

Atmospheric carbon dioxide and the ocean

U. Siegenthaler & J. L. Sarmiento

The ocean is a significant sink for anthropogenic carbon dioxide, taking up about a third of the emissions arising from fossil-fuel use and tropical deforestation. Increases in the atmospheric carbon dioxide concentration account for most of the remaining emissions, but there still appears to be a 'missing sink' which may be located in the terrestrial biosphere.

HUMAN activities have led to considerable anthropogenic emissions of greenhouse gases. In particular, for the period from 1980 to 1989 carbon dioxide emissions from fossil-fuel burning¹ and tropical deforestation^{2,3} amounted to $\sim 7.0 \pm 1.1 \text{ Gt C yr}^{-1}$ (gigatonnes carbon; $1 \text{ Gt} = 10^{15} \text{ g}$). Increases in the atmospheric CO_2 concentration can account for about half of the CO_2 emissions for this period^{4,5}. The ocean has also taken up large amounts of anthropogenic CO_2 , but there have been conflicting estimates of this uptake. Models of the global carbon cycle (which calculate oceanic CO_2 uptake by simulating downward transport of CO_2 -laden water from the ocean surface) yield a mean 1980–89 oceanic CO_2 uptake of $2.0 \pm 0.6 \text{ Gt C yr}^{-1}$ (see Table 1). By contrast, Tans *et al.*⁶ estimated an oceanic uptake for the same period of $<1 \text{ Gt C yr}^{-1}$, from surface-water $p\text{CO}_2$ measurements for the Northern Hemisphere and the interhemispheric difference in atmospheric CO_2 concentrations. This led Tans *et al.* to propose the existence of a large 'missing sink' for CO_2 , probably located in the terrestrial biosphere. It is clearly necessary to settle the question of how much CO_2 is absorbed by the oceans, before any conclusions can be drawn about the

presence and importance of other natural sinks.

Here we evaluate the various estimates of the amount of anthropogenic CO_2 taken up by the ocean that have been published in recent years. We show that the estimate of Tans *et al.* neglects several important processes, and conclude that available evidence to date supports an annual mean uptake of $\sim 2 \text{ Gt C yr}^{-1}$. Having established a 'best guess' for the oceanic CO_2 uptake, one can then show that the total accumulation of CO_2 in the atmosphere and ocean from 1980 to 1989 is significantly less than current estimates of the total CO_2 emitted during that period. This implies either that the CO_2 release from tropical deforestation is much smaller than currently estimated, or that there is indeed a 'missing sink' for the CO_2 , albeit smaller than the one proposed by Tans *et al.* Future studies are needed to improve our understanding of the magnitude and location of these respective CO_2 sinks, if we are to predict future changes in atmospheric CO_2 .

Global carbon cycle and the atmospheric record

Figure 1 shows the global carbon reservoirs and fluxes for pre-

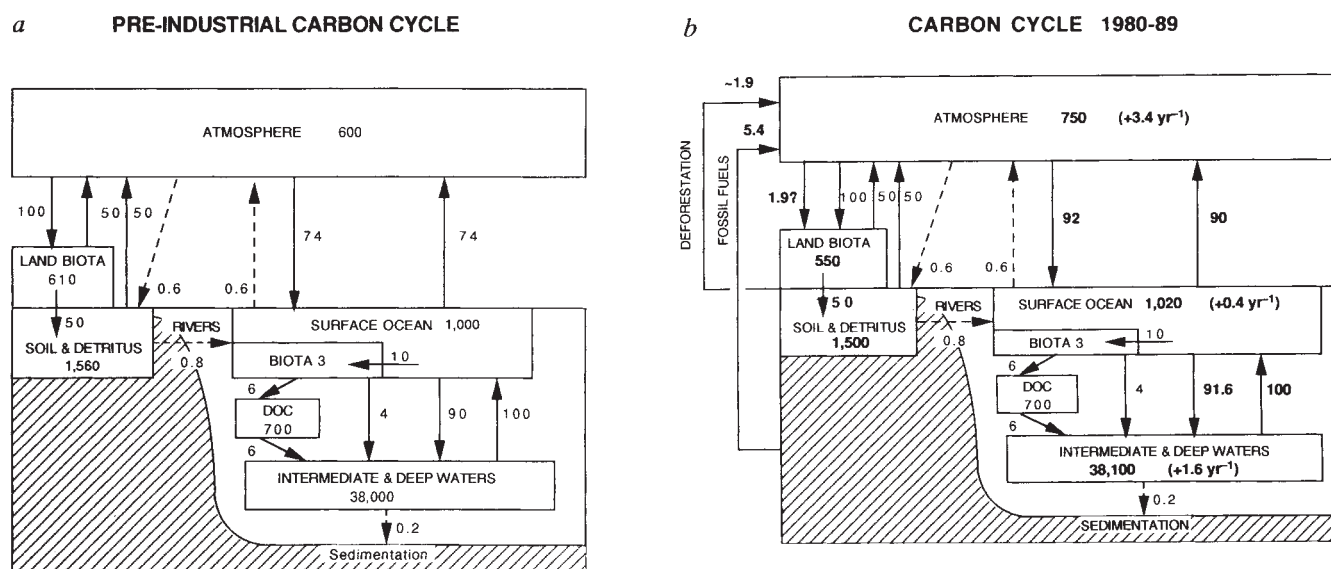


FIG. 1 Global carbon cycle reservoirs and fluxes, in Gt C and Gt C yr^{-1} , respectively ($1 \text{ Gt C} = 10^{15} \text{ g C}$). *a*, Reconstructed pre-industrial situation and *b*, present-day situation. In *b*, bold numbers denote fluxes or reservoir sizes which have changed due to human activities. The numbers in *b* correspond approximately to those given in the 1990 IPCC assessment² with the following exceptions: an oceanic pool of dissolved organic carbon (DOC) is included (E. Peltzer, personal communication). The marine biological new production (equal to particles plus DOC exported from the surface) is 10 Gt C yr^{-1} , taken from model calculations^{65,66}. The indicated transport by water circulation is much larger than in the IPCC assessment², but this is primarily a matter of

definition. The IPCC downward flux of 35 Gt C yr^{-1} corresponds roughly to global deep-water formation ($\sim 46 \times 10^6 \text{ m}^3 \text{ s}^{-1}$). Our upward flux (100 Gt C yr^{-1}) is chosen such that it is about ten times the total new production, which in a 2-box model yields a surface water ΣCO_2 deficit of 10%, as observed. Our fluxes therefore represent exchange between the surface and a depth of perhaps 1 km where most of the particles and DOC have been remineralized. The cumulative land-use effect, assumed to be -120 Gt C , is divided equally between vegetation and soils. The difference between river input and sedimentation has been closed by fluxes of 0.6 Gt C yr^{-1} from ocean to atmosphere and from atmosphere to biota (dashed arrows).

TABLE 1 Estimates of the average oceanic CO₂ uptake rate (Gt C yr⁻¹)

Model number and type*	Oceanic uptake rate†
1. Box-diffusion model (refs 55, 82)§,†	2.32
2. HILDA (ref. 35)§	2.15
3. Princeton Ocean General Circulation model (ref. 28)	≥1.9
4. Hamburg Ocean General Circulation model (M. Heimann & E. Maier-Reimer, personal communication)§	1.58

These estimates are for 1980–89, based on different carbon cycle models, normalized to a common mean penetration depth *z* for bomb-¹⁴C (*z* = (column inventory/surface concentration), refs 80, 81, calculated using the bomb-¹⁴C inventory or ref. 32).

* Models 1 and 2 are simple, parameterized ocean models. 1 is purely one-dimensional; 2 is 1.5-dimensional with a subdivision into low- and high-latitude ocean (HILDA = high-latitude exchange/interior diffusion-advection model); 3 and 4 are three-dimensional models.

† Oceanic uptake rate obtained by deconvolving the CO₂ concentration record (Siple ice core data^{15,83} and Mauna Loa observations¹³, that is by prescribing the atmospheric concentration as a function of time and calculating the corresponding flux into the ocean.

‡ Goudriaan^{84,85} used a similar model to the box-diffusion model, but with two separate ocean basins. His model was not run in the deconvolution mode, but forced by prescribed anthropogenic emissions, and the simulation did not include the period 1980–1989; Orr³³ corrected for this and obtained 2.2 Gt C yr⁻¹. However, the information about the bomb-¹⁴C simulation used is Goudriaan's model is insufficient to perform a normalization.

§ The mean bomb-¹⁴C penetration depth is 343 m from observations³² (derived from GEOSECS data, nominally 1974). The simulated penetration depth is correct for the HILDA model, version K(z); 5% too large for the box-diffusion model; 8% too small for the Hamburg model. The listed uptake values are correspondingly corrected.

|| The Princeton model has too low a bomb-¹⁴C penetration depth³¹, so that the oceanic CO₂ uptake in this model is considered as a lower limit (see ref. 28 for details).

industrial (Fig. 1a) and present (Fig. 1b) conditions. The largest pool is dissolved inorganic carbon (ΣCO₂) in the ocean, including CO₂, HCO₃⁻ and CO₃²⁻. Carbon dioxide is exchanged between atmospheric and ocean by gas transfer, and between the biota and the other reservoirs by photosynthesis and respiration. In pre-industrial times, the carbon cycle was in a roughly steady state, with the sum of all fluxes into each reservoir being equal to the sum of the fluxes out. Because of anthropogenic carbon emissions, fluxes and carbon reservoir sizes changed (bold-face numbers in Fig. 1b). The atmospheric concentration of CO₂ has increased from its pre-industrial value of 280 parts per million (p.p.m.) to 355 p.p.m. in 1992. The cycle we observe today represents a superposition of the natural situation and man-made perturbations. The recoverable fossil-fuel resources are estimated at perhaps 4,000 Gt C (ref. 7), a huge amount compared to the atmospheric reservoir (600 Gt C) and to the live vegetation (~550 Gt C). The continued combustion of fossil fuels has the potential to raise atmospheric CO₂ levels several fold, whereas the potential effect of continued deforestation is limited.

The atmospheric CO₂ concentration has been measured continuously at Mauna Loa and at the South Pole since 1958 (Fig. 2a, refs 4, 5), and later at many other monitoring stations⁶. For earlier times, the atmospheric CO₂ concentration can be reconstructed by means of analysis of air trapped in old polar ice (Fig. 2b). This concentration has grown steadily since AD 1800, which has given rise to a net CO₂ uptake by the oceans and probably by parts of the land biota. The atmospheric growth is due to emissions from combustion of fossil fuels, 5.4 Gt C yr⁻¹ for the decade 1980–1989 (refs 1, 9), and from deforestation and land use, estimated at 0.6–2.5 Gt C yr⁻¹ (refs 2, 3). The large range of the estimates of deforestation flux^{10,12} reflects the fact that

TABLE 2 Budget of annual anthropogenic CO₂ perturbations

Emissions from fossil combustion ¹	5.4 ± 0.5
Emissions from deforestation and land use ^{2,3}	0.6 to 2.5
Atmospheric accumulation ^{4,5}	3.2* ± 0.2
Uptake by the ocean	2.0 ± 0.6
Net imbalance	1.8 ± 1.3

These values are averages for the decade 1980–89. Emissions from deforestation and land use also include forest regrowth on abandoned land, but not a possible CO₂ fertilization. For the deforestation flux, a range instead of an error is given, because estimates from different authors cannot just be averaged to get a best value. For estimating the net imbalance and its error (obtained by quadratic addition), however, 1.6 ± 1.0 Gt C yr⁻¹ is adopted for deforestation.

* Average of Mauna Loa and South Pole.

terrestrial vegetation and soils are extremely heterogeneous and that it is difficult to assess changes in carbon storage per unit area cleared and regrowth of abandoned land.

The natural exchange fluxes between atmosphere, ocean and land biota are relatively large compared to the anthropogenic perturbations (see Fig. 1b). Therefore, the question has sometimes been raised whether the current increase could just be due to a natural excursion of the carbon cycle which would eventually reverse. Several arguments disprove this idea. In Fig. 2c, the annual growth of atmospheric CO₂ is compared with the estimated emissions from fossil-fuel combustion and land use. The atmospheric growth has been smaller than the fossil-fuel input in every single year from about 1900 onwards, and it has been smaller by a factor of 2–3 than the total estimated annual input since the beginning of the deforestation record. The increase from 1860 to 1989 corresponds to an airborne fraction of 40% of the estimated cumulative anthropogenic release (see legend to Fig. 2c). Thus, during all these years, ocean plus land biota together have acted as a net CO₂ sink rather than a source. A compelling piece of evidence for the relation between emissions and atmospheric increase comes from the observation that the annual mean concentration in the Northern Hemisphere, where 95% of the fossil-fuel emissions occur, has exceeded the concentrations in the Southern Hemisphere since the start of atmospheric monitoring (Fig. 2a) and that the interhemispheric difference has grown in parallel to the fossil-fuel emissions^{13,14} (Fig. 2d).

Is it possible that natural fluctuations have modulated the concentration change? During most of the Holocene period and also during the last interglacial, the atmospheric level of CO₂ was near 280 p.p.m. (refs 15–17). Variations in CO₂ levels comparable in magnitude to the anthropogenic increase are documented only for periods with drastic climatic changes, such as the transition from the last glacial to the Holocene^{15,17}. Analyses of ice cores from the South Pole, covering the time AD 1000–1800 (Fig. 2b) (ref. 18), and from other sites^{19,21} indicate that between AD 1000 and 1800, the CO₂ concentration varied within about 10 p.p.m. This variability is much less than the increase since AD 1800. It may not seem obvious that the natural fluxes are so well balanced when considering that the atmosphere exchanges more than 10% of its carbon mass every year with both the land biota and the ocean. But a large fraction of the gross fluxes consists of molecules circulated rapidly between relatively small sub-reservoirs.

On a shorter time scale, interannual variations of about 1 p.p.m., corresponding to a transfer of ≤2 Gt C yr⁻¹ into or out of the atmosphere, have been observed, correlated with El Niño Southern Oscillation (ENSO) events^{13,22,23}. They seem to be connected to carbon releases by land vegetation, due possibly to ENSO-related drought and the increased frequency of fires^{13,24}. There is good evidence that the natural atmospheric CO₂ variations are relatively small under present climatic condi-

tions. Thus, the assumption that the natural cycle has operated in a steady state in the past and continues to do so, upon which the models of the global carbon cycle discussed below are all based, seems to be a reasonable approximation.

Uptake of CO₂ by the ocean

The ocean is the largest of the rapidly exchanging global carbon reservoirs (Fig. 1) and a major sink for anthropogenic carbon. The increase of dissolved inorganic carbon (ΣCO_2) in the oceans is difficult to measure experimentally, because the annual increase is small compared to the regional and temporal variability. Therefore, the oceanic CO₂ uptake has to be estimated using ocean-atmosphere carbon-cycle models. The net air-sea flux is driven by the difference in partial pressures of CO₂ and can be written as

$$F = k_g(p\text{CO}_{2,a} - p\text{CO}_{2,s}) = k_g \Delta p\text{CO}_2 \quad (1)$$

where $p\text{CO}_{2,s}$ is the equilibrium partial pressure of CO₂ in surface sea water, $p\text{CO}_{2,a}$ is the partial pressure of CO₂ in the air and k_g is a gas exchange coefficient. Whereas the air-sea exchange occurs by means of gaseous CO₂, most of the ΣCO_2 in surface sea water is in ionic form and less than 1% is dissolved CO₂ gas. When sea water takes up additional CO₂, ΣCO_2 and $p\text{CO}_2$ both

increase, but the chemical equilibria between the carbon species (CO₂, HCO₃⁻ and CO₃²⁻) are shifted such that the relative increase of $p\text{CO}_2$ is about 10 times larger than that of ΣCO_2 . This buffer mechanism determines the uptake capacity of the ocean: the ocean contains about 65 times more carbon than the pre-industrial atmosphere, but at equilibrium it can take up only ~6.5 times as much additional carbon as the atmosphere. This capacity becomes available only when the whole ocean is chemically equilibrated with the new atmospheric CO₂ concentration, which would take roughly 1,000 yr, the turnover time of the deep sea. The dynamics of the oceanic uptake of CO₂ is therefore strongly determined by the rate of downward transport of CO₂-laden water from surface to depth. The gas-exchange rate is fast enough to ensure that surface-water $p\text{CO}_2$ is near equilibrium with the atmosphere (except in ocean regions where vertical water exchange is vigorous), with a global mean $\Delta p\text{CO}_2$ of currently ~8 p.p.m., which is small compared to the atmospheric increase of ~75 p.p.m. since pre-industrial times. The global mean $\Delta p\text{CO}_2$ is so small because surface sea water reaches chemical equilibrium with the atmospheric CO₂ concentration within typically one year²⁵, whereas the timescale for downward transport from the surface to deeper layers in the ocean is considerably longer. Thus, the main rate-determining step for oceanic

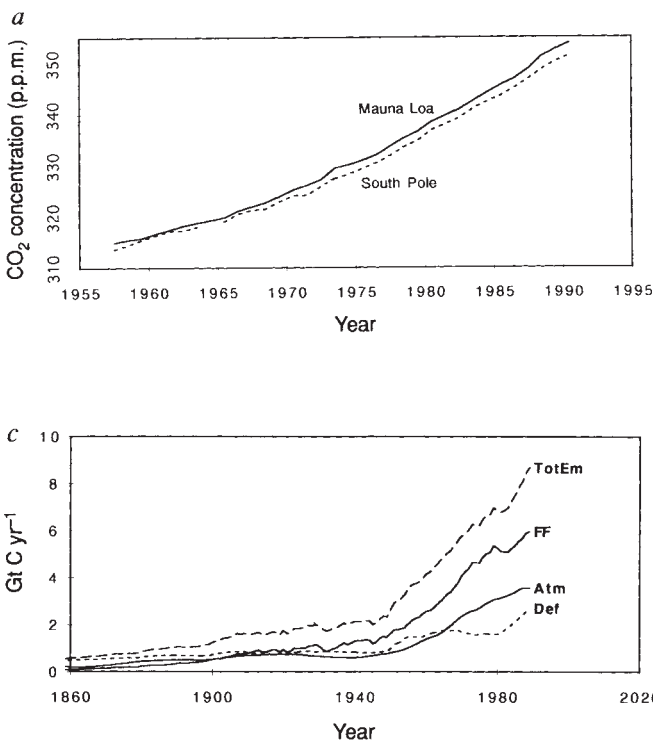
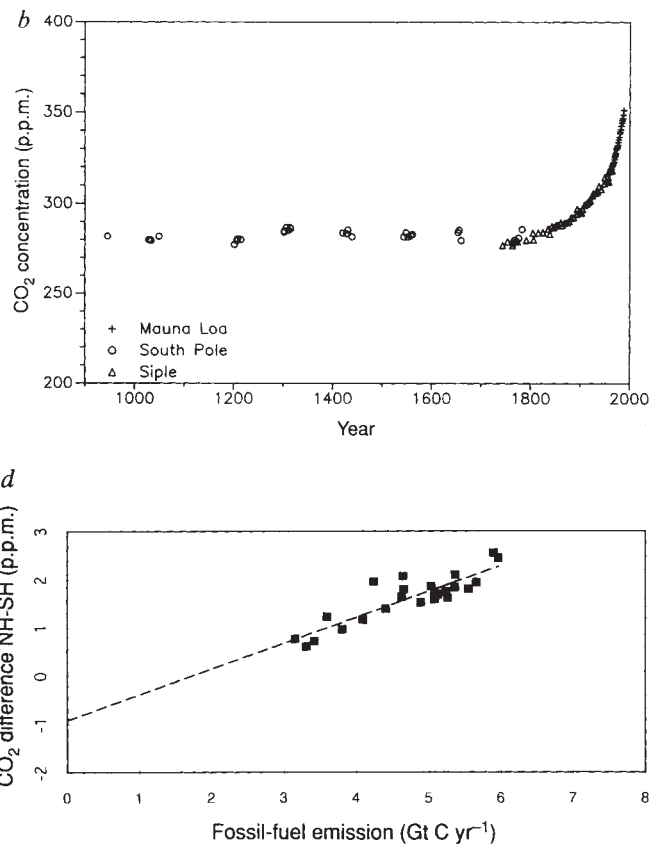


FIG. 2 a, Atmospheric CO₂ measurement at Mauna Loa, Hawaii⁵ and at the South Pole⁴. b, Record of atmospheric CO₂ for the past 1,000 yr, given by direct atmospheric observations at Mauna Loa⁵ (+), measurement on Antarctic ice cores from Siple station^{15,83} (Δ) and South Pole¹⁸ (O). c, Annual growth of amount of CO₂ in atmosphere (Atm), emissions from fossil fuel use^{1,9} (FF), an estimate of net flux due to deforestation and land use¹¹ (Def) and the sum of both emissions (TotEm). The year-to-year increase in the atmosphere has been smaller than the annual emissions from fossil fuels since about 1900 and than the total estimated annual emissions since 1850, that is the start of the deforestation record. The annual atmospheric CO₂ increase observed in the Siple ice core before 1900 cannot be explained by the fossil emissions alone, which indicates that carbon release from deforestation was significant in the 19th century, as also obtained from the direct estimates. For the whole period 1860 to 1989, the total estimated CO₂ release from fossil fuels and deforestation is about 345 Gt C, while the atmospheric increase amounted to 138 Gt C, corresponding to an average airborne



fraction of 40% of the cumulative release. (The ratio of atmospheric increase to cumulative fossil input only is 65%; our figure includes the contribution from deforestation.) The airborne fraction has varied in time, depending on the history of the emissions. For the decade 1980–1989, it is 46 ± 8%. d, Interhemispheric CO₂ concentration difference (Mauna Loa–South Pole^{4,5}) versus global fossil-fuel derived emissions. The Northern Hemisphere–Southern Hemisphere difference is the result of a balance between emissions, interhemispheric transportation through the atmosphere and surface sinks. The good correlation can be explained by the fact that most of these emissions (95%) take place in the NH. Note that if extrapolated to zero fossil-fuel emissions, the SH concentration would be ~1 p.p.m. greater than that in the NH, which, comparing with the model calculations of refs 6, 13 roughly correspond to a northward flux of ~1 Gt C yr⁻¹.

CO₂ uptake, which must be correctly simulated by carbon-cycle models, is the vertical water transport. The time needed for penetration of anthropogenic carbon into the thermocline (topmost 1,000 m) is several decades, and many centuries are needed to reach the large reservoirs of the deep sea. The behaviour of the oceanic uptake over time can be studied in a model by the progressive decay of a hypothetical CO₂ pulse into the atmosphere^{26, 28}. The model-calculated CO₂ uptake, to the present, corresponds typically to an average penetration depth of 600 m.

The models used vary in complexity from simple box-type schemes (for example refs 29, 30) to three-dimensional Ocean General Circulation Models (for example refs 27, 28). In the former, the calculation of oceanic circulation is not based on physical laws, but is prescribed in a parametric fashion, with the oceanic transport parameters determined by the use of observations of a suitable tracer such as bomb-produced ¹⁴C. Verification of the simulated pattern and rate of circulation by means of suitable tracers is essential also for three-dimensional models³¹. The results for the oceanic uptake, obtained by different models from a deconvolution of the Siple–Mauna Loa CO₂ record and normalized by the penetration depth of bomb-¹⁴C, are all in the range 1.6–2.3 Gt C yr⁻¹ (Table 1). Assuming an error ±20% for the bomb-¹⁴C inventory³² and further that the CO₂ uptake scales directly with the bomb-¹⁴C uptake (both conservative assumptions), we estimate an overall error of ±30%. We conclude that the best model-based estimate for the current oceanic uptake is 2.0 ± 0.6 Gt C yr⁻¹ (subjectively estimated confidence 90%).

Calculating air–sea CO₂ fluxes from observations. Local, instantaneous air–sea CO₂ fluxes can be estimated from equation (1), using measured air–sea *p*CO₂ differences and estimated gas exchange coefficients. Some oceanic regions such as the Equatorial Pacific release large amounts of CO₂ to the atmosphere, other regions take up CO₂ because of undersaturation. It is important to recognize that the observed distribution of source and sink regions is given by the superposition of natural and anthropogenic processes, with the natural features generally dominating the pattern. Therefore, Δ*p*CO₂ measurements do not indicate where anthropogenic CO₂ is mainly taken up, as they only yield the total flux; the net uptake of anthropogenic CO₂ (the perturbation flux) equals the present minus the pre-industrial flux. In fact, the net sequestration is larger in the Equatorial Pacific (an outgassing region) than, for example, in the subtropics, because the water that upwells at the equator is less CO₂-contaminated than surface water in the subtropical gyre regions^{27, 28}.

One problem with equation (1) is that the (wind-speed dependent) gas exchange coefficient *k_g* is not precisely known. There is a discrepancy of a factor 1.5–2 in the global mean value of *k_g* as obtained by two different methods. Estimates based on the oceanic inventories of natural or bomb-produced ¹⁴C yield an average gross exchange flux of 15–18 mol m⁻² yr⁻¹ at *p*CO₂ = 280 p.p.m. (refs 32, 34, 35), whereas a global integration of results from laboratory and field gas-exchange experiments^{36, 37}, using observed winds, yields 8–11 mol m⁻² yr⁻¹ (ref. 38). The reason for this discrepancy is not clear. One suggestion is that very high exchange fluxes occur during long-lasting heavy-wind events which are not represented in the laboratory and in most field studies³⁹. Another possibility is that compared to other gases, the gas exchange rate of CO₂ is enhanced by the enzyme carbonic anhydrase which accelerates the hydration of carbon dioxide in living cells by many orders of magnitude⁴⁰. But it is not clear whether this enzyme is present in sufficient concentrations in the open ocean⁴¹.

In principle, the net oceanic uptake of CO₂ could be obtained by globally integrating local instantaneous air–sea fluxes, calculated from measured *p*CO₂ values using equation (1), $F = k_g \Delta pCO_2$. But this method is rather inaccurate. First, the variation of surface-water *p*CO₂ in space and time is much larger than the global mean Δ*p*CO₂ of (currently) ~8 p.p.m. For

instance, *p*CO₂ exhibits a temperature-driven seasonal variation of ~80 p.p.m. near Bermuda¹⁴, and biologically-driven spatial variations of several 10 p.p.m. were observed within <100 km in the northeastern Atlantic³⁷. Therefore, a spatially and seasonally very dense *p*CO₂ data coverage would be required for a global integration of equation (1). Another serious problem is that Δ*p*CO₂ is the small difference between two large numbers, so that the computed net fluxes are very sensitive to small experimental errors in *p*CO₂. Such errors may, for example, be due to uncertainties in the chemical equilibrium constants used for back-calculating *p*CO₂ from the temperature in the measuring device (equilibrator) to sea water temperature. Attempts to estimate the oceanic sink based only on Δ*p*CO₂ measurements will therefore remain rather imprecise.

While there is little hope of obtaining the oceanic CO₂ uptake from Δ*p*CO₂ observations alone, regional Δ*p*CO₂ data sets can help to constrain the atmospheric CO₂ budget (see below).

Interhemispheric concentration difference and CO₂ sinks. The discussion of the oceanic CO₂ uptake was recently stimulated by Tans, Fung and Takahashi⁶ who combined observations of atmospheric and oceanic *p*CO₂ with an atmospheric model, and concluded that the ocean takes up less CO₂ than predicted by carbon-cycle models. The atmospheric CO₂ concentration is higher in the Northern Hemisphere (NH) than in the Southern Hemisphere (SH), because 95% of the fossil-fuel CO₂ emissions occur in the NH. The observed interhemispheric difference is, however, smaller than that predicted by atmospheric transport models that employ the conventionally assumed geographical distribution of natural and anthropogenic sources and sinks (refs 6, 42–44 and P. Kasibhatla, personal communication). This indicates that the ocean in the SH takes up less CO₂ than expected, resulting in a smaller NH–SH transport and thus a smaller interhemispheric concentration difference. For a quantitative assessment, Tans *et al.* estimated the oceanic uptake in the NH by means of Δ*p*CO₂ data and equation (1); the data coverage in the SH is inadequate to do this. They then adjusted the SH oceanic uptake and introduced a NH terrestrial sink such that the observed CO₂ distribution was reproduced by the transport model. (Δ*p*CO₂ measurements are used here to determine the flux only for a restricted area of the global ocean, and the final result is therefore less sensitive to the accuracy of Δ*p*CO₂ than a global integration discussed above.) In this way Tans *et al.* obtained a total oceanic uptake of 0.3–0.8 Gt C yr⁻¹, much less than the estimate from carbon-cycle models. In order to balance the budget, they postulated a large carbon sink in the NH land biota. In contrast, Keeling *et al.*⁴⁴ have dismissed that possibility, based on atmospheric δ¹³C observations.

The result of Tans *et al.*⁶ requires revision in three respects^{45, 46}. First, the skin temperature at the sea surface is (on average) a few tenths of a degree cooler than the bulk water temperature at which *p*CO₂ is determined, so that the mean surface *p*CO₂ is overestimated by several p.p.m. Robertson and Watson⁴⁷ estimated that the value of the air–sea flux north of 15° S, obtained by Tans *et al.* on the basis of Δ*p*CO₂, (and consequently their result for the global ocean) has to be increased by ~0.44 Gt C yr⁻¹ to correct for the skin effect. Second, the net air–sea gas exchange is the sum of the anthropogenic flux and a non-zero natural flux. Rivers transport organic and inorganic carbon from soils to the oceans (~0.8 Gt C yr⁻¹, see Fig. 1); a large part of this carbon was originally taken up from the atmosphere by photosynthesis on land. Part of the riverine load goes to the sediments, but a substantial fraction of the organic input is remineralized in the sea to inorganic carbon. In a steady state, the cycle must be closed by an outgassing flux of 0.4–0.7 Gt C yr⁻¹ from the ocean to the atmosphere^{45, 48}. This amount has to be added to the calculated gas transfer to obtain the total anthropogenic CO₂ flux to the sea (equal to the difference between the present and pre-industrial situations). Third, there is a north–south transport of carbon in the atmosphere not only by carbon dioxide, but also by carbon monoxide. If properly accounted for, this adds

$\sim 0.25 \text{ Gt C yr}^{-1}$ to the oceanic uptake⁴³. The mean estimate of Tans *et al.* for the oceanic CO_2 uptake, revised for these three corrections, is then $0.55 + 0.44 + 0.55 + 0.25 \sim 1.8 \text{ Gt C yr}^{-1}$ (with an uncertainty difficult to estimate), in agreement with the carbon-cycle models. A recent reassessment⁴⁹ of the Tans *et al.* calculation obtained an oceanic carbon uptake of $2.0 \pm 1.0 \text{ Gt C yr}^{-1}$.

These corrections do not explain why the observed interhemispheric CO_2 difference is smaller than the value predicted by models that use the conventional distribution of sources and sinks. Interestingly, an extrapolation of the NH-SH difference to zero fossil-fuel emissions (Fig. 2d) indicates that without emissions, the SH concentration would be ~ 1 p.p.m. higher than that in the NH. This difference, compared to model calculations^{6,13}, would give rise to an interhemispheric flow of approximately 1 Gt C yr^{-1} . Model results^{44,50} suggest that this natural interhemispheric difference may partly (but probably not fully) be caused by a covariance of seasonal concentration variations and atmospheric transport patterns. Thus, an atmospheric transport of order 1 Gt C yr^{-1} across the equator seems to have existed in pre-industrial time, which must have been balanced by an equal southward flow through the ocean⁴⁴. A net southward carbon flux is plausible via North Atlantic Deep Water, carrying more carbon southward than the CO_2 -depleted surface water transports northward, although geochemical esti-

mates of this flux are smaller than expected (0.4 Gt C yr^{-1} and 0.6 Gt C yr^{-1} , refs 51, 52).

In the near future, it should become possible to improve and enhance the $p\text{CO}_2$ data base. Field programmes, for example within the Joint Global Ocean Flux Study (JGOFS), will produce large numbers of high-precision observations. The combination of atmospheric and oceanic CO_2 measurements with atmospheric models will then result in a more accurate assessment of the carbon budget, with the $\Delta p\text{CO}_2$ measurements serving as constraints on the regional air-sea fluxes. In addition, observations of transient tracers (^{14}C , freons) in the ocean obtained in the World Ocean Circulation experiment (WOCE) will provide integrated information on the rate of oceanic water fluxes; these measurements are essential for validating ocean models.

Other methods for estimating the oceanic CO_2 uptake. Carbon dioxide from the burning of fossil fuels or biomass is isotopically labelled, compared to atmospheric CO_2 , by low $^{13}\text{C}/^{12}\text{C}$ ratios. Correspondingly, $^{13}\text{C}/^{12}\text{C}$ has decreased in the various carbon reservoirs, which can be used as an additional constraint on the budget of CO_2 perturbations. Quay *et al.*⁵³ made use of this by considering the partitioning of anthropogenic $^{13}\text{CO}_2$ between atmosphere, ocean and land biota in the period 1970–1990. The atmospheric ^{13}C decrease is known from measurements. The change in the oceanic amount of ^{13}C carbon comes about by a change in isotopic composition (measured) and by the increase of ΣCO_2 . Analogously, the biotic share in the isotopic perturbation is due to a change of $^{13}\text{C}/^{12}\text{C}$ (estimated using a biota model) and the change in net biotic carbon storage. The two unknown quantities, oceanic uptake and net biomass change, can in principle be calculated if the other quantities can be determined. In this way, Quay *et al.*⁵³ estimated an average oceanic uptake for 1970–1990 of $2.1 \pm 1.5 \text{ Gt C yr}^{-1}$ (2σ error) and a net biotic carbon flux of near zero. The error stems from two main sources. First, the existing oceanic and atmospheric ^{13}C measurements are insufficient to precisely determine the small isotopic changes; further high-precision ^{13}C measurements in the atmosphere and the ocean have to be done to improve this. Second, the isotopic difference between global respiration and photosynthesis cannot be measured, but has to be estimated based on biota models. How well this can be done essentially determines the precision of the CO_2 perturbation budget achievable by this method. Although the error is presently still too large, the isotopic method represents a new and independent way to assess the oceanic CO_2 uptake.

Keeling and Shertz⁵⁴ recently published results showing the decrease of atmospheric oxygen. During photosynthesis, respiration or combustion of organic matter, about 1 mole O_2 is produced for each mole CO_2 consumed (and *vice versa*). Therefore, the atmospheric CO_2 increase is accompanied by a slight O_2 decrease. In contrast to CO_2 the ocean does not buffer the O_2 decrease, because O_2 is much less soluble than CO_2 and is not affected by aquatic chemistry. High-precision monitoring of the O_2 concentration thus allows a direct assessment of the sum of fossil-fuel and biospheric sources minus sinks of carbon. The CO_2 uptake by ocean plus land biota is then obtained by subtracting the atmospheric CO_2 increase. As the O_2 decrease is very small, ~ 4 p.p.m. yr^{-1} , compared to the concentration of 210,000 p.p.m., its measurement is rather difficult. This method is only beginning; within several years, it should provide useful constraints on the carbon budget. In addition the seasonal atmospheric O_2 variations yield information on the size of the new production by the marine biota⁵⁴.

The budget of anthropogenic perturbations

Figure 3a shows the result of a model deconvolution of the Siple–Mauna Loa CO_2 record, obtained by calculating the flux into the ocean corresponding to the observed atmospheric concentration increase^{35,55}. In Fig. 3b, estimates of anthropogenic emissions are compared with the accumulation of CO_2 in the

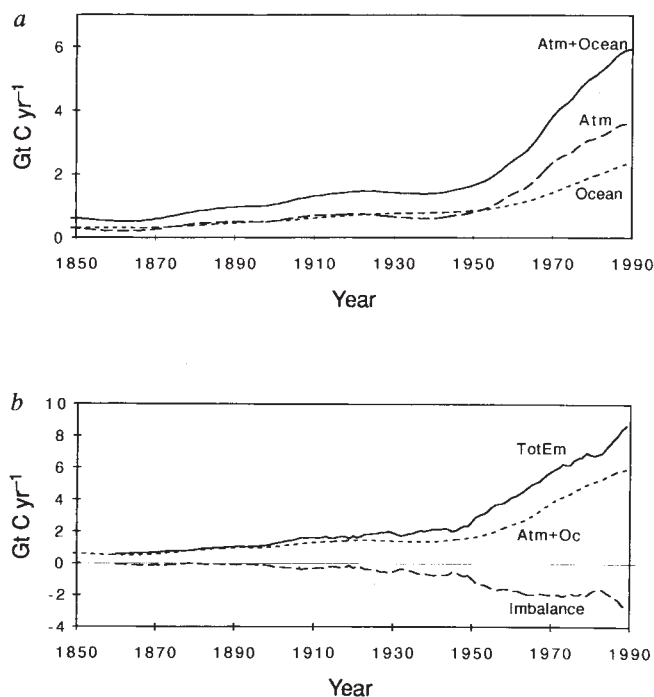


FIG. 3 a, Deconvolution of the atmospheric CO_2 record. To perform the deconvolution, the atmospheric CO_2 concentration is prescribed as a function of time (Fig. 2b) and the flux into the ocean is calculated using the HILDA model^{35,72,73}. Shown are annual CO_2 accumulations in the atmosphere (Atm; prescribed), ocean (Ocean; computed) and the sum of both (Atm + Ocean) that must be equal to the annual net flux into the atmosphere from fossil fuel combustion plus deforestation minus CO_2 fertilization of land plants plus/minus any other sources and sinks. b, Annual fluxes into the atmospheric–ocean system: estimated total anthropogenic emissions (TotEm, from Fig. 2c), CO_2 accumulation in the atmosphere plus ocean (Atm + Oc, from Fig. 3a) and difference between these quantities (Imbalance). The latter represents the imbalance or ‘missing sink’; it includes the effect of stimulation of biomass growth by fertilization (by CO_2 or nitrogen emissions and so on) and from natural fluctuations. Note that the estimate for emissions from deforestation, and therefore also the imbalance, have considerable uncertainty.

atmosphere plus the ocean. The accumulation in the atmosphere plus the ocean matches the estimated emissions until about 1920, but after this there is an increasing gap between the two, indicating that either the emission estimates are significantly too high or that there is a sink not accounted for in this balance. Table 2 summarizes best estimates for the average 1980–1989 budget of the anthropogenic CO₂ perturbations. Of the estimated annual release of 7 Gt C, 3.2 Gt C yr⁻¹ remained in the atmosphere, as determined by direct measurements, and the ocean is estimated to have taken up 2.0 Gt C yr⁻¹. This leaves 1.8 ± 1.3 Gt C yr⁻¹ of the emissions unaccounted for. Although the error limits on this number are large, it seems difficult to reconcile the estimates for sources and sinks; there seems to be a 'missing sink'. The oceanic uptake is well known from the results of carbon-cycle models, so the solution to this problem must lie elsewhere.

A recent analysis of high-resolution satellite pictures indicates that deforestation has been overestimated⁵⁶, but it seems unrealistic to assume that it was virtually zero, as required for closing the perturbation budget with the sinks of Table 2. The most plausible explanation for the imbalance is that vegetation and soils are accumulating carbon, perhaps in response to the increased CO₂ concentration—in which case this sink should have grown parallel to atmospheric CO₂—or due to man-made nitrogen compounds⁵⁷. As Fig. 3b shows, the imbalance has indeed grown with time. A stimulation of plant growth in CO₂-enriched air is well-documented in short-term laboratory experiments, but it is not clear how important this effect is in nature and over longer time periods⁵⁸. Analyses of forest growth have so far not confirmed a carbon accumulation of the required size⁵⁹, but the imbalance is only a few percent of the terrestrial net primary production of 50 Gt C yr⁻¹, and the expected small increment in carbon storage density may well have escaped observation. Indirect evidence for growing biospheric activities comes from the observation that the seasonal CO₂ amplitude at many atmospheric monitoring stations has increased significantly^{14,60}.

Another reason for the mismatch between sources and sinks could be an imbalance of the natural exchange fluxes between atmosphere and ocean. But considering that there were no major CO₂ excursions in pre-industrial time, it seems unlikely that this could explain the whole imbalance.

The role of marine biology

The marine biota act as a carbon pump by producing particulate and dissolved organic matter, which is then exported to deeper layers in the ocean where it is decomposed (Fig. 1). This provides a deep source of inorganic carbon and creates a deficit of about 10% of ΣCO₂ in surface water compared to the deep sea. The size of the export fluxes is not well known, with estimates for the particulate flux ranging from 4 to 20 Gt C yr⁻¹ (refs 61, 62). Reported measurements of dissolved organic carbon (DOC)⁶³ yielding significantly higher oceanic concentrations than previously adopted have recently been withdrawn⁶⁴. Model simulations suggest a DOC export to depth of order 10 Gt C yr⁻¹ (refs 65, 66). In the unperturbed stationary state, the biogenic fluxes are compensated by an equally large upward transport of dissolved inorganic matter by water motion, corresponding to a zero net transport (except for the small fraction that goes into the sediments). The biogenic fluxes are usually not included in carbon-cycle models designed for studying the anthropogenic perturbations. This is because according to present understanding, biological productivity is controlled by nutrients (mainly phosphorus and nitrogen), light or zooplankton grazing, but not by CO₂ concentration. Therefore, the biogenic fluxes do not sequester anthropogenic carbon, but rather act as a natural background process continuing to work as in pre-industrial times (compare Fig. 1). (New laboratory studies⁶⁷ indicate that under special conditions the growth of diatoms can be affected by the availability of CO₂, but the large-scale significance of these results remains to be assessed.)

Climatic or environmental changes might modify the natural biological fluxes, which could then feed back on the atmospheric composition. Alterations of the biological carbon pump, for example related to the documented glacial–interglacial shifts of the oceanic circulation, have been discussed as possible causes of the lower ice-age CO₂ levels^{68–70}. A particularly sensitive ocean region is the Southern Ocean where the exchange between surface and deep ocean is fast, providing a large nutrient supply from depth to the surface, while marine productivity is relatively small and does not make full use of the abundant nutrients. It has been suggested that Southern Ocean productivity might be controlled by lack of the micronutrient iron⁷¹ and that fertilizing the Southern Ocean with iron could stimulate a stronger biogenic downward export of carbon and therefore counteract the man-made atmospheric CO₂ increase. Model calculations indicate that for a business-as-usual emission scenario, iron fertilization could not stop the atmospheric CO₂ growth, even under extreme assumptions about its efficiency, but only reduce the growth rate; when the iron input ceased, CO₂ would escape again from the ocean^{72–76}. Although the role of iron as a limiting nutrient is of fundamental interest for marine biology, iron fertilization is clearly not an alternative to a control of carbon emissions.

Conceivable direct effects of climate change on the biological carbon pump include a change of productivity or a more rapid remineralization of DOC and sinking organic particles due to global warming. For large environmental changes, the composition of marine ecosystems might shift. Extreme cases of the possible influence of the marine biota on atmospheric CO₂ levels are given by model simulations which indicate that for pre-industrial conditions (unperturbed concentration of CO₂: 280 p.p.m.), a fully effective biological carbon pump, reducing surface nutrient concentrations to zero everywhere, would yield an atmospheric CO₂ level of about 160 p.p.m. Extinction of all marine life would lead to a level of ~450 p.p.m. (refs 69, 77). This can be compared to a predicted ~1,000 p.p.m. in the year 2100 (ref. 78) for the highest 1992 emission scenario of the Inter-governmental Panel on Climate Change³. Changes in the marine biota could thus significantly affect atmospheric CO₂, although their potential impact is smaller than the potential anthropogenic increase. On long timescales (millenia), interactions with marine sediments have also to be considered⁷.

Indirectly, climatic change could affect CO₂ levels in different ways. The CO₂ solubility would decrease in the case of a general warming (positive feedback on atmospheric growth). Ocean circulation could change, probably reducing the downward transport of excess carbon into the interior ocean (positive feedback). Finally, oceanic circulation influences the upward transportation of carbon and nutrients and by way of nutrients, also the biological pump, as discussed in the context of glacial–interglacial variation^{68–70} (positive or negative feedback). Preliminary model calculations suggest that significant impacts on the carbon cycle would only occur for major changes in ocean circulation.

Factors controlling future CO₂ levels

The main uncertainty about the future growth of atmospheric CO₂ levels stems from the development of anthropogenic emissions, which depend on political and socio-economic factors and cannot be predicted. For instance, there is a three-fold difference in the cumulative emissions 1990–2100 between the highest (2,127 Gt C) and the lowest (742 Gt C) of the six 1992 IPCC scenarios, all based on plausible assumptions about future developments³. These 1990–2100 emissions originate largely from fossil fuels, whereas deforestation does not play an important role (30–93 Gt C) because the biomass in tropical forests is limited. For a given emission scenario, the model predictions of future atmospheric CO₂ depend on assumptions about the 'missing sink'. Calculations based on best estimates for the sources and sinks (implying an unbalanced perturbations budget) yield higher future concentrations than calculations based on a balanced budget achieved by assuming an extra

(biospheric or oceanic) sink; the difference may be considerable, especially for low-emission scenarios⁷⁹.

To improve our ability to estimate future CO₂ concentrations, intense further research is necessary. Oceanic tracer measurements, in particular of ¹⁴C and CFCs, are needed for the validation of ocean models. The resolution of ocean carbon-cycle models has to be increased. It seems unlikely, however, that revised oceanic uptake estimates will be outside the range of current model results. An observational assessment of the net carbon fluxes to the ocean and the land biota requires high-precision observations of the spatial and temporal CO₂ and isotopic distributions in the atmosphere and the surface ocean, and a variety of models for deducing fluxes. The factors controlling marine biology are not well understood. Are the ratios in which carbon and nutrients (P, N) are built into organic tissue (the Redfield ratios) indeed constant, as generally assumed? Could CO₂ be a limiting nutrient under special circumstances? The large

oceanic data sets to be produced in programmes like JGOFS and WOCE will further progress in these areas. Important uncertainties exist about the land biota (particularly concerning growth stimulation by anthropogenic CO₂ and nitrogen compounds), reaction of photosynthesis and respiration to temperature and water cycle changes and longer term modifications of ecosystem composition due to environmental change. Finally, model studies of the anthropogenic perturbation have been based on the assumption that the oceanic carbon cycle operates in a steady state. How good this assumption is remains to be determined. □

U. Siegenthaler is at the Physics Institute, University of Bern, 3012 Bern, Switzerland. J. L. Sarmiento is at the Atmospheric and Oceanic Sciences Program, Princeton University, Princeton, New Jersey 08544, USA.

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