluctuations in APO on interannual time scales, which are interpreted by our calculations as variations in the oceanic carbon sink over different time periods, therefore, probably reflect largely variations in air–sea O<sub>2</sub> exchange rather than CO<sub>2</sub> exchange.

#### 4.6 Comparison with Sabine et al. (2004)

It is of interest to compare our estimate of oceanic CO<sub>2</sub> uptake for the 1993–2003 period ( $2.2 \pm 0.6$  Pg C yr<sup>-1</sup>) with the recent study of Sabine et al. (2004), who estimate, based on hydrographic data, that the oceans have accumulated  $118 \pm 19$  Pg C of

‘anthropogenic CO<sub>2</sub>’ from 1800 through to 1994. To allow a quantitative comparison, two additional pieces of information are needed: (1) information on the time evolution of anthropogenic CO<sub>2</sub> uptake and (2) information on additional air–sea CO<sub>2</sub> exchanges that are not counted as ‘anthropogenic’. These additional exchanges are relevant because the Sabine et al. (2004) estimate is an incomplete measure of oceanic CO<sub>2</sub> uptake, accounting for uptake that arises from the direct response of the oceans to rising atmospheric CO<sub>2</sub> levels, but neglecting uptake or releases of CO<sub>2</sub> driven by processes internal to the ocean, such as ocean warming or changes in stratification (Keeling, 2005). (Note that, by conventional usage, the term ‘anthropogenic CO<sub>2</sub>’ does not account for CO<sub>2</sub> exchange driven by anthropogenic warming. In contrast, the estimates of oceanic CO<sub>2</sub> uptake based on atmospheric O<sub>2</sub> budgets account for, in principle, uptake driven by both rising atmospheric CO<sub>2</sub> and any internal ocean processes.)

To account for the time variations in anthropogenic CO<sub>2</sub> uptake, we make use of the box-diffusion model developed by Oeschger et al. (1975), which, although simplistic, has been shown to adequately depict the ocean’s direct response to rising CO<sub>2</sub> (Joos et al., 1997). The box-diffusion model has two key free parameters: the vertical eddy diffusivity,  $K$  and the air–sea gas exchange coefficient,  $k_{as}$ . These two parameters can be fixed using two constraints: (1) the Sabine et al. (2004) estimate of anthropogenic CO<sub>2</sub> uptake and (2) the ocean accumulation of bomb-<sup>14</sup>C (Peacock, 2004). By trial and error, we find that these constraints are satisfied with  $K = 6080 \text{ m}^2 \text{ yr}^{-1}$  and  $k_{as} = 1/10 \text{ yr}$  ( $k_{as}$  is measured here as the reciprocal atmospheric lifetime). With these parameters, the model yields an average oceanic uptake of  $2.4 \pm 0.4 \text{ Pg C yr}^{-1}$  for 1993–2003, where the uncertainty is dominated by uncertainty in the Sabine et al. (2004) estimate because the result is rather insensitive to the bomb-<sup>14</sup>C constraint.

To account for the non-anthropogenic contributions, we first consider the direct effect of ocean warming on CO<sub>2</sub> solubility, which, considered alone, causes CO<sub>2</sub> to be released from the oceans. Using the box-diffusion model, we estimate an average outgassing rate of  $0.3 \text{ Pg C yr}^{-1}$  for 1993–2003. This estimate is based on driving the box-diffusion model, tuned as above, with the global average sea-surface temperature, as computed from a  $5^\circ \times 5^\circ$  global data set (Jones and Moberg, 2003).

Warming is also expected to cause increased upper-ocean stratification thereby causing a net uptake of CO<sub>2</sub> from the atmosphere via increased efficiency of the marine biological pump. Models suggest this effect should be about  $0.1$  to  $0.2 \text{ Pg C yr}^{-1}$ , opposing the solubility effect, although this estimate is poorly constrained (Sarmiento et al., 1998; Plattner et al., 2001). Stratification is also expected to slow the uptake of anthropogenic CO<sub>2</sub>, by reducing the transport from surface to deeper waters. Here we neglect this and several other effects which appear to be less important, at least at this time (Plattner et al., 2001).

Combining the box-diffusion model results with the adjustments for warming yields a net uptake of  $\sim 2.2 \text{ Pg C yr}^{-1}$  for the

1993–2003 period. The overall uncertainty in this adjusted estimate is hard to estimate, but is clearly larger than  $\pm 0.4 \text{ Pg C yr}^{-1}$ , considering that the warming corrections are uncertain and considering that additional decadal variability may be present. This hydrographic/model-based result is in excellent agreement with our atmospheric-based result of  $2.2 \pm 0.6 \text{ Pg C yr}^{-1}$ . The agreement is slightly better with the adjustments for warming and stratification. The comparison, therefore, supports the hypothesis that climate feedbacks may be causing a slight reduction in oceanic CO<sub>2</sub> uptake in recent years, rather than an enhancement, but the uncertainties are too large to draw firm conclusions.

#### 4.7. Reducing uncertainties in global carbon sink estimates

In calculations of average oceanic and land biotic carbon sinks estimated from atmospheric O<sub>2</sub>/N<sub>2</sub> ratios and CO<sub>2</sub> concentrations presented here and elsewhere, typical uncertainties are between 30% and 50% and greater than  $\pm 0.5 \text{ Pg C yr}^{-1}$ . Le Quéré et al. (2003) claimed that it will be difficult to reduce these uncertainties below  $\pm 0.7 \text{ Pg C yr}^{-1}$  when estimated from O<sub>2</sub>/N<sub>2</sub> ratio measurements. With the background of the discussions above, we assess here the principal contributing factors to these uncertainties, and thus suggest areas for future work in order to reduce them. In Table 5, we summarize, for decadal averages, our best estimates of the uncertainties in the contributing factors.

For the land biotic carbon sink, the largest source of uncertainty arises from fossil fuel burning statistics. We attribute  $\pm 6\%$  uncertainty to this trend, corresponding to  $\pm 0.5 \text{ Pg C yr}^{-1}$  uncertainty in the land biotic sink. In contrast, however, this fossil fuel uncertainty corresponds to only  $\pm 0.1 \text{ Pg C yr}^{-1}$  uncertainty in the oceanic sink. This is because when using our calculation methodology, the oceanic sink is calculated from APO data, which decrease due to fossil fuel combustion only by a factor of  $(\alpha_F - \alpha_B)$ ,  $\sim 0.3$ , in contrast to O<sub>2</sub>/N<sub>2</sub> ratios, which decrease from fossil fuel combustion by a factor of  $\alpha_F$ ,  $\sim 1.4$ .

The largest source of uncertainty in the oceanic carbon sink, and contributing equal (but opposite) uncertainty to the land biotic sink are our estimates for oceanic O<sub>2</sub> outgassing, discussed in Section 4.3 above. Our calculation effectively adopts the null hypothesis that O<sub>2</sub> (and N<sub>2</sub>) outgassing is proportional to the net flux of heat into the ocean, but this is indeed a hypothesis, rather than an observed fact. A better approach, and probably the only approach that can substantially reduce uncertainties, is to make direct observations of dissolved O<sub>2</sub> in the oceans with long-term observing programs and with global coverage. As an example, a sustained O<sub>2</sub> outgassing of  $0.4 \times 10^{14} \text{ mol O}_2 \text{ yr}^{-1}$  (approximately what we expect in coming years) would correspond to a change of  $0.7 \mu\text{mol O}_2/\text{kg}$  per decade, if spread uniformly over the global oceans to a depth of 2000 m (Keeling and Garcia, 2002). To observe such changes against natural variability is feasible, but will require a high measurement density, both spatially and temporally (Keeling and Garcia, 2002). The task

Table 5. Contributions to uncertainties in decadal oceanic and land biotic carbon sinks

Parameter	Uncertainty	Oceanic sink (Pg C yr <sup>-1</sup> )	Land biotic sink (Pg C yr <sup>-1</sup> )
Fossil fuel trend	±6% <sup>a</sup>	±0.1	±0.5
Z <sub>eff</sub>	–	~ ±0.5	~ ±0.5
α <sub>B</sub>	±0.05	±0.06	±0.06
α <sub>F</sub>	±0.04	±0.2	±0.2
Atmospheric measurements <sup>b</sup> :			
Synoptic variability <sup>c</sup>	±0.13 per meg yr <sup>-1</sup>	±0.18	±0.18
Calibration cylinder drift	±0.41 per meg yr <sup>-1</sup>		
Different stations <sup>d</sup>	±0.20 per meg yr <sup>-1</sup>	±0.08	±0.09
Quadrature sum of all observational uncertainties		±0.6	±0.7

<sup>a</sup>Uncertainty over a 10-yr period.

<sup>b</sup>Uncertainty given is for global APO trend, taking into account our uncertainties in both O<sub>2</sub>/N<sub>2</sub> ratios and CO<sub>2</sub> concentrations.

<sup>c</sup>Also includes a small contribution from sampling and analysis errors.

<sup>d</sup>Largest differences found in Table 1 when a different number of stations are used in calculating APO global trends, where at least one station from each hemisphere is used.

is made more difficult because oceanic O<sub>2</sub> outgassing is most likely not uniform. For example, in the North Pacific (Emerson et al., 2001), North Atlantic (Garcia et al., 1998) and South Pacific (Matear et al., 2000; Watanabe et al., 2001) dissolved O<sub>2</sub> decreases ranging between 5 and 15 μmol O<sub>2</sub>/kg per decade have been found. On the other hand, spatial patterns of changes in dissolved O<sub>2</sub> are informative as indicators of variations and trends in ocean circulation and biological activity, so programs to track these changes would serve multiple purposes.

Also contributing to the uncertainty in oceanic O<sub>2</sub> outgassing is natural interannual variability in air–sea O<sub>2</sub> fluxes. Our approach, which computes the outgassing based on observed air–sea heat flux, effectively assumes that this variability is proportional to heat flux, with the same scaling as long-term warming. This assumption has support from modelling studies (Bopp et al., 2002; Plattner et al., 2002), but has not been tested observationally. Our overall uncertainty for the oceanic O<sub>2</sub> outgassing term of ±0.5 Pg C yr<sup>-1</sup> (used in our 1993–2003 estimates) reflects our estimates of the combined uncertainties due to natural interannual variability and long-term warming. The uncertainties associated with interannual variability in air–sea O<sub>2</sub> exchange are reduced by integrating over longer time periods, and could be further reduced by incorporating constraints based on direct observations of changes in dissolved O<sub>2</sub> in the oceans, which would constrain the total air–sea O<sub>2</sub> flux, whether due to long-term warming or interannual variability.

Hypothetically, if the uncertainty in oceanic O<sub>2</sub> outgassing were reduced from ±0.5 Pg C yr<sup>-1</sup> to ±0.2 Pg C yr<sup>-1</sup>, then the total uncertainty in the oceanic and land biotic sinks reported in Table 5 would be reduced to ±0.4 and ±0.6, respectively. Thus if atmospheric O<sub>2</sub> and CO<sub>2</sub> measurements were paired

with an ocean observing system with tight constraints on long-term O<sub>2</sub> exchange, the uncertainties in the sinks could be reduced considerably.

The estimated global value for α<sub>B</sub> of 1.10 ± 0.05 is based only on a small number of plant and soil laboratory chamber analyses carried out by Severinghaus (1995). The uncertainty assigned of ±0.05 is little more than a guess, and we can say very little about the spatial or temporal homogeneity of this ratio. However, a globally weighted (and time-invariant) offset of 10% in the estimate for α<sub>B</sub> translates into opposing effects on decadal averaged oceanic and land biotic sink estimates of only about 0.1 Pg C yr<sup>-1</sup>. This effect increases however, in direct proportion to the size of the land biotic carbon sink, thus uncertainty in α<sub>B</sub> has more relevance to studies of the interannual variability in carbon sinks, and analyses of sinks on regional scales.

A few exploratory studies have been made to examine α<sub>B</sub> from canopy or regionally integrated air masses. From 3 days of flask sample collections at different times of year in a forest in southern England, Marca (2004) found an average value of 1.04; from 1 week of continuous atmospheric data from Baring Head, New Zealand when the sampled air masses were travelling over temperate forest, Manning (2001) derived a ratio of 1.08; and from short studies at sites in north-eastern USA and Scotland, Seibt et al. (2004) found daily-averaged ratios of 1.0. Seibt et al. (2004) also conducted field chamber experiments measuring photosynthetic and respiratory ratios ranging from 0.7 to 1.6. Despite the good agreement of the air mass studies, their exploratory nature and their sparse representation of the diversity of global ecosystems provides us with little confidence in either our estimate for α<sub>B</sub> or its uncertainty. Furthermore, from a

simple one-box modelling study, Seibt et al. (2004) found evidence to suggest that  $O_2$  and  $CO_2$  measurements from above-canopy air masses may not be an appropriate method for determining  $O_2/CO_2$  exchange ratios of net ecosystem fluxes.

Although less pertinent to global carbon sink estimates, improved understanding of the spatial and temporal variability in land biotic  $O_2:CO_2$  exchange ratios will assist regional carbon flux studies. Thus, we suggest research analysing air samples both above and below canopy, in concert with field and laboratory chamber measurements. However, chamber measurements suffer from sampling artefacts, which have yet to be overcome, and interpretations of canopy air measurements require improvements in our understanding of local micro-meteorology. Another promising approach may be controlled laboratory combustion of biotic samples and measuring the  $O_2$  depletion and  $CO_2$

produced. The challenge here would be to correlate such a complete combustion process to the oxidation states of biotic matter found in natural systems.

The global average fossil-fuel  $O_2:CO_2$  combustion ratio,  $\alpha_F$ , depends not only on the ratio of each fuel type (e.g. coal, petroleum, natural gas and gas flaring) but also on the relative contribution of each fuel type to the global mix. The overall uncertainty of  $\pm 0.04$  is dominated by uncertainty in the fuel relative contributions, as related to uncertainty in the production figures for each fuel type (Keeling, 1988a; Marland et al., 2002). This uncertainty translates into uncertainties in our decadal oceanic and land biotic sink estimates of  $\pm 0.2 \text{ Pg C yr}^{-1}$ . The changes in  $\alpha_F$  from year to year shown in Table 3, although much smaller than  $\pm 0.04$ , may nevertheless be significant because the changes in fuel production from year to year are resolvable to a finer

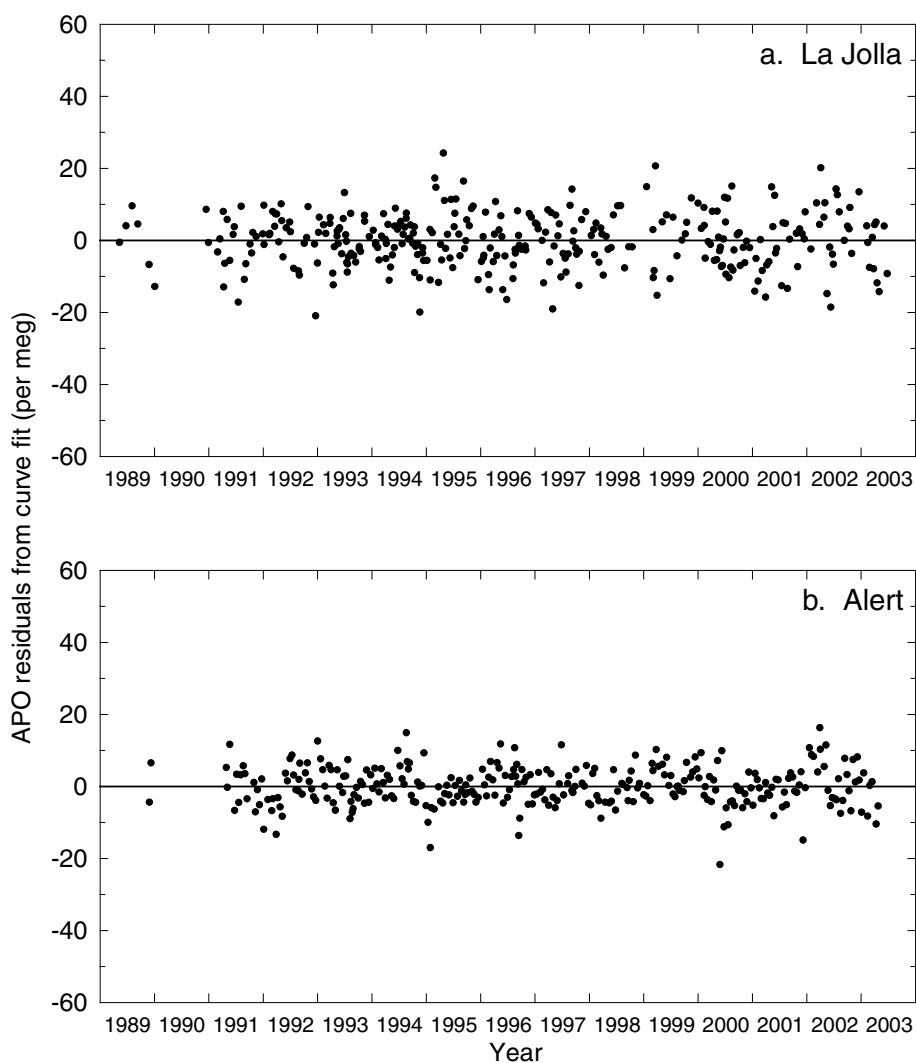


Fig. 4. APO residuals from the curve fits for La Jolla and Alert. These residuals give a measure of the uncertainty to assign in the calculation of global oceanic and land biotic carbon sinks. The figure also shows that early 1989 data are not more variable than more recent parts of the record.



degree than the total production in any given year (Marland et al., 2002).

The global atmospheric trends in both  $O_2/N_2$  ratios and  $CO_2$  concentrations are well constrained. As shown in Table 5, we estimate our uncertainty in the APO global trend due to synoptic variability and sample collection and analysis errors to be  $\pm 0.13$  per meg  $yr^{-1}$ . This uncertainty was estimated by calculating the standard error of the residuals of flask samples from our curve fits (described in Section 3). We repeat this calculation for each station used in constructing the global average trend, and calculate the total uncertainty by quadrature sum of the errors. Fig. 4 shows an example of flask residuals from the curve fits for Alert and La Jolla stations.

The uncertainty in our measurements caused by possible drift in our calibration cylinders is much greater, estimated at  $\pm 0.41$  per meg  $yr^{-1}$ . This was calculated for APO by considering the drifts in both  $O_2/N_2$  ratio and  $CO_2$  concentration as reported by Keeling et al. (2005). Combined, these uncertainties translate to uncertainties in both oceanic and land biotic sinks of  $\pm 0.18$  Pg C  $yr^{-1}$ . Any additional systematic errors in the long-term trends are not included here, however, our interlaboratory comparisons, discussed above, support the conclusion that these are much smaller than the uncertainty in calibration cylinder drift.

We have also shown that, on time scales greater than 5 yr, global atmospheric trends in  $O_2/N_2$  ratios (and APO) can be precisely estimated from only three or four (well chosen) measurement stations. Typical uncertainties related to station choices translate to  $\pm 0.09$  Pg C  $yr^{-1}$  or less in global carbon sinks, when between three and seven stations are used in the global average (so long as at least one Southern Hemisphere station is used, and where the wider CMDL network is used for global  $CO_2$  trends).

Finally, we caution that the oceanic and land biotic carbon sinks reported here over specific time windows are not necessarily representative of sinks over shorter or longer time windows due to natural variability. This is especially true of our estimates for the land biotic carbon sink, which appears to be highly variable from year to year and from decade to decade. We have shown that even for decadal averages, offsetting the 10-yr average by only 6 months can potentially change the average land biotic sink by as much as 0.32 Pg C  $yr^{-1}$ . The estimates for the oceanic carbon sink show more stability, with a maximum observed change of 0.17 Pg C  $yr^{-1}$  with a 6-month offset in the decadal average. This suggests that we may be closer to being able to track systematic variations in the oceanic sink from decade to decade using  $O_2/N_2$  data.

## 5. Summary

In this paper we have formalized the definitions and relations used in atmospheric  $O_2/N_2$  work, including providing a detailed accounting of our calculation methodology for deriving global oceanic and land biotic carbon sinks. We have presented the data and calculations that were used in deriving the 1990–2000

average global carbon sinks given in the IPCC Third Assessment Report (Prentice et al., 2001). Since this report, improved, but sometimes contrasting, estimates have been made of oceanic  $O_2$  outgassing, and we have reviewed and discussed these here. We suggest that the best estimate of the effect of oceanic  $O_2$  outgassing on the global carbon sinks from 1990 to 2000 is  $0.3 \pm 0.5$  Pg C  $yr^{-1}$ . This results in our best estimate of a corrected global budget from 1990 to 2000 of an oceanic carbon sink of  $1.9 \pm 0.6$  Pg C  $yr^{-1}$  and a land biotic carbon sink of  $1.2 \pm 0.8$  Pg C  $yr^{-1}$ . These estimates represent a shift of 0.2 Pg C  $yr^{-1}$  from the IPCC estimates, with a larger oceanic sink and smaller land biotic sink.

For the 10-yr period from 1993 to 2003, we calculated an oceanic carbon sink of  $2.2 \pm 0.6$  Pg C  $yr^{-1}$  and a land biotic carbon sink of  $0.5 \pm 0.7$  Pg C  $yr^{-1}$ . These values include a correction of 0.5 Pg C  $yr^{-1}$  representing our best estimate for oceanic outgassing of  $O_2$  over this period. We presented global sinks over this different time period because of significant improvements in our gas handling procedures after 1992 (Keeling et al., 2005). These results provide further support demonstrating the relative stability of the oceanic carbon sink of about 2 Pg C  $yr^{-1}$ , when integrated over time periods of about 10 yr. In contrast, the land biotic carbon sink shows much greater natural variability, and thus global average values obtained are highly dependent on both the time period chosen and the length of the time period. Our results demonstrate a 0.7 Pg C  $yr^{-1}$  decrease in the land biotic carbon sink associated only with a 3-yr shift in the decadal average.

One of the main conclusions in Battle et al. (2000) was that their data, between mid-1991 and mid-1997, demonstrated a large ( $1.4$  Pg C  $yr^{-1}$ ) global land biotic carbon sink in comparison to the average computed for the 1980s of approximately zero. We have demonstrated that the Battle et al. (2000) computation was biased due to splicing  $O_2/N_2$  ratio data together from two different Northern Hemisphere stations, which only in hindsight appears to be problematic. Our own results over the same time period indicate an even larger land biotic carbon sink of 2.2 Pg C  $yr^{-1}$ . However, both of these calculations did not take into account oceanic  $O_2$  outgassing, which probably would have reduced the land biotic carbon sink by 0.2–0.3 Pg C  $yr^{-1}$ . In addition, there was relatively strong uptake by the land biota in the early 1990s (Schimel et al., 2001), and thus the average land biotic sink over the longer period for the entire 1990s decade (and taking into account oceanic  $O_2$  outgassing) was smaller as we have shown here.

We have found that our oceanic carbon uptake estimate of 2.2 Pg C  $yr^{-1}$  is consistent with the Sabine et al. (2004) inventory estimate of accumulated anthropogenic  $CO_2$ , to within the uncertainties, and the agreement is better once warming corrections are applied to the inventory-based estimate. This comparison was achieved by assuming that the inventory-based estimate, which is for the period 1800–1994, varied over time as predicted by a box-diffusion model (Oeschger et al., 1975), thus providing

supporting evidence that the oceanic sink has varied over time more or less as predicted by this model.

We have demonstrated that global carbon sinks averaged over time periods greater than 5 yr can be constrained with measurements from as few as three well chosen long-term monitoring stations sampling  $O_2/N_2$  ratios and  $CO_2$  concentrations. However, for assessing interannual and regional variability in these sinks, a much higher-density network is needed. We have also shown that care must be taken when considering trends in decadal averages of global sinks, for example, as given in Le Quéré et al. (2003), since natural variability can cause differences in such averages by as much as  $0.3 \text{ Pg C yr}^{-1}$  with as little as a 6-month offset in the 10-yr period used for the average.

Although atmospheric trends in  $O_2/N_2$  ratios and  $CO_2$  concentrations are presently well measured by several programs, continuing interlaboratory comparison programs is essential to ensure that no artefacts are introduced in these trends. Absolute  $O_2/N_2$  ratio standards should also be developed to solve long-term calibration issues as discussed in Keeling et al. (2005). Finally, the adoption of a standard methodology for interpreting fluxes from atmospheric  $O_2/N_2$  and  $CO_2$  data would be helpful in allowing results to be compared, because methodological differences can result in discrepancies in oceanic and land biotic carbon sinks as large as  $0.2 \text{ Pg C yr}^{-1}$ .

If we continue to use atmospheric  $O_2/N_2$  ratio measurements to constrain the global oceanic and land biotic carbon sinks, it is essential that we focus our efforts in several areas if we wish to constrain these sinks to  $\pm 0.5 \text{ Pg C yr}^{-1}$  or better. The most important areas to focus our attention on to reduce uncertainties are: (1) improved quantification of global fossil fuel emission trends, including improved estimates of the  $O_2:CO_2$  ratios of the source fuels; (2) obtaining long-term and global coverage observations of dissolved  $O_2$  concentrations in the world oceans and (3) maintaining strict sampling, analysis, and calibration protocols, and increasing the number of interlaboratory comparisons.

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## 7. Appendix: Calibration Scale Uncertainties and Additional Considerations for the 1990–2000 Calculations

The observed long-term changes in  $O_2/N_2$  ratio in flask samples are based on comparisons with a suite of long-lived reference gases stored in high-pressure cylinders. The methods for comparing  $O_2/N_2$  ratios in flasks and cylinders are discussed in Keeling et al. (1998a), and a detailed examination of the stability of  $O_2/N_2$  ratios in the air delivered from the long-lived cylinders is discussed in Keeling et al. (1998a) and Keeling et al. (2005). The stability improved in 1992, when measures were taken to reduce thermal and gravimetric fractionation by orienting the cylinders horizontally in a thermally insulated enclosure. By examining relative drift between cylinders used at different rates and between cylinders of different sizes and material types, we estimate that our scale has been stable to within  $\pm 6$  per meg from 1990 to 2000 and  $\pm 4$  per meg from 1993 to 2003 (Keeling et al., 2005). The analysis upon which these stability estimates are based considered a range of possible drift mechanisms, including regulator effects, cylinder corrosion, thermal diffusion, orifice effects, tank leakage and surface adsorption effects.

Here we provide further details on additional considerations that were necessary to arrive at the global oceanic and land biotic sinks calculated in Section 4.2 for the period 1990–2000 and used in the IPCC report (Prentice et al., 2001). We also detail how we arrived at the uncertainties given for these sinks. In the La Jolla data set we discarded some data from flask samples collected in 1990. This is pertinent to any comparison made to Keeling and Shertz (1992), where our 1990 data were also used. In 1989 and 1990, some of the stopcocks on the glass flasks sealed with Teflon o-rings, rather than Viton o-rings. Keeling and Shertz (1992), observing very low  $O_2$  concentrations in some flask samples, realized that they were contaminated, and attributed this problem to preferential diffusion of  $O_2$  relative to  $N_2$  through the Teflon o-rings. Keeling and Shertz (1992) discarded many, but not all, of the samples collected in these flasks. With the longer data set now available, we were able to show that the Teflon o-ring-sealed flasks retained by Keeling and Shertz (1992) also exhibited a small negative  $O_2$  anomaly from the apparent baseline. Therefore, we discarded

all remaining samples collected in Teflon o-ring-sealed flasks. Although CO<sub>2</sub> concentrations were not affected by the Teflon o-ring-sealed flasks, we removed CO<sub>2</sub> data obtained from the same flasks also, so as not to cause inconsistent aliasing of the two data sets. This removed seven sampling dates in 1990 from the data set, leaving a total of five dates when samples were collected from La Jolla in 1989 and three in 1990 (in 1991 our regular sampling program was initiated and, for example in this year 18 samples were collected). The data retained, calculated as APO, were shown previously in Fig. 2a. These data, which are seasonally detrended, are the data used to compute annual means.

Because of the sparseness of the early part of the La Jolla record, we then proceeded to look in more detail at the Alert record. If the Alert record shows a similar long-term trend as La Jolla, then this will provide greater confidence in the La Jolla data. Flask samples were collected on two dates at Alert in 1989, none in 1990 and 15 in 1991 when a regular sampling program was begun. Fig. 2b shows the Alert seasonally detrended APO.

In order to include the Alert data in the oceanic and land biotic sink calculations, annual averages centred on 1 January 1990 and 1 January 2000 are needed, therefore, requiring data back to 1 July 1989 and up to 1 July 2000 in our normal calculation methodology. Since in 1989 we only have data from samples collected in November and December, our procedure to calculate an 'annual' average was as follows: The Fortran program used for calculating curve fits to the data also reports monthly values of the curve fit on the 15th of each month, and reports seasonally adjusted values for each month. Therefore, we averaged four seasonally adjusted monthly values, from November and December 1989, based on flask samples, and from January and February 1990, based on interpolated monthly values of the curve fit, resulting in an average centred on 1 January 1990.

The advantages of using APO data instead of O<sub>2</sub>/N<sub>2</sub> ratio data have been mentioned in Section 2 above. For the unique case of these IPCC calculations, using APO is even more advantageous, helping reduce additional uncertainty that could have arisen both

due to the sparseness of the early La Jolla and Alert records, and the necessary interpolation of the early Alert record. This becomes apparent when we compare long-term trends at La Jolla and Alert in O<sub>2</sub>/N<sub>2</sub> ratios and APO over different time periods. For a 9-yr period starting in 1991 when sampling programs were in full operation at both stations, the O<sub>2</sub>/N<sub>2</sub> ratio trends (shown in Fig. 1) differed by about 5 per meg over the 9 yr. Whereas with the interpolated Alert data set, and the sparse early record of La Jolla added, the difference in the trends doubles to 10 per meg over just 10 yr. However, APO data over the same intervals (shown in Fig. 2) show only a 2 per meg difference in the Alert and La Jolla trends over 9 yr, and also a 2 per meg difference over the longer 10-yr period. Thus these findings provide confidence both in the use of APO data, and in the Alert interpolation technique and subsequent averaging of Alert and La Jolla stations to obtain a Northern Hemisphere proxy.

The final consideration in the IPCC calculation is the lack of Southern Hemisphere O<sub>2</sub>/N<sub>2</sub> data in computing the 'global' oceanic carbon sink. Not only is there an interhemispheric gradient in O<sub>2</sub>/N<sub>2</sub> ratios and APO (Stephens et al., 1998), but these gradients exhibit significant interannual variability. This makes it problematic to use only Northern Hemisphere stations in calculating a global APO average. We attempted to quantify this additional error by comparing the Cape Grim trend to the Alert and La Jolla trends over the time period for which we have Cape Grim data, which is a 9.5-yr measurement period from January 1991 to July 2000. Over this time period, O<sub>2</sub>/N<sub>2</sub> ratios at Cape Grim decreased by about 15 per meg more than at the two Northern Hemisphere stations. In APO the difference was less, but still high at about 10 per meg. Since in a true global calculation the Southern Hemisphere would contribute a weighting of one-half to the global trend, we decided to add ±3 per meg uncertainty to the reported APO trend because of this lack of Southern Hemisphere data.

A summary of the uncertainties assigned to the different variables used in the global sinks calculation for the period from 1990 to 2000 is shown in Table 6. The total uncertainty in the

Table 6. Uncertainties in 1990–2000 global oceanic and land biotic sink calculations

Quantity	Value	Uncertainty	Source
$\alpha_B$	1.1	±0.05	(Severinghaus, 1995)
$\alpha_F$	1.391	±0.04	(Keeling, 1988)
Fossil fuel emissions	6.33 Pg C yr <sup>-1</sup>	±0.38 Pg C yr <sup>-1</sup>	(Marland et al., 2002)
CO <sub>2</sub> trend	3.21 Pg C yr <sup>-1</sup>	±0.13 Pg C yr <sup>-1</sup>	(Conway et al., 1994)
Oceanic O <sub>2</sub> degassing	1.64 × 10 <sup>13</sup> mol yr <sup>-1</sup>	±1.64 × 10 <sup>13</sup> mol yr <sup>-1</sup>	This study
APO trend:			
From 'typical' trend calculation		±6 per meg	This study
Lack of Southern Hemisphere data		±3 per meg	This study
Additional La Jolla		±3.2 per meg	This study
Additional Alert		±3.4 per meg	This study
Total	-80.4 per meg	±8.2 per meg	This study

assigned global APO trend is  $\pm 8.2$  per meg. This was derived from a quadrature sum of the  $\pm 6$  per meg uncertainty for a typical global  $O_2/N_2$  (or APO) trend computation (Keeling et al., 1996),  $\pm 3$  per meg attributed to the lack of Southern Hemisphere data,  $\pm 3.4$  per meg additional uncertainty attributed to sparse data in the early Alert record and the Alert interpolation, and  $\pm 3.2$  per meg attributed to the sparse La Jolla data in 1989 and 1990. These latter two uncertainties were calculated by considering the residuals of the flask data from the curve fits of the full Alert and La Jolla records. These residuals are shown in Fig. 4. The standard deviations of these residuals were calculated for the full records, then the standard errors were calculated by considering how many flask samples were used in deriving the 1990 annual averages. Fig. 4 is also informative in verifying that the 1989 and 1990 data are not unusual in terms of their residuals from the fitted curves.

There are two minor differences in the calculations presented here for 1990–2000 compared to that of Manning (2001) and IPCC. First, Manning (2001) did not have available fossil fuel emission data from Marland et al. (2002) through to the end of 1999, instead using data from British Petroleum for emissions in 1998 and 1999 (H. Kheshgi, personal communication). Second, at that time the Alert record went only as far as May 2000, 2 months short of the July 2000 required to achieve an annual average centred on 1 January 2000. Therefore, a slightly different technique was used to obtain this year 2000 annual average. The resulting difference between the oceanic and land biotic sinks of Manning (2001) and those presented here was only 0.03 Pg C/y (1.68 and 1.44 Pg C yr<sup>-1</sup> for oceanic and land biotic sinks, respectively). Therefore, to a precision of one decimal place, as presented in the IPCC report, the results are the same.

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