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The Carbon Cycle and Atmospheric Carbon Dioxide

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Executive Summary

CO_2 concentration trends and budgets

Before the Industrial Era, circa 1750, atmospheric carbon dioxide (CO_2) concentration was 280 ± 10 ppm for several thousand years. It has risen continuously since then, reaching 367 ppm in 1999.

The present atmospheric CO_2 concentration has not been exceeded during the past 420,000 years, and likely not during the past 20 million years. The rate of increase over the past century is unprecedented, at least during the past 20,000 years.

The present atmospheric CO_2 increase is caused by anthropogenic emissions of CO_2. About three-quarters of these emissions are due to fossil fuel burning. Fossil fuel burning (plus a small contribution from cement production) released on average 5.4 ± 0.3 PgC/yr during 1980 to 1989, and 6.3 ± 0.4 PgC/yr during 1990 to 1999. Land use change is responsible for the rest of the emissions.

The rate of increase of atmospheric CO_2 content was 3.3 ± 0.1 PgC/yr during 1980 to 1989 and 3.2 ± 0.1 PgC/yr during 1990 to 1999. These rates are less than the emissions, because some of the emitted CO_2 dissolves in the oceans, and some is taken up by terrestrial ecosystems. Individual years show different rates of increase. For example, 1992 was low (1.9 PgC/yr), and 1998 was the highest (6.0 PgC/yr) since direct measurements began in 1957. This variability is mainly caused by variations in land and ocean uptake.

Statistically, high rates of increase in atmospheric CO_2 have occurred in most El Niño years, although low rates occurred during the extended El Niño of 1991 to 1994. Surface water CO_2 measurements from the equatorial Pacific show that the natural source of CO_2 from this region is reduced by between 0.2 and 1.0 PgC/yr during El Niño events, counter to the atmospheric increase. It is likely that the high rates of CO_2 increase during most El Niño events are explained by reductions in land uptake, caused in part by the effects of high temperatures, drought and fire on terrestrial ecosystems in the tropics.

Land and ocean uptake of CO_2 can now be separated using atmospheric measurements (CO_2, oxygen (O_2) and $^{13}CO_2$). For 1980 to 1989, the ocean-atmosphere flux is estimated as -1.9 ± 0.6 PgC/yr and the land-atmosphere flux as -0.2 ± 0.7 PgC/yr based on CO_2 and O_2 measurements (negative signs denote net uptake). For 1990 to 1999, the ocean-atmosphere flux is estimated as -1.7 ± 0.5 PgC/yr and the land-atmosphere flux as -1.4 ± 0.7 PgC/yr. These figures are consistent with alternative budgets based on CO_2 and $^{13}CO_2$ measurements, and with independent estimates based on measurements of CO_2 and $^{13}CO_2$ in sea water. The new 1980s estimates are also consistent with the ocean-model based carbon budget of the IPCC WGI Second Assessment Report (IPCC, 1996a) (hereafter SAR). The new 1990s estimates update the budget derived using SAR methodologies for the IPCC Special Report on Land Use, Land Use Change and Forestry (IPCC, 2000a).

The net CO_2 release due to land-use change during the 1980s has been estimated as 0.6 to 2.5 PgC/yr (central estimate 1.7 PgC/yr). This net CO_2 release is mainly due to deforestation in the tropics. Uncertainties about land-use changes limit the accuracy of these estimates. Comparable data for the 1990s are not yet available.

The land-atmosphere flux estimated from atmospheric observations comprises the *balance* of net CO_2 release due to land-use changes and CO_2 uptake by terrestrial systems (the "residual terrestrial sink"). The residual terrestrial sink is estimated as -1.9 PgC/yr (range -3.8 to $+0.3$ PgC/yr) during the 1980s. It has several likely causes, including changes in land management practices and fertilisation effects of increased atmospheric CO_2 and nitrogen (N) deposition, leading to increased vegetation and soil carbon.

Modelling based on atmospheric observations (inverse modelling) enables the land-atmosphere and ocean-atmosphere fluxes to be partitioned between broad latitudinal bands. The sites of anthropogenic CO_2 uptake in the ocean are not resolved by inverse modelling because of the large, natural background air-sea fluxes (outgassing in the tropics and uptake in high latitudes). Estimates of the land-atmosphere flux north of 30°N during 1980 to 1989 range from -2.3 to -0.6 PgC/yr; for the tropics, -1.0 to $+1.5$ PgC/yr. These results imply substantial terrestrial sinks for anthropogenic CO_2 in the northern extra-tropics, and in the tropics (to balance deforestation). The pattern for the 1980s persisted into the 1990s.

Terrestrial carbon inventory data indicate carbon sinks in northern and tropical forests, consistent with the results of inverse modelling.

East-west gradients of atmospheric CO_2 concentration are an order of magnitude smaller than north-south gradients. Estimates of continental-scale CO_2 balance are possible in principle but are poorly constrained because there are too few well-calibrated CO_2 monitoring sites, especially in the interior of continents, and insufficient data on air-sea fluxes and vertical transport in the atmosphere.

The global carbon cycle and anthropogenic CO_2

The global carbon cycle operates through a variety of response and feedback mechanisms. The most relevant for decade to century time-scales are listed here.

Responses of the carbon cycle to changing CO_2 concentrations
- Uptake of anthropogenic CO_2 by the ocean is primarily governed by ocean circulation and carbonate chemistry. So long as atmospheric CO_2 concentration is increasing there is net uptake of carbon by the ocean, driven by the atmosphere-ocean difference in partial pressure of CO_2. The fraction of anthropogenic CO_2 that is taken up by the ocean declines with increasing CO_2 concentration, due to reduced buffer capacity of the carbonate system. The fraction taken up by the ocean also declines with the rate of increase of atmospheric CO_2, because the rate of mixing between deep water and surface water limits CO_2 uptake.
- Increasing atmospheric CO_2 has no significant fertilisation effect on marine biological productivity, but it decreases pH. Over a century, changes in marine biology brought about by changes in calcification at low pH could increase the ocean uptake of CO_2 by a few percentage points.

- Terrestrial uptake of CO_2 is governed by net biome production (NBP), which is the balance of net primary production (NPP) and carbon losses due to heterotrophic respiration (decomposition and herbivory) and fire, including the fate of harvested biomass. NPP increases when atmospheric CO_2 concentration is increased above present levels (the "fertilisation" effect occurs directly through enhanced photosynthesis, and indirectly through effects such as increased water use efficiency). At high CO_2 concentration (800 to 1,000 ppm) any further direct CO_2 fertilisation effect is likely to be small. The effectiveness of terrestrial uptake as a carbon sink depends on the transfer of carbon to forms with long residence times (wood or modified soil organic matter). Management practices can enhance the carbon sink because of the inertia of these "slow" carbon pools.

Feedbacks in the carbon cycle due to climate change
- Warming reduces the solubility of CO_2 and therefore reduces uptake of CO_2 by the ocean.
- Increased vertical stratification in the ocean is likely to accompany increasing global temperature. The likely consequences include reduced outgassing of upwelled CO_2, reduced transport of excess carbon to the deep ocean, and changes in biological productivity.
- On short time-scales, warming increases the rate of heterotrophic respiration on land, but the extent to which this effect can alter land-atmosphere fluxes over longer time-scales is not yet clear. Warming, and regional changes in precipitation patterns and cloudiness, are also likely to bring about changes in terrestrial ecosystem structure, geographic distribution and primary production. The net effect of climate on NBP depends on regional patterns of climate change.

Other impacts on the carbon cycle
- Changes in management practices are very likely to have significant effects on the terrestrial carbon cycle. In addition to deforestation and afforestation/reforestation, more subtle management effects can be important. For example, fire suppression (e.g., in savannas) reduces CO_2 emissions from burning, and encourages woody plant biomass to increase. On agricultural lands, some of the soil carbon lost when land was cleared and tilled can be regained through adoption of low-tillage agriculture.
- Anthropogenic N deposition is increasing terrestrial NPP in some regions; excess tropospheric ozone (O_3) is likely to be reducing NPP.
- Anthropogenic inputs of nutrients to the oceans by rivers and atmospheric dust may influence marine biological productivity, although such effects are poorly quantified.

Modelling and projection of CO_2 concentration

Process-based models of oceanic and terrestrial carbon cycling have been developed, compared and tested against *in situ* measurements and atmospheric measurements. The following are consistent results based on several models.
- Modelled ocean-atmosphere flux during 1980 to 1989 was in the range -1.5 to -2.2 PgC/yr for the 1980s, consistent with earlier model estimates and consistent with the atmospheric budget.
- Modelled land-atmosphere flux during 1980 to 1989 was in the range -0.3 to -1.5 PgC/yr, consistent with or slightly more negative than the land-atmosphere flux as indicated by the atmospheric budget. CO_2 fertilisation and anthropogenic N deposition effects contributed significantly: their combined effect was estimated as -1.5 to -3.1 PgC/yr. Effects of climate change during the 1980s were small, and of uncertain sign.
- In future projections with ocean models, driven by CO_2 concentrations derived from the IS92a scenario (for illustration and comparison with earlier work), ocean uptake becomes progressively larger towards the end of the century, but represents a smaller fraction of emissions than today. When climate change feedbacks are included, ocean uptake becomes less in all models, when compared with the situation without climate feedbacks.
- In analogous projections with terrestrial models, the rate of uptake by the land due to CO_2 fertilisation increases until mid-century, but the models project smaller increases, or no increase, after that time. When climate change feedbacks are included, land uptake becomes less in all models, when compared with the situation without climate feedbacks. Some models have shown a rapid decline in carbon uptake after the mid-century.

Two simplified, fast models (ISAM and Bern-CC) were used to project future CO_2 concentrations under IS92a and six SRES scenarios, and to project future emissions under five CO_2 stabilisation scenarios. Both models represent ocean and terrestrial climate feedbacks, in a way consistent with process-based models, and allow for uncertainties in climate sensitivity and in ocean and terrestrial responses to CO_2 and climate.

- The reference case projections (which include climate feedbacks) of both models under IS92a are, by coincidence, close to those made in the SAR (which neglected feedbacks).
- The SRES scenarios lead to divergent CO_2 concentration trajectories. Among the six emissions scenarios considered, the projected range of CO_2 concentrations at the end of the century is 550 to 970 ppm (ISAM model) or 540 to 960 ppm (Bern-CC model).
- Variations in climate sensitivity and ocean and terrestrial model responses add at least -10 to $+30\%$ uncertainty to these values, and to the emissions implied by the stabilisation scenarios.
- The net effect of land and ocean climate feedbacks is always to increase projected atmospheric CO_2 concentrations. This is equivalent to reducing the allowable emissions for stabilisation at any one CO_2 concentration.
- New studies with general circulation models including interactive land and ocean carbon cycle components also indicate that climate feedbacks have the potential to increase atmospheric CO_2 but with large uncertainty about the magnitude of the terrestrial biosphere feedback.

Implications

CO_2 emissions from fossil fuel burning are virtually certain to be the dominant factor determining CO_2 concentrations during the 21st century. There is scope for land-use changes to increase or decrease CO_2 concentrations on this time-scale. If all of the carbon so far released by land-use changes could be restored to the terrestrial biosphere, CO_2 at the end of the century would be 40 to 70 ppm less than it would be if no such intervention had occurred. By comparison, global deforestation would add two to four times more CO_2 to the atmosphere than reforestation of all cleared areas would subtract.

There is sufficient uptake capacity in the ocean to incorporate 70 to 80% of foreseeable anthropogenic CO_2 emissions to the atmosphere, this process takes centuries due to the rate of ocean mixing. As a result, even several centuries after emissions occurred, about a quarter of the increase in concentration caused by these emissions is still present in the atmosphere.

CO_2 stabilisation at 450, 650 or 1,000 ppm would require global anthropogenic CO_2 emissions to drop below 1990 levels, within a few decades, about a century, or about two centuries respectively, and continue to steadily decrease thereafter. Stabilisation requires that net anthropogenic CO_2 emissions ultimately decline to the level of persistent natural land and ocean sinks, which are expected to be small (<0.2 PgC/yr).

3.1 Introduction

The concentration of CO_2 in the atmosphere has risen from close to 280 parts per million (ppm) in 1800, at first slowly and then progressively faster to a value of 367 ppm in 1999, echoing the increasing pace of global agricultural and industrial development. This is known from numerous, well-replicated measurements of the composition of air bubbles trapped in Antarctic ice. Atmospheric CO_2 concentrations have been measured directly with high precision since 1957; these measurements agree with ice-core measurements, and show a continuation of the increasing trend up to the present.

Several additional lines of evidence confirm that the recent and continuing increase of atmospheric CO_2 content is caused by anthropogenic CO_2 emissions – most importantly fossil fuel burning. First, atmospheric O_2 is declining at a rate comparable with fossil fuel emissions of CO_2 (combustion consumes O_2). Second, the characteristic isotopic signatures of fossil fuel (its lack of ^{14}C, and depleted content of ^{13}C) leave their mark in the atmosphere. Third, the increase in observed CO_2 concentration has been faster in the northern hemisphere, where most fossil fuel burning occurs.

Atmospheric CO_2 is, however, increasing only at about half the rate of fossil fuel emissions; the rest of the CO_2 emitted either dissolves in sea water and mixes into the deep ocean, or is taken up by terrestrial ecosystems. Uptake by terrestrial ecosystems is due to an excess of primary production (photosynthesis) over respiration and other oxidative processes (decomposition or combustion of organic material). Terrestrial systems are also an anthropogenic source of CO_2 when land-use changes (particularly deforestation) lead to loss of carbon from plants and soils. Nonetheless, the global balance in terrestrial systems is currently a net uptake of CO_2.

The part of fossil fuel CO_2 that is taken up by the ocean and the part that is taken up by the land can be calculated from the changes in atmospheric CO_2 and O_2 content because terrestrial processes of CO_2 exchange involve exchange of oxygen whereas dissolution in the ocean does not. Global carbon budgets based on CO_2 and O_2 measurements for the 1980s and 1990s are shown in Table 3.1. The human influence on the fluxes of carbon among the three "reservoirs" (atmosphere, ocean, and terrestrial biosphere) represent a small but significant perturbation of a huge global cycle (Figure 3.1).

This chapter summarises current knowledge of the global carbon cycle, with special reference to the fate of fossil fuel CO_2 and the factors that influence the uptake or release of CO_2 by the oceans and land. These factors include atmospheric CO_2 concentration itself, the naturally variable climate, likely climate changes caused by increasing CO_2 and other greenhouse gases, changes in ocean circulation and biology, fertilising effects of atmospheric CO_2 and nitrogen deposition, and direct human actions such as land conversion (from native vegetation to agriculture and vice versa), fire suppression and land management for carbon storage as provided for by the Kyoto Protocol (IPCC, 2000a). Any changes in the function of either the terrestrial biosphere or the ocean – whether intended or not – could potentially have significant effects, manifested within years to decades, on the fraction of fossil fuel CO_2 that stays in the atmosphere. This perspective has

a) Main components of the natural carbon cycle

ATMOSPHERE *[730]*

90

OCEAN *[38,000]*

SEDIMENT

burial 0.2

0.6

weathering 0.2

river transport 0.8

weathering 0.2

120

0.4

Soil *[1500]* : Plants *[500]*
LAND

DOC export 0.4

Fossil organic carbon : Rock carbonates
GEOLOGICAL RESERVOIRS

vulcanism < 0.1

b) The human perturbation

ATMOSPHERE

ocean uptake 1.9

OCEAN

SEDIMENT

land-use change 1.7

land uptake 1.9

5.4

LAND

cement production 0.1

fossil fuel burning 5.3

Fossil organic carbon : Rock carbonates
GEOLOGICAL RESERVOIRS

c) Carbon cycling in the ocean

zoo-plankton

phyto-plankton

detritus

NPP 45

GPP 103

autotrophic respiration 58

heterotrophic respiration 34

CaCO₃ 0.7

CaCO₃ 0.1

export of soft tissue 11

export of CaCO₃ 0.4

coastal sediment

CaCO₃ 0.2

0.1

0.3

DOC/POC

heterotrophic respiration 11

dissolution 0.2

DIC

physical transport 33

CO₂ + H₂O + CO₃²⁻ ⇌ 2HCO₃⁻
DIC in surface water

90

88

42

thermocline 100 m

lysocline 3,500 m

sediment

0.01

d) Carbon cycling on land

heterotrophic respiration 55

autotrophic respiration 60

Animals

DETRITUS τ <10yr [300]

NPP 60

GPP 120

combustion

4

MODIFIED SOIL CARBON τ=10 to 1000yr [1050]

DOC export 0.4

'INERT' CARBON τ>1000yr [150]

< 0.1

?

driven a great deal of research during the years since the IPCC WGI Second Assessment report (IPCC, 1996) (hereafter SAR) (Schimel *et al.,* 1996; Melillo *et al.,* 1996; Denman *et al.,* 1996). Some major areas where advances have been made since the SAR are as follows:

- Observational research (atmospheric, marine and terrestrial) aimed at a better quantification of carbon fluxes on local, regional and global scales. For example, improved precision and repeatability in atmospheric CO_2 and stable isotope measurements; the development of highly precise methods to measure changes in atmospheric O_2 concentrations; local terrestrial CO_2 flux measurements from towers, which are now being performed continuously in many terrestrial ecosystems; satellite observations of global land cover and change; and enhanced monitoring of geographical, seasonal and interannual variations of biogeochemical parameters in the sea, including measurements of the partial pressure of CO_2 (pCO_2) in surface waters.

- Experimental manipulations, for example: laboratory and greenhouse experiments with raised and lowered CO_2 concentrations; field experiments on ecosystems using free-air carbon dioxide enrichment (FACE) and open-top chamber studies of raised CO_2 effects, studies of soil warming and nutrient enrichment effects; and *in situ* fertilisation experiments on marine ecosystems and associated pCO_2 measurements.

- Theory and modelling, especially applications of atmospheric transport models to link atmospheric observations to surface fluxes (inverse modelling); the development of process-based models of terrestrial and marine carbon cycling and programmes to compare and test these models against observations; and the use of such models to project climate feedbacks on the uptake of CO_2 by the oceans and land.

As a result of this research, there is now a more firmly based knowledge of several central features of the carbon cycle. For example:

- Time series of atmospheric CO_2, O_2 and $^{13}CO_2$ measurements have made it possible to observationally constrain the partitioning of CO_2 between terrestrial and oceanic uptake and to confirm earlier budgets, which were partly based on model results.

- *In situ* experiments have explored the nature and extent of CO_2 responses in a variety of terrestrial ecosystems (including forests), and have confirmed the existence of iron limitations on marine productivity.

- Process-based models of terrestrial and marine biogeochemical processes have been used to represent a complex array of feedbacks in the carbon cycle, allowing the net effects of these processes to be estimated for the recent past and for future scenarios.

Figure 3.1: The global carbon cycle: storages (PgC) and fluxes (PgC/yr) estimated for the 1980s. (a) *Main components of the natural cycle*. The thick arrows denote the most important fluxes from the point of view of the contemporary CO_2 balance of the atmosphere: gross primary production and respiration by the land biosphere, and physical air-sea exchange. These fluxes are approximately balanced each year, but imbalances can affect atmospheric CO_2 concentration significantly over years to centuries. The thin arrows denote additional natural fluxes (dashed lines for fluxes of carbon as $CaCO_3$), which are important on longer time-scales. The flux of 0.4 PgC/yr from atmospheric CO_2 via plants to inert soil carbon is approximately balanced on a time-scale of several millenia by export of dissolved organic carbon (DOC) in rivers (Schlesinger, 1990). A further 0.4 PgC/yr flux of dissolved inorganic carbon (DIC) is derived from the weathering of $CaCO_3$, which takes up CO_2 from the atmosphere in a 1:1 ratio. These fluxes of DOC and DIC together comprise the river transport of 0.8 PgC/yr. In the ocean, the DOC from rivers is respired and released to the atmosphere, while $CaCO_3$ production by marine organisms results in half of the DIC from rivers being returned to the atmosphere and half being buried in deep-sea sediments – which are the precursor of carbonate rocks. Also shown are processes with even longer time-scales: burial of organic matter as fossil organic carbon (including fossil fuels), and outgassing of CO_2 through tectonic processes (vulcanism). Emissions due to vulcanism are estimated as 0.02 to 0.05 PgC/yr (Williams *et al.,* 1992; Bickle, 1994). (b) *The human perturbation* (data from Table 3.1). Fossil fuel burning and land-use change are the main anthropogenic processes that release CO_2 to the atmosphere. Only a part of this CO_2 stays in the atmosphere; the rest is taken up by the land (plants and soil) or by the ocean. These uptake components represent imbalances in the large natural two-way fluxes between atmosphere and ocean and between atmosphere and land. (c) *Carbon cycling in the ocean*. CO_2 that dissolves in the ocean is found in three main forms (CO_2, CO_3^{2-}, HCO_3^-, the sum of which is DIC). DIC is transported in the ocean by physical and biological processes. Gross primary production (GPP) is the total amount of organic carbon produced by photosynthesis (estimate from Bender *et al.,* 1994); net primary production (NPP) is what is what remains after autotrophic respiration, i.e., respiration by photosynthetic organisms (estimate from Falkowski *et al.,* 1998). Sinking of DOC and particulate organic matter (POC) of biological origin results in a downward flux known as export production (estimate from Schlitzer, 2000). This organic matter is tranported and respired by non-photosynthetic organisms (heterotrophic respiration) and ultimately upwelled and returned to the atmosphere. Only a tiny fraction is buried in deep-sea sediments. Export of $CaCO_3$ to the deep ocean is a smaller flux than total export production (0.4 PgC/yr) but about half of this carbon is buried as $CaCO_3$ in sediments; the other half is dissolved at depth, and joins the pool of DIC (Milliman, 1993). Also shown are approximate fluxes for the shorter-term burial of organic carbon and $CaCO_3$ in coastal sediments and the re-dissolution of a part of the buried $CaCO_3$ from these sediments. (d) *Carbon cycling on land*. By contrast with the ocean, most carbon cycling through the land takes place locally within ecosystems. About half of GPP is respired by plants. The remainer (NPP) is approximately balanced by heterotrophic respiration with a smaller component of direct oxidation in fires (combustion). Through senescence of plant tissues, most of NPP joins the detritus pool; some detritus decomposes (i.e., is respired and returned to the atmosphere as CO_2) quickly while some is converted to modified soil carbon, which decomposes more slowly. The small fraction of modified soil carbon that is further converted to compounds resistant to decomposition, and the small amount of black carbon produced in fires, constitute the "inert" carbon pool. It is likely that biological processes also consume much of the "inert" carbon as well but little is currently known about these processes. Estimates for soil carbon amounts are from Batjes (1996) and partitioning from Schimel *et al.* (1994) and Falloon *et al.* (1998). The estimate for the combustion flux is from Scholes and Andreae (2000). 'τ' denotes the turnover time for different components of soil organic matter.

Box 3.1: Measuring terrestrial carbon stocks and fluxes.

Estimating the carbon stocks in terrestrial ecosystems and accounting for changes in these stocks requires adequate information on land cover, carbon density in vegetation and soils, and the fate of carbon (burning, removals, decomposition). Accounting for changes in all carbon stocks in all areas would yield the net carbon exchange between terrestrial ecosystems and the atmosphere (NBP).

Global land cover maps show poor agreement due to different definitions of cover types and inconsistent sources of data (de Fries and Townshend, 1994). Land cover changes are difficult to document, uncertainties are large, and historical data are sparse. Satellite imagery is a valuable tool for estimating land cover, despite problems with cloud cover, changes at fine spatial scales, and interpretation (for example, difficulties in distinguishing primary and secondary forest). Aerial photography and ground measurements can be used to validate satellite-based observations.

The carbon density of vegetation and soils has been measured in numerous ecological field studies that have been aggregated to a global scale to assess carbon stocks and NPP (e.g., Atjay *et al.,* 1979; Olson *et al.,* 1983; Saugier and Roy, 2001; Table 3.2), although high spatial and temporal heterogeneity and methodological differences introduce large uncertainties. Land inventory studies tend to measure the carbon stocks in vegetation and soils over larger areas and/or longer time periods. For example, the United Nations Food and Agricultural Organisation (FAO) has been compiling forest inventories since 1946 providing detailed data on carbon stocks, often based on commercial wood production data. Inventory studies include managed forests with mixed age stands, thus average carbon stock values are often lower than those based on ecological site studies, which have generally been carried out in relatively undisturbed, mature ecosystems. Fluxes of carbon can be estimated from changes in inventoried carbon stocks (e.g., UN-ECE/FAO, 2000), or from combining data on land-use change with methods to calculate changes in carbon stock (e.g., Houghton, 1999). The greatest uncertainty in both methods is in estimating the fate of the carbon: the fraction which is burned, rates of decomposition, the effect of burning and harvesting on soil carbon, and subsequent land management.

Ecosystem-atmosphere CO_2 exchange on short time-scales can be measured using micrometeorological techniques such as eddy covariance, which relies on rapidly responding sensors mounted on towers to resolve the net flux of CO_2 between a patch of land and the atmosphere (Baldocchi *et al.*, 1988). The annual integral of the measured CO_2 exchange is approximately equivalent to NEP (Wofsy *et al.*, 1993; Goulden *et. al*, 1996; Aubinet *et al.,* 2000). This innovation has led to the establishment of a rapidly expanding network of long-term monitoring sites (FLUXNET) with many sites now operating for several years, improving the understanding of the physiological and ecological processes that control NEP (e.g., Valentini *et al.,* 2000). The distribution of sites is currently biased toward regrowing forests in the Northern Hemisphere, and there are still technical problems and uncertainties, although these are being tackled. Current flux measurement techniques typically integrate processes at a scale less than 1 km^2.

Table 3.1: *Global CO_2 budgets (in PgC/yr) based on intra-decadal trends in atmospheric CO_2 and O_2. Positive values are fluxes to the atmosphere; negative values represent uptake from the atmosphere. The fossil fuel emissions term for the 1980s (Marland et al., 2000) has been slightly revised downward since the SAR. Error bars denote uncertainty ($\pm 1\sigma$), not interannual variability, which is substantially greater.*

	1980s	**1990s**
Atmospheric increase	3.3 ± 0.1	3.2 ± 0.1
Emissions (fossil fuel, cement)	5.4 ± 0.3	6.3 ± 0.4
Ocean-atmosphere flux	-1.9 ± 0.6	-1.7 ± 0.5
Land-atmosphere flux[*]	-0.2 ± 0.7	-1.4 ± 0.7
[*]*partitioned as follows*		
Land-use change	1.7 (0.6 to 2.5)	NA
Residual terrestrial sink	-1.9 (-3.8 to 0.3)	NA

[*] The land-atmosphere flux represents the balance of a positive term due to land-use change and a residual terrestrial sink. The two terms cannot be separated on the basis of current atmospheric measurements. Using independent analyses to estimate the land-use change component for the 1980s based on Houghton (1999), Houghton and Hackler (1999), Houghton *et al.* (2000), and the CCMLP (McGuire *et al.*, 2001) the residual terrestrial sink can be inferred for the 1980s. Comparable global data on land-use changes through the 1990s are not yet available.

3.2 Terrestrial and Ocean Biogeochemistry: Update on Processes

3.2.1 Overview of the Carbon Cycle

The first panel of Figure 3.1 shows the major components of the carbon cycle, estimates of the current storage in the active compartments, and estimates of the gross fluxes between compartments. The second panel shows best estimates of the additional flux (release to the atmosphere – positive; uptake – negative) associated with the human perturbation of the carbon cycle during the 1980s. Note that the gross amounts of carbon annually exchanged between the ocean and atmosphere, and between the land and atmosphere, represent a sizeable fraction of the atmospheric CO_2 content – and are many times larger than the total anthropogenic CO_2 input. In consequence, an imbalance in these exchanges could easily lead to an anomaly of comparable magnitude to the direct anthropogenic perturbation. This implies that it is important to consider how these fluxes may be changing in response to human activities.

To understand how the changing global environment may alter the carbon cycle, it is necessary to further analyse the fluxes and examine the physicochemical and biological processes that determine them. The remaining two panels of Figure 3.1 indicate the main constituent fluxes in the terrestrial and marine systems, with current estimates of their magnitude. The following sections explain the controls on these fluxes, with special reference to processes by which anthropogenic changes may influence the overall carbon balance of the land and oceans on time-scales from years to centuries.

3.2.2 Terrestrial Carbon Processes

3.2.2.1 Background

Higher plants acquire CO_2 by diffusion through tiny pores (stomata) into leaves and thus to the sites of photosynthesis. The total amount of CO_2 that dissolves in leaf water amounts to about 270 PgC/yr, i.e., more than one-third of all the CO_2 in the atmosphere (Farquhar *et al.,* 1993; Ciais *et al.,* 1997). This quantity is measurable because this CO_2 has time to exchange oxygen atoms with the leaf water and is imprinted with the corresponding ^{18}O "signature" (Francey and Tans, 1987; Farquhar *et al.,* 1993). Most of this CO_2 diffuses out again without participating in photosynthesis. The amount that is "fixed" from the atmosphere, i.e., converted from CO_2 to carbohydrate during photosynthesis, is known as gross primary production (GPP). Terrestrial GPP has been estimated as about 120 PgC/yr based on ^{18}O measurements of atmospheric CO_2 (Ciais *et al.,* 1997). This is also the approximate value necessary to support observed plant growth, assuming that about half of GPP is incorporated into new plant tissues such as leaves, roots and wood, and the other half is converted back to atmospheric CO_2 by autotrophic respiration (respiration by plant tissues) (Lloyd and Farquhar, 1996; Waring *et al.,* 1998).

Annual plant growth is the difference between photosynthesis and autotrophic respiration, and is referred to as net primary production (NPP). NPP has been measured in all major ecosystem types by sequential harvesting or by measuring plant biomass (Hall *et al.,* 1993). Global terrestrial NPP has been estimated at about 60 PgC/yr through integration of field measurements (Table 3.2) (Atjay *et al.,* 1979; Saugier and Roy, 2001). Estimates from remote sensing and atmospheric CO_2 data (Ruimy *et al.,* 1994; Knorr and Heimann, 1995) concur with this value, although there are large uncertainties in all methods. Eventually, virtually all of the carbon fixed in NPP is returned to the atmospheric CO_2 pool through two processes: heterotrophic respiration (Rh) by decomposers (bacteria and fungi feeding on dead tissue and exudates) and herbivores; and combustion in natural or human-set fires (Figure 3.1d).

Most dead biomass enters the detritus and soil organic matter pools where it is respired at a rate that depends on the chemical composition of the dead tissues and on environmental conditions (for example, low temperatures, dry conditions and flooding slow down decomposition). Conceptually, several soil carbon pools are distinguished. Detritus and microbial biomass have a short turnover time (<10 yr). Modified soil organic carbon has decadal to centennial turnover time. Inert (stable or recalcitrant) soil organic carbon is composed of molecules more or less resistant to further decomposition. A very small fraction of soil organic matter, and a small fraction of burnt biomass, are converted into inert forms (Schlesinger, 1990; Kuhlbusch *et al.,* 1996). Natural processes and management regimes may reduce or increase the amount of carbon stored in pools with turnover times on the order of tens to hundreds of years (living wood, wood products and modified soil organic matter) and thus influence the time evolution of atmospheric CO_2 over the century.

The difference between NPP and Rh determines how much carbon is lost or gained by the ecosystem in the absence of disturbances that remove carbon from the ecosystem (such as harvest or fire). This carbon balance, or net ecosystem production (NEP), can be estimated from changes in carbon stocks, or by measuring the fluxes of CO_2 between patches of land and the atmosphere (see Box 3.1). Annual NEP flux measurements are in the range 0.7 to 5.9 MgC/ha/yr for tropical forests and 0.8 to 7.0 MgC/ha/yr for temperate forests; boreal forests can reach up to 2.5 MgC/ha/yr although they have been shown to be carbon-neutral or to release carbon in warm and/or cloudy years (Valentini *et al.,* 2000). Integration of these and other results leads to an estimated global NEP of about 10 PgC/yr, although this is likely to be an overestimate because of the current biased distribution of flux measuring sites (Bolin *et al.,* 2000).

When other losses of carbon are accounted for, including fires, harvesting/removals (eventually combusted or decomposed), erosion and export of dissolved or suspended organic carbon (DOC) by rivers to the oceans (Schlesinger and Melack, 1981; Sarmiento and Sundquist; 1992), what remains is the net biome production (NBP), i.e., the carbon accumulated by the terrestrial biosphere (Schulze and Heimann, 1998). This is what the atmosphere ultimately "sees" as the net land uptake on a global scale over periods of a year or more. NBP is estimated in this chapter to have averaged -0.2 ± 0.7 PgC/yr during the 1980s and -1.4 ± 0.7 PgC/yr during the 1990s, based on atmospheric measurements of CO_2 and O_2 (Section 3.5.1 and Table 3.1).

Box 3.2: Maximum impacts of reforestation and deforestation on atmospheric CO_2.

Rough upper bounds for the impact of reforestation on atmospheric CO_2 concentration over a century time-scale can be calculated as follows. Cumulative carbon losses to the atmosphere due to land-use change during the past 1 to 2 centuries are estimated as 180 to 200 PgC (de Fries *et al.*, 1999) and cumulative fossil fuel emissions to year 2000 as 280 PgC (Marland *et al.,* 2000), giving cumulative anthropogenic emissions of 480 to 500 PgC. Atmospheric CO_2 content has increased by 90 ppm (190 PgC). Approximately 40% of anthropogenic CO_2 emissions has thus remained in the atmosphere; the rest has been taken up by the land and oceans in roughly equal proportions (see main text). Conversely, if land-use change were completely reversed over the 21st century, a CO_2 reduction of $0.40 \times 200 = 80$ PgC (about 40 ppm) might be expected. This calculation assumes that future ecosystems will not store more carbon than pre-industrial ecosystems, and that ocean uptake will be less because of lower CO_2 concentration in the atmosphere (see Section 3.2.3.1) .

A higher bound can be obtained by assuming that the carbon taken up by the land during the past 1 to 2 centuries, i.e. about half of the carbon taken up by the land and ocean combined, will be retained there. This calculation yields a CO_2 reduction of $0.70 \times 200 = 140$ PgC (about 70 ppm). These calculations are not greatly influenced by the choice of reference period. Both calculations require the extreme assumption that a large proportion of today's agricultural land is returned to forest.

The maximum impact of total deforestation can be calculated in a similar way. Depending on different assumptions about vegetation and soil carbon density in different ecosystem types (Table 3.2) and the proportion of soil carbon lost during deforestation (20 to 50%; IPCC, 1997), complete conversion of forests to climatically equivalent grasslands would add 400 to 800 PgC to the atmosphere. Thus, global deforestation could theoretically add two to four times more CO_2 to the atmosphere than could be subtracted by reforestation of cleared areas.

Table 3.2: Estimates of terrestrial carbon stocks and NPP (global aggregated values by biome).

Biome	Area (10^9 ha)		Global Carbon Stocks (PgC)[f]						Carbon density (MgC/ha)				NPP (PgC/yr)	
	WBGU[a]	MRS[b]	WBGU[a]			MRS[b]	IGBP[e]		WBGU[a]		MRS[b]	IGBP[c]	Atjay[a]	MRS[b]
			Plants	Soil	Total	Plants	Soil	Total	Plants	Soil	Plants	Soil		
Tropical forests	1.76	1.75	212	216	428	340	213	553	120	123	194	122	13.7	21.9
Temperate forests	1.04	1.04	59	100	159	139[e]	153	292	57	96	134	147	6.5	8.1
Boreal forests	1.37	1.37	88[d]	471	559	57	338	395	64	344	42	247	3.2	2.6
Tropical savannas & grasslands	2.25	2.76	66	264	330	79	247	326	29	117	29	90	17.7	14.9
Temperate grasslands & shrublands	1.25	1.78	9	295	304	23	176	199	7	236	13	99	5.3	7.0
Deserts and semi deserts	4.55[h]	2.77	8	191	199	10	159	169	2	42	4	57	1.4	3.5
Tundra	0.95	0.56	6	121	127	2	115	117	6	127	4	206	1.0	0.5
Croplands	1.60	1.35	3	128	131	4	165	169	2	80	3	122	6.8	4.1
Wetlands[g]	0.35	–	15	225	240	–	–	–	43	643	–	–	4.3	–
Total	15.12	14.93[h]	466	2011	2477	654	1567	2221					59.9	62.6

[a] WBGU (1988): forest data from Dixon *et al. (*1994); other data from Atjay *et al.* (1979).

[b] MRS: Mooney, Roy and Saugier (MRS) (2001). Temperate grassland and Mediterranean shrubland categories combined.

[c] IGBP-DIS (International Geosphere-Biosphere Programme – Data Information Service) soil carbon layer (Carter and Scholes, 2000) overlaid with De Fries *et al.* (1999) current vegetation map to give average ecosystem soil carbon.

[d] WBGU boreal forest vegetation estimate is likely to be to high, due to high Russian forest density estimates including standing dead biomass.

[e] MRS temperate forest estimate is likely to be too high, being based on mature stand density.

[f] Soil carbon values are for the top 1 m, although stores are also high below this depth in peatlands and tropical forests.

[g] Variations in classification of ecosystems can lead to inconsistencies. In particular, wetlands are not recognised in the MRS classification.

[h] Total land area of 14.93×10^9 ha in MRS includes 1.55×10^9 ha ice cover not listed in this table. InWBGU, ice is included in deserts and semi-deserts category.

By definition, for an ecosystem in steady state, Rh and other carbon losses would just balance NPP, and NBP would be zero. In reality, human activities, natural disturbances and climate variability alter NPP and Rh, causing transient changes in the terrestrial carbon pool and thus non-zero NBP. If the rate of carbon input (NPP) changes, the rate of carbon output (Rh) also changes, in proportion to the altered carbon content; but there is a time lag between changes in NPP and changes in the slower responding carbon pools. For a *step* increase in NPP, NBP is expected to increase at first but to relax towards zero over a period of years to decades as the respiring pool "catches up". The globally averaged lag required for Rh to catch up with a change in NPP has been estimated to be of the order of 10 to 30 years (Raich and Schlesinger, 1992). A *continuous* increase in NPP is expected to produce a sustained positive NBP, so long as NPP is still increasing, so that the increased terrestrial carbon has not been processed through the respiring carbon pools (Taylor and Lloyd, 1992; Friedlingstein *et al.,* 1995a; Thompson *et al.,* 1996; Kicklighter *et al.,* 1999), and provided that the increase is not outweighed by compensating increases in mortality or disturbance.

The terrestrial system is currently acting as a global sink for carbon (Table 3.1) despite large releases of carbon due to deforestation in some regions. Likely mechanisms for the sink are known, but their relative contribution is uncertain. Natural climate variability and disturbance regimes (including fire and herbivory) affect NBP through their impacts on NPP, allocation to long- versus short-lived tissues, chemical and physical properties of litter, stocks of living biomass, stocks of detritus and soil carbon, environmental controls on decomposition and rates of biomass removal. Human impacts occur through changes in land use and land management, and through indirect mechanisms including climate change, and fertilisation due to elevated CO_2 and deposition of nutrients (most importantly, reactive nitrogen). These mechanisms are discussed individually in the following sections.

3.2.2.2 Effects of changes in land use and land management
Changes in land use and management affect the amount of carbon in plant biomass and soils. Historical cumulative carbon losses due to changes in land use have been estimated to be 180 to 200 PgC by comparing maps of "natural" vegetation in the absence of human disturbance (derived from ground-based information (Matthews, 1983) or from modelled potential vegetation based on climate (Leemans, 1990)) to a map of current vegetation derived from 1987 satellite data (de Fries *et al.,* 1999). Houghton (1999, 2000) estimated emissions of 121 PgC (approximately 60% in tropical areas and 40% in temperate areas) for the period 1850 to 1990 from statistics on land-use change, and a simple model tracking rates of decomposition from different pools and rates of regrowth on abandoned or reforested land. There was substantial deforestation in temperate areas prior to 1850, and this may be partially reflected in the difference between these two analyses. The estimated land-use emissions during 1850 to 1990 of 121 PgC (Houghton, 1999, 2000) can be compared to estimated net terrestrial flux of 39 PgC to the atmosphere over the same period inferred from an atmospheric

increase of 144 PgC (Etheridge *et al.,* 1996; Keeling and Whorf, 2000), a release of 212 PgC due to fossil fuel burning (Marland *et al.,* 2000), and a modelled ocean-atmosphere flux of about −107 PgC (Gruber, 1998, Sabine *et al.*, 1999, Feely *et al.*, 1999a). The difference between the net terrestrial flux and estimated land-use change emissions implies a residual land-atmosphere flux of −82 PgC (i.e., a terrestrial sink) over the same period. Box 3.2 indicates the theoretical upper bounds for additional carbon storage due to land-use change, similar bounds for carbon loss by continuing deforestation, and the implications of these calculations for atmospheric CO_2.

Land use responds to social and economic pressures to provide food, fuel and wood products, for subsistence use or for export. Land clearing can lead to soil degradation, erosion and leaching of nutrients, and may therefore reduce the subsequent ability of the ecosystem to act as a carbon sink (Taylor and Lloyd, 1992). Ecosystem conservation and management practices can restore, maintain and enlarge carbon stocks (IPCC, 2000a). Fire is important in the carbon budget of some ecosystems (e.g., boreal forests, grasslands, tropical savannas and woodlands) and is affected directly by management and indirectly by land-use change (Apps *et al.,* 1993). Fire is a major short-term source of carbon, but adds to a small longer-term sink (<0.1 PgC/yr) through production of slowly decomposing and inert black carbon.

Forests
Deforestation has been responsible for almost 90% of the estimated emissions due to land-use change since 1850, with a 20% decrease of the global forest area (Houghton, 1999). Deforestation appears to be slowing slightly in tropical countries (FAO, 1997; Houghton, 2000), and some deforested areas in Europe and North America have been reforested in recent decades (FAO, 1997). Managed or regenerated forests generally store less carbon than natural forests, even at maturity. New trees take up carbon rapidly, but this slows down towards maturity when forests can be slight sources or sinks (Buchmann and Schulze, 1999). To use land continuously in order to take up carbon, the wood must be harvested and turned into long-lived products and trees must be re-planted. The trees may also be used for biomass energy to avoid future fossil fuel emissions (Hall *et al.,* 2000). Analysis of scenarios for future development show that expanded use of biomass energy could reduce the rate of atmospheric CO_2 increase (IPCC 1996b; Leemans *et al.,* 1996; Edmonds *et al.,* 1996; Ishitani *et al.,* 1996; IPCC, 2000a). IPCC (1996b) estimated that slowing deforestation and promoting natural forest regeneration and afforestation could increase carbon stocks by about 60 to 87 PgC over the period 1995 to 2050, mostly in the tropics (Brown *et al.,* 1996).

Savannas and grasslands – fire and grazing
Grasslands and mixed tree-grass systems are vulnerable to subtle environmental and management changes that can lead to shifts in vegetation state (Scholes and Archer, 1997; House and Hall, 2001). Livestock grazing on these lands is the land use with the largest global areal extent (FAO, 1993a). Extensive clearing of trees (for agricultural expansion) has occurred in some areas. In

other areas, fire suppression, eradication of indigenous browsers and the introduction of intensive grazing and exotic trees and shrubs have caused an increase in woody plant density known as woody encroachment or tree thickening (Archer *et al.,* 2001). This process has been estimated to result in a CO_2 sink of up to 0.17 PgC/yr in the USA during the 1980s (Houghton *et al.,* 1999) and at least 0.03 PgC/yr in Australia (Burrows, 1998). Grassland ecosystems have high root production and store most of their carbon in soils where turnover is relatively slow, allowing the possibility of enhancement through management (e.g., Fisher *et al.,* 1994).

Peatlands/wetlands

Peatlands/wetlands are large reserves of carbon, because anaerobic soil conditions and (in northern peatlands) low temperatures reduce decomposition and promote accumulation of organic matter. Total carbon stored in northern peatlands has been estimated as about 455 PgC (Gorham, 1991) with a current uptake rate in extant northern peatlands of 0.07 PgC/yr (Clymo *et al.,* 1998). Anaerobic decomposition releases methane (CH_4) which has a global warming potential (GWP) about 23 times that of CO_2 (Chapter 6). The balance between CH_4 release and CO_2 uptake and release is highly variable and poorly understood. Draining peatlands for agriculture increases total carbon released by decomposition, although less is in the form of CH_4. Forests grown on drained peatlands may be sources or sinks of CO_2 depending on the balance of decomposition and tree growth (Minkkinen and Laine, 1998).

Agricultural land

Conversion of natural vegetation to agriculture is a major source of CO_2, not only due to losses of plant biomass but also, increased decomposition of soil organic matter caused by disturbance and energy costs of various agricultural practices (e.g., fertilisation and irrigation; Schlesinger, 2000). Conversely, the use of high-yielding plant varieties, fertilisers, irrigation, residue management and reduced tillage can reduce losses and enhance uptake within managed areas (Cole *et al.,* 1996; Blume *et al.*, 1998). These processes have led to an estimated increase of soil carbon in agricultural soils in the USA of 0.14 PgC/yr during the 1980s (Houghton *et al.,* 1999). IPCC (1996b) estimated that appropriate management practices could increase carbon sinks by 0.4 to 0.9 PgC/yr , or a cumulative carbon storage of 24 to 43 PgC over 50 years; energy efficiency improvements and production of energy from dedicated crops and residues would result in a further mitigation potential of 0.3 to 1.4 PgC/yr, or a cumulative carbon storage of 16 to 68 PgC over 50 years (Cole *et al.,* 1996).

Scenarios

The IPCC Special Report on Land Use, Land-Use Change and Forestry (IPCC, 2000a) (hereafter SRLULUCF) derived scenarios of land-use emissions for the period 2008 to 2012. It was estimated that a deforestation flux of 1.79 PgC/yr is likely to be offset by reforestation and afforestation flux of −0.20 to −0.58 PgC/yr, yielding a net release of 1.59 to 1.20 PgC/yr (Schlamadinger *et al.,* 2000). The potential for net carbon storage from several "additional activities" such as improved land management and other land-use changes was estimated to amount to a global land-atmosphere flux in the region of −1.3 PgC/yr in 2010 and −2.5 PgC/yr in 2040, not including wood products and bioenergy (Sampson *et al.,* 2000).

3.2.2.3 Effects of climate

Solar radiation, temperature and available water affect photosynthesis, plant respiration and decomposition, thus climate change can lead to changes in NEP. A substantial part of the interannual variability in the rate of increase of CO_2 is likely to reflect terrestrial biosphere responses to climate variability (Section 3.5.3). Warming may increase NPP in temperate and arctic ecosystems where it can increase the length of the seasonal and daily growing cycles, but it may decrease NPP in water-stressed ecosystems as it increases water loss. Respiratory processes are sensitive to temperature; soil and root respiration have generally been shown to increase with warming in the short term (Lloyd and Taylor, 1994; Boone *et al.,* 1998) although evidence on longer-term impacts is conflicting (Trumbore, 2000; Giardina and Ryan, 2000; Jarvis and Linder, 2000). Changes in rainfall pattern affect plant water availability and the length of the growing season, particularly in arid and semi-arid regions. Cloud cover can be beneficial to NPP in dry areas with high solar radiation, but detrimental in areas with low solar radiation. Changing climate can also affect the distribution of plants and the incidence of disturbances such as fire (which could increase or decrease depending on warming and precipitation patterns, possibly resulting under some circumstances in rapid losses of carbon), wind, and insect and pathogen attacks, leading to changes in NBP. The global balance of these positive and negative effects of climate on NBP depends strongly on regional aspects of climate change.

The climatic sensitivity of high northern latitude ecosystems (tundra and taiga) has received particular attention as a consequence of their expanse, high carbon density, and observations of disproportionate warming in these regions (Chapman and Walsh, 1993; Overpeck *et al.,* 1997). High-latitude ecosystems contain about 25% of the total world soil carbon pool in the permafrost and the seasonally-thawed soil layer. This carbon storage may be affected by changes in temperature and water table depth. High latitude ecosystems have low NPP, in part due to short growing seasons, and slow nutrient cycling because of low rates of decomposition in waterlogged and cold soils. Remotely sensed data (Myneni *et al.,* 1997) and phenological observations (Menzel and Fabian, 1999) independently indicate a recent trend to longer growing seasons in the boreal zone and temperate Europe. Such a trend might be expected to have increased annual NPP. A shift towards earlier and stronger spring depletion of atmospheric CO_2 has also been observed at northern stations, consistent with earlier onset of growth at mid- to high northern latitudes (Manning, 1992; Keeling *et al.,* 1996a; Randerson, 1999). However, recent flux measurements at individual high-latitude sites have generally failed to find appreciable NEP (Oechel *et al.,* 1993; Goulden *et al.,* 1998; Schulze *et al.,* 1999; Oechel *et al.,* 2000). These studies suggest that, at least in the short term, any direct effect of warming on NPP may be more than offset by an increased respiration of soil

carbon caused by the effects of increased depth of soil thaw. Increased decomposition, may, however also increase nutrient mineralisation and thereby indirectly stimulate NPP (Melillo *et al.,* 1993; Jarvis and Linder, 2000; Oechel *et al.,* 2000).

Large areas of the tropics are arid and semi-arid, and plant production is limited by water availability. There is evidence that even evergreen tropical moist forests show reduced GPP during the dry season (Malhi *et al.,* 1998) and may become a carbon source under the hot, dry conditions of typical El Niño years. With a warmer ocean surface, and consequently generally increased precipitation, the global trend in the tropics might be expected to be towards increased NPP, but changing precipitation patterns could lead to drought, reducing NPP and increasing fire frequency in the affected regions.

3.2.2.4 Effects of increasing atmospheric CO_2

CO_2 and O_2 compete for the reaction sites on the photosynthetic carbon-fixing enzyme, Rubisco. Increasing the concentration of CO_2 in the atmosphere has two effects on the Rubisco reactions: increasing the rate of reaction with CO_2 (carboxylation) and decreasing the rate of oxygenation. Both effects increase the rate of photosynthesis, since oxygenation is followed by photorespiration which releases CO_2 (Farquhar *et al.,* 1980). With increased photsynthesis, plants can develop faster, attaining the same final size in less time, or can increase their final mass. In the first case, the overall rate of litter production increases and so the soil carbon stock increases; in the second case, both the below-ground and above-ground carbon stocks increase. Both types of growth response to elevated CO_2 have been observed (Masle, 2000).

The strength of the response of photosynthesis to an increase in CO_2 concentration depends on the photosynthetic pathway used by the plant. Plants with a photosynthetic pathway known as C_3 (all trees, nearly all plants of cold climates, and most agricultural crops including wheat and rice) generally show an increased rate of photosynthesis in response to increases in CO_2 concentration above the present level (Koch and Mooney, 1996; Curtis, 1996; Mooney *et al.*, 1999). Plants with the C_4 photosynthetic pathway (tropical and many temperate grasses, some desert shrubs, and some crops including maize and sugar cane) already have a mechanism to concentrate CO_2 and therefore show either no direct photosynthetic response, or less response than C_3 plants (Wand *et al.*, 1999). Increased CO_2 has also been reported to reduce plant respiration under some conditions (Drake *et al.*, 1999), although this effect has been questioned.

Increased CO_2 concentration allows the partial closure of stomata, restricting water loss during transpiration and producing an increase in the ratio of carbon gain to water loss ("water-use efficiency", WUE) (Field *et al.,* 1995a; Drake *et al.,* 1997; Farquhar, 1997; Körner, 2000). This effect can lengthen the duration of the growing season in seasonally dry ecosystems and can increase NPP in both C_3 and C_4 plants.

Nitrogen-use efficiency also generally improves as carbon input increases, because plants can vary the ratio between carbon and nitrogen in tissues and require lower concentrations of photosynthetic enzymes in order to carry out photosynthesis

at a given rate; for this reason, low nitrogen availability does not consistently limit plant responses to increased atmospheric CO_2 (McGuire *et al.,* 1995; Lloyd and Farquhar, 1996; Curtis and Wang, 1998; Norby *et al.,* 1999; Körner, 2000). Increased CO_2 concentration may also stimulate nitrogen fixation (Hungate *et al.*, 1999; Vitousek and Field, 1999). Changes in tissue nutrient concentration may affect herbivory and decomposition, although long-term decomposition studies have shown that the effect of elevated CO_2 in this respect is likely to be small (Norby and Cortufo, 1998) because changes in the C:N ratio of leaves are not consistently reflected in the C:N ratio of leaf litter due to nitrogen retranslocation (Norby *et al.,* 1999).

The process of CO_2 "fertilisation" thus involves direct effects on carbon assimilation and indirect effects such as those via water saving and interactions between the carbon and nitrogen cycles. Increasing CO_2 can therefore lead to structural and physiological changes in plants (Pritchard *et al.,* 1999) and can further affect plant competition and distribution patterns due to responses of different species. Field studies show that the relative stimulation of NPP tends to be greater in low-productivity years, suggesting that improvements in water- and nutrient-use efficiency can be more important than direct NPP stimulation (Luo *et al.,* 1999).

Although NPP stimulation is not automatically reflected in increased plant biomass, additional carbon is expected to enter the soil, via accelerated ontogeny, which reduces lifespan and results in more rapid shoot death, or by enhanced root turnover or exudation (Koch and Mooney, 1996; Allen *et al.,* 2000). Because the soil microbial community is generally limited by the availability of organic substrates, enhanced addition of labile carbon to the soil tends to increase heterotrophic respiration unless inhibited by other factors such as low temperature (Hungate *et al.*, 1997; Schlesinger and Andrews, 2000). Field studies have indicated increases in soil organic matter, and increases in soil respiration of about 30%, under elevated CO_2 (Schlesinger and Andrews, 2000). The potential role of the soil as a carbon sink under elevated CO_2 is crucial to understanding NEP and long-term carbon dynamics, but remains insufficiently well understood (Trumbore, 2000).

C_3 crops show an average increase in NPP of around 33% for a doubling of atmospheric CO_2 (Koch and Mooney, 1996). Grassland and crop studies combined show an average biomass increase of 14%, with a wide range of responses among individual studies (Mooney *et al.,* 1999). In cold climates, low temperatures restrict the photosynthetic response to elevated CO_2. In tropical grasslands and savannas, C_4 grasses are dominant, so it has been assumed that trees and C_3 grasses would gain a competitive advantage at high CO_2 (Gifford, 1992; Collatz *et al.,* 1998). This is supported by carbon isotope evidence from the last glacial maximum, which suggests that low CO_2 favours C_4 plants (Street-Perrott *et al.,* 1998). However, field experiments suggest a more complex picture with C_4 plants sometimes doing better than C_3 under elevated CO_2 due to improved WUE at the ecosystem level (Owensby *et al.,* 1993; Polley *et al.,* 1996). Highly productive forest ecosystems have the greatest potential for *absolute* increases in productivity due to CO_2 effects. Long-term field studies on young trees have

typically shown a stimulation of photosynthesis of about 60% for a doubling of CO_2 (Saxe *et al.,* 1998; Norby *et al.,* 1999). A FACE experiment in a fast growing young pine forest showed an increase of 25% in NPP for an increase in atmospheric CO_2 to 560 ppm (DeLucia *et al.*, 1999). Some of this additional NPP is allocated to root metabolism and associated microbes; soil CO_2 efflux increases, returning a part (but not all) of the extra NPP to the atmosphere (Allen *et al.,* 2000). The response of mature forests to increases in atmospheric CO_2 concentration has not been shown experimentally; it may be different from that of young forests for various reasons, including changes in leaf C:N ratios and stomatal responses to water vapour deficits as trees mature (Curtis and Wang, 1998; Norby *et al.,* 1999).

At high CO_2 concentrations there can be no further increase in photosynthesis with increasing CO_2 (Farquhar *et al.,* 1980), except through further stomatal closure, which may produce continued increases in WUE in water-limited environments. The shape of the response curve of global NPP at higher CO_2 concentrations than present is uncertain because the response at the level of gas exchange is modified by incompletely understood plant- and ecosystem-level processes (Luo *et al.,* 1999). Based on photosynthetic physiology, it is likely that the additional carbon that could be taken up globally by enhanced photosynthsis as a direct consequence of rising atmospheric CO_2 concentration is small at atmospheric concentrations above 800 to 1,000 ppm. Experimental studies indicate that some ecosystems show greatly reduced CO_2 fertilisation at lower concentrations than this (Körner, 2000).

3.2.2.5 Effects of anthropogenic nitrogen deposition

Nitrogen availability is an important constraint on NPP (Vitousek *et al.,* 1997), although phosphorus and calcium may be more important limiting nutrients in many tropical and sub-tropical regions (Matson, 1999). Reactive nitrogen is released into the atmosphere in the form of nitrogen oxides (NO_x) during fossil fuel and biomass combustion and ammonia emitted by industrial regions, animal husbandry and fertiliser use (Chapter 4). This nitrogen is then deposited fairly near to the source, and can act as a fertiliser for terrestrial plants. There has been a rapid increase in reactive nitrogen deposition over the last 150 years (Vitousek *et al.*, 1997; Holland *et al.,* 1999). Much field evidence on nitrogen fertilisation effects on plants (e.g., Chapin, 1980; Vitousek and Howarth, 1991; Bergh *et al.*, 1999) supports the hypothesis that additional nitrogen deposition will result in increased NPP, including the growth of trees in Europe (Spiecker *et al.*, 1996). There is also evidence (Fog, 1988; Bryant *et al.,* 1998) that N fertilisation enhances the formation of modified soil organic matter and thus increases the residence time of carbon in soils.

Tracer experiments with addition of the stable isotope ^{15}N provide insight into the short-term fate of deposited reactive nitrogen (Gundersen *et al.*, 1998). It is clear from these experiments that most of the added N added to the soil surface is retained in the ecosystem rather than being leached out via water transport or returned to the atmosphere in gaseous form (as N_2, NO, N_2O or NH_3). Studies have also shown that the tracer is found initially in the soil

(Nadelhoffer *et al.,* 1999), but that it enters the vegetation after a few years (Clark 1977; Schimel and Chapin, 1996; Delgado *et al.,* 1996; Schulze, 2000).

There is an upper limit to the amount of added N that can fertilise plant growth. This limit is thought to have been reached in highly polluted regions of Europe. With nitrogen saturation, ecosystems are no longer able to process the incoming nitrogen deposition, and may also suffer from deleterious effects of associated pollutants such as ozone (O_3), nutrient imbalance, and aluminium toxicity (Schulze *et al.,* 1989; Aber *et al.,* 1998).

3.2.2.6 Additional impacts of changing atmospheric chemistry

Current tropospheric O_3 concentrations in Europe and North America cause visible leaf injury on a range of crop and tree species and have been shown to reduce the growth and yield of crops and young trees in experimental studies. The longer-term effects of O_3 on forest productivity are less certain, although significant negative associations between ozone exposure and forest growth have been reported in North America (Mclaughlin and Percy, 2000) and in central Europe (Braun *et al.*, 2000). O_3 is taken up through stomata, so decreased stomatal conductance at elevated CO_2 may reduce the effects of O_3 (Semenov *et al.*, 1998, 1999). There is also evidence of significant interactions between O_3 and soil water availability in effects on stem growth or NPP from field studies (e.g., Mclaughlin and Downing, 1995) and from modelling studies (e.g., Ollinger *et al.*, 1997). The regional impacts of O_3 on NPP elsewhere in the world are uncertain, although significant impacts on forests have been reported close to major cities. Fowler *et al.* (2000) estimate that the proportion of global forests exposed to potentially damaging ozone concentrations will increase from about 25% in 1990 to about 50% in 2100.

Other possible negative effects of industrially generated pollution on plant growth include effects of soil acidification due to deposition of NO_3^- and SO_4^{2-}. Severe forest decline has been observed in regions with high sulphate deposition, for instance in parts of eastern Europe and southern China. The wider effects are less certain and depend on soil sensitivity. Fowler *et al.* (2000) estimate that 8% of global forest cover received an annual sulphate deposition above an estimated threshold for effects on acid sensitive soils, and that this will increase to 17% in 2050. The most significant long-term effect of continued acid deposition for forest productivity may be through depletion of base cations, with evidence of both increased leaching rates and decreased foliar concentrations (Mclaughlin and Percy, 2000), although the link between these changes in nutrient cycles and NPP needs to be quantified.

3.2.2.7 Additional constraints on terrestrial CO_2 uptake

It is very likely that there are upper limits to carbon storage in ecosystems due to mechanical and resource constraints on the amount of above ground biomass and physical limits to the amount of organic carbon that can be held in soils (Scholes *et al.,* 1999). It is also generally expected that increased above-ground NPP (production of leaves and stem) will to some extent be counterbalanced by an increased rate of turnover of the biomass as upper limits are approached.

3.2.3 Ocean Carbon Processes

3.2.3.1 Background

The total amount of carbon in the ocean is about 50 times greater than the amount in the atmosphere, and is exchanged with the atmosphere on a time-scale of several hundred years. Dissolution in the oceans provides a large sink for anthropogenic CO_2, due in part to its high solubility, but above all because of its dissociation into ions and interactions with sea water constituents (see Box 3.3).

The annual two-way gross exchange of CO_2 between the atmosphere and surface ocean is about 90 PgC/yr, mediated by molecular diffusion across the air-sea interface. Net CO_2 transfer can occur whenever there is a partial pressure difference of CO_2 across this interface. The flux can be estimated as the product of a gas transfer coefficient, the solubility of CO_2, and the partial pressure difference of CO_2 between air and water. The gas transfer coefficient incorporates effects of many physical factors but is usually expressed as a non-linear function of wind speed alone. There is considerable uncertainty about this function (Liss and Merlivat, 1986; Wanninkhof, 1992; Watson *et al.*, 1995). Improvements in the ability to measure CO_2 transfer directly (e.g., Wanninkhof and McGillis, 1999) may lead to a better knowledge of gas transfer coefficients.

Despite extensive global measurements conducted during the 1990s, measurements of surface water pCO_2 remain sparse, and extensive spatial and temporal interpolation is required in order to produce global fields. Takahashi *et al.* (1999) interpolated data collected over three decades in order to derive monthly values of surface water pCO_2 over the globe for a single "virtual" calendar year (1995). A wind speed dependent gas transfer coefficient was used to calculate monthly net CO_2 fluxes. The resulting estimates, although subject to large uncertainty, revealed clear regional and seasonal patterns in net fluxes.

Regional net CO_2 transfers estimated from contemporary surface water pCO_2 data should not be confused with the uptake of anthropogenic CO_2. The uptake of anthropogenic CO_2 is the *increase* in net transfer over the pre-industrial net transfer, and is therefore superimposed on a globally varying pattern of relatively large natural transfers. The natural transfers result from heating and cooling, and biological production and respiration. Carbon is transferred within the ocean from natural sink regions to natural source regions via ocean circulation and the sinking of carbon rich particles. This spatial separation of natural sources and sinks dominates the regional distribution of net annual air-sea fluxes.

CO_2 solubility is temperature dependent, hence air-sea heat transfer contributes to seasonal and regional patterns of air-sea CO_2 transfer (Watson *et al.*, 1995). Net cooling of surface waters tends to drive CO_2 uptake; net warming drives outgassing. Regions of cooling and heating are linked via circulation, producing vertical gradients and north-south transports of carbon within the ocean (e.g., of the order 0.5 to 1 PgC/yr southward transport in the Atlantic Basin; Broecker and Peng, 1992; Keeling and Peng, 1995; Watson *et al.*, 1995; Holfort *et al.*, 1998).

Biological processes also drive seasonal and regional distributions of CO_2 fluxes (Figure 1c). The gross primary production by ocean phytoplankton has been estimated by Bender *et al.* (1994) to be 103 PgC/yr. Part of this is returned to DIC through autotrophic respiration, with the remainder being net primary production, estimated on the basis of global remote sensing data

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Box 3.3: The varying CO_2 uptake capacity of the ocean.

Because of its solubility and chemical reactivity, CO_2 is taken up by the ocean much more effectively than other anthropogenic gases (e.g., chlorofluorocarbons (CFCs) and CH_4). CO_2 that dissolves in seawater is found in three main forms. The sum of these forms constitutes dissolved inorganic carbon (DIC). The three forms are: (1) dissolved CO_2 (non-ionic, about 1% of the total) which can be exchanged with the atmosphere until the partial pressure in surface water and air are equal, (2) bicarbonate ion (HCO_3^-, about 91%); and (3) carbonate ion (CO_3^{2-}, about 8%). As atmospheric CO_2 increases, the dissolved CO_2 content of surface seawater increases at a similar rate, but most of the added CO_2 ends up as HCO_3^-. Meanwhile, the CO_3^{2-} content decreases, since the net effect of adding CO_2 is a reaction with CO_3^{2-} to form HCO_3^- (Figure 3.1). There is therefore less available CO_3^{2-} to react with further CO_2 additions, causing an increasing proportion of the added CO_2 to remain in its dissolved form. This restricts further uptake, so that the overall ability of surface sea water to take up CO_2 decreases at higher atmospheric CO_2 levels. The effect is large. For a 100 ppm increase in atmospheric CO_2 above today's level (i.e., from 370 to 470 ppm) the DIC concentration increase of surface sea water is already about 40% smaller than would have been caused by a similar 100 ppm increase relative to pre-industrial levels (i.e., from 280 to 380 ppm). The contemporary DIC increase is about 60% greater than would result if atmospheric CO_2 were to increase from 750 to 850 ppm.

The uptake capacity for CO_2 also varies significantly due to additional factors, most importantly seawater temperature, salinity and alkalinity (the latter being a measurable quantity approximately equal to $[HCO_3^-] + 2 \times [CO_3^{2-}]$). Alkalinity is influenced primarily by the cycle of $CaCO_3$ formation (in shells and corals) and dissolution (see Figure 3.1c).

to be about 45 PgC/yr (Longhurst *et al.*, 1995; Antoine *et al.*, 1996; Falkowski *et al.*, 1998; Field *et al.*, 1998; Balkanski *et al.*, 1999). About 14 to 30% of the total NPP occurs in coastal areas (Gattuso *et al.*, 1998). The resulting organic carbon is consumed by zooplankton (a quantitatively more important process than herbivory on land) or becomes detritus. Some organic carbon is released in dissolved form (DOC) and oxidised by bacteria (Ducklow, 1999) with a fraction entering the ocean reservoir as net DOC production (Hansell and Carlson, 1998). Sinking of particulate organic carbon (POC) composed of dead organisms and detritus together with vertical transfer of DOC create a downward flux of organic carbon from the upper ocean known as "export production". Recent estimates for global export production range from roughly 10 to 20 PgC/yr (Falkowski *et al.*, 1998; Laws *et al.*, 2000). An alternative estimate for global export production of 11 PgC/yr has been derived using an inverse model of physical and chemical data from the world's oceans (Schlitzer, 2000). Only a small fraction (about 0.1 PgC) of the export production sinks in sediments, mostly in the coastal ocean (Gattuso *et al.,* 1998). Heterotrophic respiration at depth converts the remaining organic carbon back to DIC. Eventually, and usually at another location, this DIC is upwelled into the ocean's surface layer again and may re-equilibrate with the atmospheric CO_2. These mechanisms, often referred to as the biological pump, maintain higher DIC concentrations at depth and cause atmospheric CO_2 concentrations to be about 200 ppm lower than would be the case in the absence of such mechanisms (Sarmiento and Toggweiler, 1984; Maier-Reimer *et al.*, 1996).

Marine organisms also form shells of solid calcium carbonate ($CaCO_3$) that sink vertically or accumulate in sediments, coral reefs and sands. This process depletes surface CO_3^{2-}, reduces alkalinity, and tends to increase pCO_2 and drive more outgassing of CO_2 (see Box 3.3 and Figure 3.1). The effect of $CaCO_3$ formation on surface water pCO_2 and air-sea fluxes is therefore counter to the effect of organic carbon production. For the surface ocean globally, the ratio between the export of organic carbon and the export of calcium carbonate (the "rain ratio") is a critical factor controlling the overall effect of biological activity on surface ocean pCO_2 (Figure 3.1; Archer and Maier-Reimer, 1994). Milliman (1993) estimated a global production of $CaCO_3$ of 0.7 PgC/yr, with roughly equivalent amounts produced in shallow water and surface waters of the deep ocean. Of this total, approximately 60% accumulates in sediments. The rest re-dissolves either in the water column or within the sediment. An estimate of $CaCO_3$ flux analogous to the export production of organic carbon, however, should include sinking out of the upper layers of the open ocean, net accumulation in shallow sediments and reefs, and export of material from shallow systems into deep sea environments. Based on Milliman's (1993) budget, this quantity is about 0.6 PgC/yr (± 25 to 50 % at least). The global average rain ratio has been variously estimated from models of varying complexity to be 4 (Broecker and Peng, 1982), 3.5 to 7.5 (Shaffer, 1993), and 11 (Yamanaka and Tajika, 1996). (It should be noted that rain ratios are highly depth dependent due to rapid oxidation of organic carbon at shallow depth compared to the

depths at which sinking $CaCO_3$ starts to dissolve.) If one accepts an organic carbon export production value of 11 PgC/yr (Schlitzer, 2000), then only Yamanaka and Tajika's (1996) value for the rain ratio approaches consistency with the observation-based estimates of the export of $CaCO_3$ and organic carbon from the ocean surface layer.

The overall productivity of the ocean is determined largely by nutrient supply from deep water. There are multiple potentially limiting nutrients: in practice nitrate and/or phosphate are commonly limiting (Falkowski *et al.*, 1998; Tyrell, 1999). Silicate plays a role in limiting specific types of phytoplankton and hence in determining the qualitative nature of primary production, and potentially the depth to which organic carbon sinks. A role for iron in limiting primary productivity in regions with detectable phosphate and nitrate but low productivity (HNLC or "high nutrient, low chlorophyll regions") has been experimentally demonstrated in the equatorial Pacific (Coale *et al.*, 1996) and the Southern Ocean (Boyd *et al.*, 2000). In both regions artificial addition of iron stimulated phytoplankton growth, resulting in decreased surface-water pCO_2. In HLNC regions, the supply of iron from deep water, while an important source, is generally insufficient to meet the requirements of phytoplankton. An important additional supply of iron to surface waters far removed from sediment and riverine sources is aeolian transport and deposition (Duce and Tindale, 1991; Fung *et al.*, 2000; Martin, 1990). This aeolian supply of iron may limit primary production in HNLC regions, although the effect is ultimately constrained by the availability of nitrate and phosphate. Iron has been hypothesised to play an indirect role over longer time-scales (e.g., glacial-interglacial) through limitation of oceanic nitrogen fixation and, consequently, the oceanic content of nitrate (Falkowski *et al.*, 1998; Broecker and Henderson, 1998; Box 3.4). The regional variability of oceanic nitrogen fixation (Gruber and Sarmiento, 1997) and its temporal variability and potential climate-sensitivity have recently become apparent based on results from long time-series and global surveys (Karl *et al.*, 1997; Hansell and Feely, 2000).

Carbon (organic and inorganic) derived from land also enters the ocean via rivers as well as to some extent via groundwater. This transport comprises a natural carbon transport together with a significant anthropogenic perturbation. The global natural transport from rivers to the ocean is about 0.8 PgC/yr, half of which is organic and half inorganic (Meybeck 1982, 1993; Sarmiento and Sundquist 1992; Figure 3.1). Additional fluxes due to human activity have been estimated (Meybeck, 1993) to be about 0.1 PgC/yr (mainly organic carbon). Much of the organic carbon is deposited and/or respired and outgassed close to land, mostly within estuaries (Smith and Hollibaugh, 1993).The outgassing of anthropogenic carbon from estuaries can be a significant term in comparison with regional CO_2 emissions estimates (e.g., 5 to 10% for Western Europe; Frankignoulle *et al.*, 1998). The natural DIC transport via rivers, however, is part of a large-scale cycling of carbon between the open ocean and land associated with dissolution and precipitation of carbonate minerals. This natural cycle drives net outgassing from the ocean of the order 0.6 PgC/yr globally,

which should be included in any assessment of net air-sea and atmosphere-terrestrial biosphere transfers (Sarmiento and Sundquist, 1992) and ocean transports (e.g., Holfort *et al.*, 1998).

3.2.3.2 Uptake of anthropogenic CO_2

Despite the importance of biological processes for the ocean's natural carbon cycle, current thinking maintains that the oceanic uptake of anthropogenic CO_2 is primarily a physically and chemically controlled process superimposed on a biologically driven carbon cycle that is close to steady state. This differs from the situation on land because of the different factors which control marine and terrestrial primary productivity. On land, experiments have repeatedly shown that current CO_2 concentrations are limiting to plant growth (Section 3.2.2.4). In the ocean, experimental evidence is against control of productivity by CO_2 concentrations, except for certain species at lower than contemporary CO_2 concentrations (Riebesell *et al.*, 1993; Falkowski, 1994). Further, deep ocean concentrations of major nutrients and DIC are tightly correlated, with the existing ratios closely (but not exactly, see Section 3.2.3.3) matching the nutritional requirements of marine organisms (the "Redfield ratios": Redfield *et al.*, 1963). This implies that as long as nutrients that are mixed into the ocean surface layer are largely removed by organic carbon production and export, then there is little potential to drive a net air-sea carbon transfer simply through alteration of the global rate of production. Terrestrial ecosystems show greater variability in this respect because land plants have multiple ways to acquire nutrients, and have greater plasticity in their chemical composition (Melillo and Gosz, 1983). There are, however, extensive regions of the ocean surface where major nutrients are not fully depleted, and changes in these regions may play a significant role in altering atmosphere-ocean carbon partitioning (see Section 3.2.3.3).

The increase of atmospheric pCO_2 over pre-industrial levels has tended to increase uptake into natural CO_2 sink regions and decreased release from natural outgassing regions. Contemporary net air-sea fluxes comprise spatially-varying mixtures of natural and anthropogenic CO_2 flux components and cannot be equated with anthropogenic CO_2 uptake, except on a global scale. Uptake of anthropogenic CO_2 is strongest in regions where "old" waters, which have spent many years in the ocean interior since their last contact with the atmosphere, are re-exposed at the sea surface to a contemporary atmosphere which now contains anthropogenic CO_2 (e.g., Sarmiento *et al.*, 1992; Doney, 1999). In an upwelling region, for example, the natural component of the air-sea flux may be to outgas CO_2 to the atmosphere. The higher atmospheric pCO_2 of the contemporary atmosphere acts to reduce this outgassing relative to the natural state, implying that more carbon remains in the ocean. This represents uptake of anthropogenic CO_2 by a region which is a source of CO_2 to the atmosphere. The additional carbon in the ocean resulting from such uptake is then transported by the surface ocean circulation, and eventually stored as surface waters sink, or are mixed, into the deep ocean interior. Whereas upwelling into the surface layer is quantitatively balanced on a global scale by sinking, the locations where deep waters rise and sink can be separated by large horizontal distances.

Air-sea gas transfer allows older waters to approach a new steady state with higher atmospheric CO_2 levels after about a year at the sea surface. This is fast relative to the rate of ocean mixing, implying that anthropogenic CO_2 uptake is limited by the rate at which "older" waters are mixed towards the air-sea interface. The rate of exposure of older, deeper waters is therefore a critical factor limiting the uptake of anthropogenic CO_2. In principle, there is sufficient uptake capacity (see Box 3.3) in the ocean to incorporate 70 to 80% of anthropogenic CO_2 emissions to the atmosphere, even when total emissions of up to 4,500 PgC are considered (Archer *et al.*, 1997). The finite rate of ocean mixing, however, means that it takes several hundred years to access this capacity (Maier-Reimer and Hasselmann, 1987; Enting *et al.*, 1994; Archer *et al.*, 1997). Chemical neutralisation of added CO_2 through reaction with $CaCO_3$ contained in deep ocean sediments could potentially absorb a further 9 to 15% of the total emitted amount, reducing the airborne fraction of cumulative emissions by about a factor of 2; however the response time of deep ocean sediments is in the order of 5,000 years (Archer *et al.*, 1997).

Using time-series and global survey data, the increasing oceanic carbon content has been directly observed, although the signal is small compared to natural variability and requires extremely accurate measurements (Sabine *et al.*, 1997). A long-term increase of surface water CO_2 levels tracking the mean atmospheric CO_2 increase has been observed in the ocean's subtropical gyres (Bates *et al.*, 1996; Winn *et al.*, 1998) and the equatorial Pacific (Feely *et al.*, 1999b). However, very few such time-series exist and the response of other important oceanic regions to the atmospheric pCO_2 increase cannot yet be assessed. Inter-decadal increases in DIC concentrations at depth have been resolved from direct measurements (Wallace, 1995; Peng *et al.*, 1998; Ono *et al.*, 1998; Sabine *et al.*, 1999). The total amounts of anthropogenic CO_2 accumulated in the ocean since the pre-industrial era can also be estimated from measurements using recent refinements (Gruber *et al.*, 1996) of long-standing methods for separating the natural and anthropogenic components of oceanic DIC. A comparison of such analyses with ocean model results is presented in Section 3.6.3.

3.2.3.3 Future changes in ocean CO_2 uptake

This section lists processes that may be important for the future uptake of anthropogenic CO_2. These changes can represent changes in anthropogenic CO_2 uptake itself (mainly physical and chemical processes), or changes in the natural biologically-linked cycling of carbon between the atmosphere and ocean.

Physical and chemical processes

Buffering changes. The capacity of surface waters to take up anthropogenic CO_2 is decreasing as CO_2 levels increase (see Box 3.3). The magnitude of this effect is substantial. This decrease in uptake capacity of the ocean makes atmospheric CO_2 more sensitive to anthropogenic emissions and other changes in the natural cycling of carbon.

Emissions rate. Even assuming no other changes to the carbon cycle, the proportion of emitted CO_2 that can be taken up by the ocean decreases as the rate of emission increases. This is due to the finite rate of exposure of 'older', deeper waters to the anthropogenic CO_2 contained in the atmosphere.

Warming. CO_2 is less soluble in warmer water, and the equilibrium pCO_2 in seawater increases by about 10 to 20 ppm per °C temperature increase. Warming of surface water would therefore tend to increase surface water pCO_2, driving CO_2 from the surface ocean to the atmosphere. The expected effect of such warming on atmospheric CO_2 may be smaller, depending on the rate of exchange between ocean surface waters and the deep ocean at high latitudes (e.g., Bacastow, 1993).

Vertical mixing and stratification. Several coupled atmosphere-ocean models have shown global warming to be accompanied by an increase in vertical stratification (see Chapter 7). Such a change would reduce the rate of mixing between surface and deep waters, and therefore reduce the effective volume of the ocean that is exposed to high atmospheric CO_2. On its own, this effect would tend to reduce the ocean CO_2 uptake. However, changes in stratification may also drive changes in the natural carbon cycle. The magnitude and even the sign of changes in the natural cycle are much more difficult to predict because of the complexity of ocean biological processes (Sarmiento *et al.,* 1998; Matear and Hirst, 1999).

Biologically-linked processes

Qualitative and quantitative changes in carbon uptake arising from changes in marine ecosystems are more speculative (Denman *et al.*, 1996; Falkowski *et al.,* 1998; Watson and Liss, 1998), but are likely to have occurred over glacial-interglacial time-scales (Section 3.3). Falkowski *et al.* (1998) listed three major classes of biologically linked factors that can in principal alter the air-sea partitioning of CO_2: (1) changes in surface nutrient utilisation (e.g., in HNLC areas); (2) changes in total ocean content of major nutrients; (3) changes in the elemental composition of biogenic material (including the rain ratio). Our incomplete understanding of present day nutrient controls on productivity limits our ability to predict future changes in ocean biology and their effect on CO_2 levels. For example, the possible identification of changes in deep ocean C:N:P ratios (Pahlow and Riebesell, 2000) leaves open the question of the extent to which ocean biological carbon cycling is in steady state, or is likely to remain so in the future.

Changes in surface nutrient utilisation. Changes in the utilisation of surface nutrients in HNLC regions have the potential to alter export production and carbon storage in the ocean interior. Most attention focuses on the role of inadvertent or deliberate changes in the external supply of iron to such regions. The sign of possible future responses of ocean biota due to iron supply changes is difficult to assess. Future iron supply may increase due to erosion (enhanced by agriculture and urbanisation) which tends to increase dust export and aeolian iron deposition (Tegen and Fung, 1995). Conversely, a globally enhanced hydrological cycle and increased water-use efficiency of terrestrial plants may tend to reduce future dust export (Harrison *et al.*, 2001). The delivery of dust to the HNLC regions will be sensitive to regional changes in erosion and the hydrological cycle, affecting the important regions of dust export, rather than to global scale changes (Dai *et al.*, 1998).

Surface nutrient supply could be reduced if ocean stratification reduces the supply of major nutrients carried to the surface waters from the deep ocean (Sarmiento *et al.*, 1998). The impact of strati-

fication on marine productivity depends on the limiting factor. In regions limited by deep ocean nutrients, stratification would reduce marine productivity and the strength of the export of carbon by biological processes. Conversely, stratification also increases the light exposure of marine organisms, which would increase productivity in regions where light is limiting.

Changes in total ocean content of major nutrients. Changes in the delivery of the major biologically limiting nutrients (N, P, Fe, Si) from riverine, atmospheric or sedimentary sources, or changes in removal rates (e.g., denitrification), could alter oceanic nutrient inventories and hence export production and ocean carbon storage. On the global scale, the upward fluxes of major nutrients are slightly depleted in N relative to P with respect to the nutrient requirements of phytoplankton (Fanning, 1992). This relative supply of N versus P may be sensitive to climate and circulation related changes in the rate of fixed-nitrogen removal by denitrification (Ganeshram *et al.*, 1995) or via changes in the rate of nitrogen fixation. Changes in river flow and composition are also affecting the supply of nutrients (Frankignoulle *et al.*, 1998). The hypothesised link between nitrogen fixation in certain ocean regions and the external iron supply (Falkowski, 1997; Wu *et al.*, 2000) could play a role in future nutrient and carbon budgets. Nitrogen fixation rates may also be affected by changes in stratification and mixing. For example, Karl *et al.* (1997) have identified interannual variability in nitrogen fixation rates in the subtropical Pacific which are apparently linked to ENSO variability in upper ocean dynamics.

Changes in the elemental composition of biogenic material. The structure and biogeochemistry of marine ecosystems can be affected by numerous climate-related factors including temperature, cloudiness, nutrient availability, mixed-layer physics and sea-ice extent. In turn the structure of marine ecosystems, and particularly the species composition of phytoplankton, exert a control on the partitioning of carbon between the ocean and the atmosphere. For example, a change in distribution of calcareous versus siliceous planktonic organisms could affect CO_2 uptake in the future, as it may have done in the past (Archer and Maier-Reimer, 1994). Precipitation of $CaCO_3$ by marine organisms (calcification) removes dissolved CO_3^{2-}, thus decreasing surface water alkalinity and reducing the capacity of sea water to dissolve atmospheric CO_2 (see Box 3.3). Recent experimental evidence suggests that as a direct result of increasing atmospheric and surface water pCO_2 levels, oceanic calcification will decrease significantly over the next 100 years. Model-based calculations suggest that decreases in coral reef calcification rates of the order 17 to 35% relative to pre-industrial rates are possible (Kleypas *et al.*, 1999). Experimental studies with corals have confirmed such effects (Langdon *et al.*, 2000). Field and laboratory studies have shown that planktonic calcification is also highly sensitive to pCO_2 levels. The calcification rate of coccolithophorids decreases by 16 to 83% at pCO_2 levels of 750 ppm (Riebesell *et al.*, 2000). Such an effect would tend to favour CO_2 storage in the upper ocean and act as a negative feedback on atmospheric growth rates of CO_2. However, long-term predictions of such biological responses are hampered by a lack of understanding concerning physiological acclimation and genetic adaptations of species to increasing pCO_2.
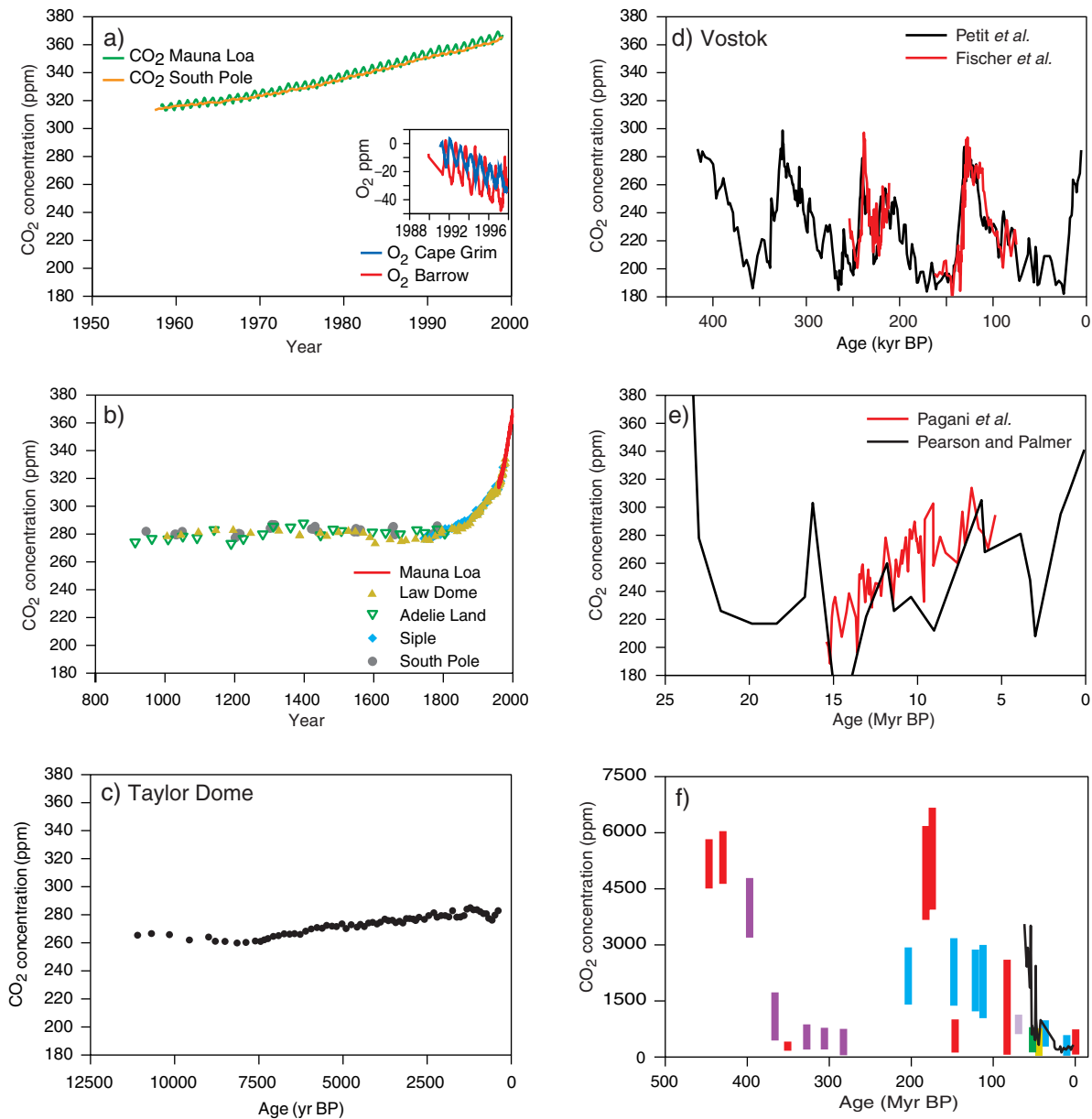
Figure 3.2: Variations in atmospheric CO_2 concentration on different time-scales. (a) Direct measurements of atmospheric CO_2 concentration (Keeling and Whorf, 2000), and O_2 from 1990 onwards (Battle *et al.,* 2000). O_2 concentration is expressed as the change from an arbitrary standard. (b) CO_2 concentration in Antarctic ice cores for the past millenium (Siegenthaler *et al.,* 1988; Neftel *et al.,* 1994; Barnola *et al.,* 1995; Etheridge *et al.,* 1996). Recent atmospheric measurements at Mauna Loa (Keeling and Whorf, 2000) are shown for comparison. (c) CO_2 concentration in the Taylor Dome Antarctic ice core (Indermühle *et al.,* 1999). (d) CO_2 concentration in the Vostok Antarctic ice core (Petit *et al.,* 1999; Fischer *et al.,* 1999). (e) Geochemically inferred CO_2 concentrations, from Pagani *et al.* (1999a) and Pearson and Palmer (2000). (f) Geochemically inferred CO_2 concentrations: coloured bars represent different published studies cited by Berner (1997). The data from Pearson and Palmer (2000) are shown by a black line. (BP = before present.)

3.3 Palaeo CO_2 and Natural Changes in the Carbon Cycle

3.3.1 Geological History of Atmospheric CO_2

Atmospheric CO_2 concentration has varied on all time-scales during the Earth's history (Figure 3.2). There is evidence for very high CO_2 concentrations (>3,000 ppm) between 600 and 400 Myr BP and between 200 and 150 Myr BP (Figure 3.2f). On long time-scales, atmospheric CO_2 content is determined by the balance among geochemical processes including organic carbon burial in sediments, silicate rock weathering, and vulcanism (Berner, 1993, 1997). In particular, terrestrial vegetation has enhanced the rate of silicate weathering, which consumes CO_2 while releasing base cations that end up in the ocean. Subsequent deep-sea burial of Ca and Mg (as carbonates, for example $CaCO_3$) in the shells of marine organisms removes CO_2. The net effect of slight imbalances in the carbon cycle over tens to hundreds of millions of years has been to reduce

Box 3.4: Causes of glacial/inter-glacial changes in atmospheric CO_2.

One family of hypotheses to explain glacial/inter-glacial variations of atmospheric CO_2 relies on physical mechanisms that could change the dissolution and outgassing of CO_2 in the ocean. The solubility of CO_2 is increased at low temperature, but reduced at high salinity. These effects nearly cancel out over the glacial/inter-glacial cycle, so simple solubility changes are not the answer. Stephens and Keeling (2000) have proposed that extended winter sea ice prevented outgassing of upwelled, CO_2-rich water around the Antarctic continent during glacial times. A melt-water "cap" may have further restricted outgassing of CO_2 during summer (François *et al.,* 1997). These mechanisms could explain the parallel increases of Antarctic temperature and CO_2 during deglaciation. However, they require less vertical mixing to occur at low latitudes than is normally assumed. The relative importance of high and low latitudes for the transport of CO_2 by physical processes is not well known, and may be poorly represented in most ocean carbon models (Toggweiler, 1999; Broecker *et al.,* 1999).

Several authors have hypothesised increased utilisation of surface nutrients by marine ecosystems in high latitudes, leading to stronger vertical gradients of DIC and thus reduced atmospheric CO_2 during glacial times (Sarmiento and Toggweiler, 1984; Siegenthaler and Wenk, 1984; Knox and McElroy, 1984). Other hypotheses call for an increased external supply of nutrients to the ocean (McElroy, 1983; Martin *et al.,* 1990; Broecker and Henderson, 1998). The supply of iron-rich dust to the Southern Ocean is increased during glacial periods, due to expanded deserts in the Patagonian source region (Andersen *et al.,* 1998; Mahowald *et al.,* 1999; Petit *et al.,* 1999); dust-borne iron concentration in Antarctic ice is also increased (Edwards *et al.,* 1998). Fertilisation of marine productivity by iron from this source could have influenced atmospheric CO_2. Most of these mechanisms, however, can only account for about 30 ppm, or less, of the change (Lefèvre and Watson, 1999; Archer and Johnson, 2000). Palaeo-nutrient proxies have also been used to argue against large changes in total high latitude productivity (Boyle, 1988; Rickaby and Elderfield, 1999; Elderfield and Rickaby, 2000), even if the region of high productivity in the Southern Ocean may have been shifted to the north (Kumar *et al.,* 1995; François *et al.,* 1997). Increased productivity over larger regions might have been caused by decreased denitrification (Altabet *et al.,* 1995; Ganeshram *et al.,* 1995) or iron stimulated N_2 fixation (Broecker and Henderson, 1998) leading to an increase in the total ocean content of reactive nitrogen.

Another family of hypotheses invokes ocean alkalinity changes by a variety of mechanisms (Opdyke and Walker, 1992; Archer and Maier-Reimer, 1994; Kleypas, 1997), including increased silica supply through dust, promoting export production by siliceous rather than calcareous phytoplankton (Harrison, 2000). Although there is geochemical evidence for higher ocean pH during glacial times (Sanyal *et al.,* 1995), a large increase in alkalinity would result in a much deeper lysocline, implying an increase in $CaCO_3$ preservation that is not observed in deep-sea sediments (Catubig *et al.,* 1998; Sigman *et al.,* 1998; Archer *et al.,* 2000).

Given the complex timing of changes between climate changes and atmospheric CO_2 on glacial-interglacial time-scales, it is plausible that more than one mechanism has been in operation; and indeed most or all of the hypotheses encounter difficulties if called upon individually to explain the full magnitude of the change.

atmospheric CO_2. The rates of these processes are extremely slow, hence they are of limited relevance to the atmospheric CO_2 response to emissions over the next hundred years.

It is pertinent, however, that photosynthesis evolved at a time when O_2 concentrations were far less than at present. O_2 has accumulated in the atmosphere over geological time because photosynthesis results in the burial of reduced chemical species: pyrite (FeS_2) derived from sulphur-reducing bacteria, and organic carbon. This accumulation has consequences for terrestrial and marine ecosystems today. Primary production is carbon limited in terrestrial ecosystems in part because of (geologically speaking) low CO_2 concentrations, and in part because Rubisco (the enzyme that fixes CO_2 in all plants) also has an affinity for O_2 that reduces its efficiency in photosynthesis (see Section 3.2.2.4). Primary production is iron limited in some marine ecosystems mainly because of the extreme insolubility of Fe(III), the predominant form of iron in the present, O_2-rich environment. These difficulties faced by contemporary organisms represent a legacy of earlier evolution under very different biogeochemical conditions.

In more recent times, atmospheric CO_2 concentration continued to fall after about 60 Myr BP and there is geochemical evidence that concentrations were <300 ppm by about 20 Myr BP

(Pagani *et al.,* 1999a; Pearson and Palmer, 1999, 2000; Figure 3.2e). Low CO_2 concentrations may have been the stimulus that favoured the evolution of C_4 plants, which increased greatly in abundance between 7 and 5 Myr BP (Cerling *et al.,* 1993, 1997; Pagani *et al.,* 1999b). Although contemporary CO_2 concentrations were exceeded during earlier geological epochs, they are likely higher now than at any time during the past 20 million years.

3.3.2 Variations in Atmospheric CO_2 during Glacial/inter-glacial Cycles

The purity of Antarctic ice allows the CO_2 concentration in trapped air bubbles to be accurately measured (Tschumi and Stauffer, 2000). The CO_2 record from the Vostok ice core is the best available for the glacial/inter-glacial time-scale and covers the past four glacial/inter-glacial cycles (420 kyr) with a resolution of 1 to 2 kyr (Petit *et al.,* 1999; Fischer *et al.,* 1999). The general pattern is clear (Figure 3.2d): atmospheric CO_2 has been low (but $\geq$ 180 ppm) during glacial periods, and higher (but $\leq$300 ppm) during interglacials. Natural processes during the glacial-interglacial cycles have maintained CO_2 concentrations within

these bounds, despite considerable variability on multi-millenial time-scales. The present CO_2 concentration is higher than at any time during the 420 kyr period covered by the Vostok record.

The terrestrial biosphere stores 300 to 700 Pg *more* carbon during interglacial periods than during glacial periods, based on a widely accepted interpretation of the $\delta^{13}C$ record in deep-sea sediments (Shackleton, 1977; Bird *et al.,* 1994; Crowley, 1995). Terrestrial modelling studies (e.g., Friedlingstein *et al.,* 1995b; Peng *et al.,* 1998) have reached the same conclusion. Thus, the terrestrial biosphere does not cause the difference in atmospheric CO_2 between glacial and interglacial periods. The cause must lie in the ocean, and indeed the amount of atmospheric change to be accounted for must be augmented to account for a fraction of the carbon transferred between the land and ocean. The mechanism remains controversial (see Box 3.4). In part this is because a variety of processes that could be effective in altering CO_2 levels on a century time-scale can be largely cancelled on multi-millenial time-scales by changes in $CaCO_3$ sedimentation or dissolution, as discussed in Section 3.2.3.1.

Orbital variations (Berger, 1978) are the pacemaker of climate change on multi-millenial time-scales (Hays *et al.,* 1976). Atmospheric CO_2 is one of many Earth system variables that show the characteristic "Milankovitch" periodicities, and has been implicated as a key factor in locking natural climate changes to the 100 kyr eccentricity cycle (Shackleton, 2000). Whatever the mechanisms involved, lags of up to 2,000 to 4,000 years in the drawdown of CO_2 at the start of glacial periods suggests that the low CO_2 concentrations during glacial periods amplify the climate change but do not initiate glaciations (Lorius and Oeschger, 1994; Fischer *et al.,* 1999). Once established, the low CO_2 concentration is likely to have enhanced global cooling (Hewitt and Mitchell, 1997). During the last deglaciation, rising CO_2 paralleled Southern Hemisphere warming and was ahead of Northern Hemisphere warming (Chapter 2).

During glacial periods, the atmospheric CO_2 concentration does not track the "fast" changes in climate (e.g., decade to century scale warming events) associated with Dansgaard-Oeschger events, although there are CO_2 fluctuations of up to 20 ppm associated with the longer-lived events (Stauffer *et al.,* 1998; Indermühle *et al.*, 2000) (see Chapter 2 for explanations of these terms). During the last deglaciation, atmospheric CO_2 concentration continued to increase, by about 12 ppm, through the Younger Dryas cold reversal (12.7 to 11.6 kyr BP) seen in Northern Hemisphere palaeoclimate records (Fischer *et al.,* 1999; Smith *et al.,* 1999). Palaeo-oceanographic evidence shows that the Younger Dryas event was marked by a prolonged shut-down of the thermo-haline circulation, which is likely to have been triggered by the release of melt water into the North Atlantic. Similar behaviour, with a slight rise in CO_2 accompanying a major Northern Hemisphere cooling and shutdown of North Atlantic Deep Water production, has been produced in a coupled atmosphere-ocean model (Marchal *et al.,* 1998). The observed CO_2 rise during the Younger Dryas period was modest, suggesting that atmospheric CO_2 has, under natural conditions, been well buffered against abrupt changes in climate, including thermohaline collapse. This buffering is a direct consequence of the large reservoir of DIC in the ocean.

3.3.3 Variations in Atmospheric CO_2 during the Past 11,000 Years

Natural variations in CO_2 during the past 11,000 years (Figure 3.2c) have been small (about 20 ppm) according to the best available measurements, which are from the Taylor Dome ice core (Smith *et al.,* 1999; Indermühle *et al.,* 1999). These measurements show a short-lived maximum around 11 kyr BP, followed by a slight fall, which may have been caused by increasing carbon storage in the terrestrial biosphere. Atmospheric CO_2 concentration was about 260 ppm at its Holocene minimum around 8 kyr BP and increased towards about 280 ppm in the pre-industrial period. The same pattern and the same CO_2 concentration levels over the past 8 kyr have also been shown in another ice core, BH7 near Vostok (Peybernès *et al.,* 2000). The causes of these changes are not known. Preliminary $\delta^{13}C$ measurements (see Box 3.6) suggest that this increase may have been due to a gradual reduction in terrestrial carbon storage (Indermühle *et al.,* 1999; Smith *et al.,* 1999) but others have considered an oceanic explanation more likely.

Atmospheric CO_2 concentrations have also been reconstructed indirectly, from stomatal index measurements on sub-fossil leaves (Van de Water *et al.,* 1994; Beerling *et al.,* 1995; Rundgren and Beerling, 1999; Wagner *et al.,* 1999). Stomatal density and stomatal index of many species respond to atmospheric CO_2 (Woodward, 1987; Woodward and Bazzaz, 1988) but are influenced by other environmental variables as well (Poole *et al.,* 1996). One recent stomatal index record, interpreted as implying high (up to 350 ppm) and rapidly fluctuating CO_2 concentrations in the early Holocene (Wagner *et al.,* 1999), is clearly incompatible with the ice core record of Indermühle *et al.* (1999), whereas a continuous stomatal index record from 9 kyr BP onwards (Rundgren and Beerling, 1999) has shown concentration trends consistent with the ice-core records.

Figure 3.2b shows the excellent agreement among different high-resolution Antarctic ice cores covering the past 1,000 years. Atmospheric CO_2 concentration fell by about 8 to 10 ppm during the Little Ice Age (from 1280 to 1860, see Chapter 2) (Figure. 3.2b, c; Barnola *et al.,* 1995; Etheridge *et al.,* 1996; Indermühle *et al.,* 1999; Rundgren and Beerling, 1999). A slight contemporaneous increase in $\delta^{13}C$ of atmospheric CO_2 has led to the suggestion that this effect was caused by enhanced carbon storage on land (Francey *et al.,* 1999b; Trudinger *et al.,* 1999).

3.3.4 Implications

The Vostok record of atmospheric CO_2 and Antarctic climate is consistent with a view of the climate system in which CO_2 concentration changes amplify orbitally-induced climate changes on glacial/inter-glacial time-scales (Shackleton, 2000). Changes during the present inter-glacial (until the start of the anthropogenic CO_2 rise) have been small by comparison. Although complete explanations for these changes in the past are lacking, high-resolution ice core records establish that the human-induced increase of atmospheric CO_2 over the past century is at least an order of magnitude faster than has occurred during the preceeding 20,000 years.

3.4 Anthropogenic Sources of CO_2

3.4.1 Emissions from Fossil Fuel Burning and Cement Production

Current anthropogenic emissions of CO_2 are primarily the result of the consumption of energy from fossil fuels. Estimates of annual global emissions from fossil fuel burning and cement production have been made for the period from 1751 through 1999. Figure 3.3 summarises emissions over the period from 1959 to 1999 (Keeling and Whorf, 2000).

Estimates of annual global emissions from fossil fuel burning and cement production by Marland *et al.* (2000) span the period from 1751 through to 1997, reaching a maximum in 1997 of 6.6 PgC/yr (0.2 PgC/yr of this was from cement production). The primary data for these estimates are annual energy statistics compiled by the United Nations (2000). Emissions for 1998 and 1999 have been estimated based on energy statistics compiled by British Petroleum (2000). Emission factors (IPCC, 1997) were applied to consumption statistics (British Petroleum, 2000) to calculate emissions over the period 1990 to 1999. Emissions were then scaled to match the estimates for emissions from fossil fuel burning and cement production from Marland *et al.* (2000) over the overlap period from 1990 to 1997. The scaled emission estimates, therefore, implicitly include emissions from cement production.

The average value of emissions for the 1980s given by Marland *et al.* (2000) is 5.44 ± 0.3 PgC/yr, revised from the earlier estimate (Marland *et al.* 1994; Andres *et al.* 2000) of 5.46 ± 0.3 PgC/yr used in the SAR and in the Special Report on Radiative Forcing (IPCC, 1994) (hereafter SRRF). Estimated emissions rose from 6.1 PgC/yr in 1990 to 6.5 PgC/yr in 1999. The average value of emissions in the 1990s was 6.3 ± 0.4 PgC/yr.

3.4.2 Consequences of Land-use Change

About 10 to 30% of the current total anthropogenic emissions of CO_2 are estimated to be caused by land-use conversion. Such estimates rely on land cover data sets which are highly variable, and estimates of average carbon density of vegetation types, which are also highly variable with stand age and local conditions (see Box 3.1). Hence they cannot be specified as accurately as is possible for fossil fuel emissions. Historical emissions are treated in Section 3.2.2.2; this section focuses on the contemporary situation.

Net land-use flux, comprising the balance of positive terms due to deforestation and negative terms due to regrowth on abandoned agricultural land, has been estimated based on land-use statistics and simple models of rates of decomposition and regrowth, excluding possible climate, CO_2 and N fertilisation effects (Houghton, 1999). Not all land-use emissions are included, for example mining of peatlands. The analysis of Houghton (1999) indicated that the net flux due to land-use change was 2.0 ± 0.8 PgC/yr during the 1980s, almost entirely due to deforestation of tropical regions. Temperate forests were found to show an approximate balance between carbon uptake in regrowing forests and carbon lost in oxidation of wood
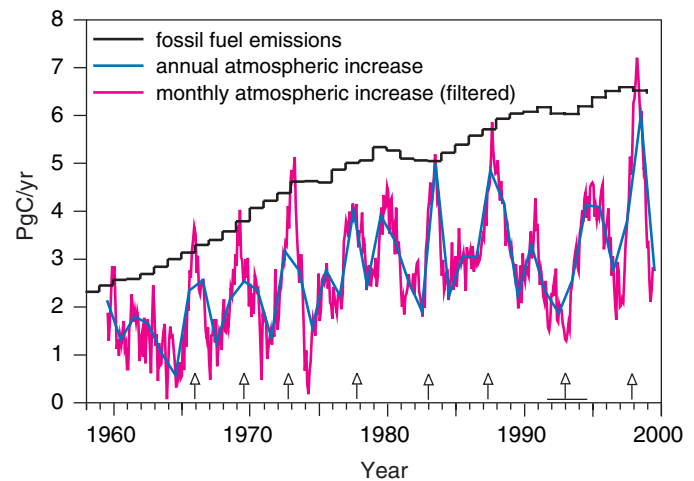

Figure 3.3: Fossil fuel emissions and the rate of increase of CO_2 concentration in the atmosphere. The annual atmospheric increase is the measured increase during a calendar year. The monthly atmospheric increases have been filtered to remove the seasonal cycle. Vertical arrows denote El Niño events. A horizontal line defines the extended El Niño of 1991 to 1994. Atmospheric data are from Keeling and Whorf (2000), fossil fuel emissions data are from Marland *et al.* (2000) and British Petroleum (2000), see explanations in text.

products, except in Europe, which showed a small net accumulation. The estimate of 2.0 PgC/yr is somewhat higher than Houghton and Hackler's (1995) earlier estimate of 1.6 PgC/yr for the same period, which was used in the SAR, because of a reanalysis of data from tropical Asia (Houghton and Hackler, 1999). However, other recent analyses by the same authors reduce the estimated emissions from the Brazilian Amazon by half (Houghton *et al.*, 2000), and point to other previously unaccounted for sinks of carbon in the USA such as fire suppression and woody encroachment, and changes in the management of agricultural soils (Houghton *et al.*, 1999). Consideration of these additional studies brings the overall total back down to 1.7 ± 0.8 PgC/yr (Houghton, 2000), as given in the SRLULUCF.

An independent analysis (see Section 3.6.2.2) by the Carbon Cycle Model Linkage Project (CCMLP) also calculated the marginal effects of land-use changes on the global terrestrial carbon budget (McGuire *et al.*, 2001). Land-use change data (conversions between native vegetation and crops) were derived from Ramankutty and Foley (2000). The estimates obtained for net land-use flux during the 1980s were between 0.6 and 1.0 PgC/yr, i.e., substantially smaller than the fluxes calculated by Houghton (1999). The reasons for this discrepancy are unclear. The CCMLP estimates may be too low because they neglected conversions to pasture. However, data presented in Houghton (1999) indicate that the main changes during recent decades were due to land conversion for crops. A more important difference may lie in the timing of deforestation in different regions in the tropics, where Ramankutty and Foley (2000) show higher overall rates in the 1970s and lower rates in the 1980s than Houghton does (1999).

Box 3.5: The use of O_2 measurements to assess the fate of fossil fuel CO_2.

The amount of CO_2 that remains in the atmosphere each year has been consistently less than the amount emitted by fossil fuel burning. This is because some CO_2 dissolves and mixes in the ocean, and some is taken up by the land. These two modes of uptake have different effects on the concentration of O_2 in the atmosphere. Fossil fuel burning consumes O_2 and causes a decline in atmospheric O_2 concentration (Figure 3.4). Dissolution of CO_2 in the ocean has no effect on atmospheric O_2. Terrestrial uptake of CO_2, by contrast, implies that photosynthesis (which releases O_2) is exceeding respiration and other oxidation processes, including fire (which consume O_2). Thus, net terrestrial uptake of CO_2 implies a net release of O_2, in a known stochiometric ratio. This difference can be used to partition the total CO_2 uptake into land and ocean components, as shown graphically in Figure 3.4. Strictly speaking, the atmospheric $O_2 – CO_2$ budget method can only distinguish between net non-biological ocean uptake and net biospheric uptake, which in principle includes both the terrestrial and the marine biosphere. However, since biological oxygen uptake is not expected to have changed significantly during recent decades because of nutrient limitations in most parts of the ocean (see Section 3.2.3.2), this inferred biospheric uptake is attributed to the land.

Measurement of changes in O_2 presents a technical challenge because changes of a few ppm caused by fossil fuel burning have to be determined against a background concentration of 209,000 ppm (about 21%). For technical reasons, O_2 is measured relative to N_2, the main constituent of the atmosphere, as a reference gas. For simplicity this chapter refers to O_2 concentrations, although strictly it is $O_2 : N_2$ ratios that are measured. The impact of nitrification-denitrification changes on atmospheric N_2 content are assumed not to be problematic because they are small and the inventory of N_2 is very large. Increases in ocean temperatures (Levitus *et al.*, 2000), because of their effect on the temperature dependent solubility, induce small outgassing fluxes of O_2 and N_2 (Keeling *et al.*, 1993) that have to be taken into account (see Figure 3.4) although their magnitude is only approximately known. Impacts on atmospheric O_2 caused by changes in the ventilation of deeper, oxygen depleted waters have been observed on interannual time-scales (Keeling *et al.*, 1993, Bender *et al.*, 1996). They could also occur on longer time-scales, e.g., through increased ocean stratification induced by ocean warming.

Another analysis calculated a substantially higher net source due to land-use change in the tropics of 2.4 ± 1.0 PgC/yr during the 1980s (Fearnside, 2000). This analysis did not deal with temperate regions, and is not used in the global budget estimates.

No complete global assessment of deforestation effects covering the 1990s is available. Rates of deforestation appear to be declining. The FAO (1997) tropical forest assessment reported annual losses of 15.5×10^6 ha in the 1980s, and 13.7×10^6 ha in 1990 to 1995. Independent studies show a significant decline in deforestation rates in the Amazon region (Skole and Tucker, 1993; Fearnside, 2000). The annual flux of carbon from land-use change for the period from 1990 to 1995 has been estimated to be 1.6 PgC/yr from 1990 to 1995, consisting of a source of 1.7 PgC/yr in the tropics and a small sink in temperate and boreal areas (Houghton, 2000).

3.5 Observations, Trends and Budgets

3.5.1 Atmospheric Measurements and Global CO_2 Budgets

Continuous time-series of highly precise measurements of the atmospheric composition are of central importance to current understanding of the contemporary carbon cycle. CO_2 has been measured at the Mauna Loa and South Pole stations since 1957 (Keeling *et al.*, 1995; Figure 3.2a), and through a global surface sampling network developed in the 1970s that is becoming progressively more extensive and better inter-calibrated (Conway *et al.*, 1994; Keeling *et al.*, 1995). Associated measurements of $\delta^{13}C$ in atmospheric CO_2 began in 1977 (Francey *et al.*, 1995, Keeling *et al.*, 1995, Trolier *et al.*, 1996). More recently, comple-

mentary information has been available from O_2 concentrations (measured as ratios of $O_2:N_2$, see Box 3.5), which have been regularly measured since the early 1990s (Keeling and Shertz, 1992; Keeling *et al.*, 1993; Bender *et al.*, 1996; Keeling *et al.*, 1996b; Battle *et al.*, 2000; Manning, 2001; Figure 3.2a). O_2 concentration data for the 1980s have been gleaned by two methods: sampling of archived air flasks that were collected during the 1980s (Langenfelds *et al.*, 1999), and measuring the air trapped in Antarctic firn (Battle *et al.*, 1996).

In addition to fossil fuel CO_2 emissions, Figure 3.3 shows the observed seasonally corrected growth rate of the atmospheric CO_2 concentrations, based on the two longest running atmospheric CO_2 recording stations (Keeling and Whorf, 2000). It is evident from this comparison that a part of the anthropogenic CO_2 has not remained in the atmosphere; in other words, CO_2 has been taken up by the land or the ocean or both. This comparison also shows that there is considerable interannual variability in the total rate of uptake.

O_2 and CO_2 measurements are used here to provide observationally-based budgets of atmospheric CO_2 (Table 3.1). CO_2 budgets are presented here (Table 3.1) for the 1980s (for comparison with previous work; Table 3.3), and for the 1990s. The reported error ranges are based on uncertainties of global fossil fuel emissions, determination of the decadal average changes in the atmospheric CO_2 concentration, and $O_2:N_2$ ratio; and uncertainties in the assumed $O_2:CO_2$ stoichiometric ratios in the combustion of fossil fuels and in photosynthesis and respiration. The error ranges reflect *uncertainties* of the decadal mean averaged values; they do not reflect interannual variability in annual values, which far exceeds uncertainty in
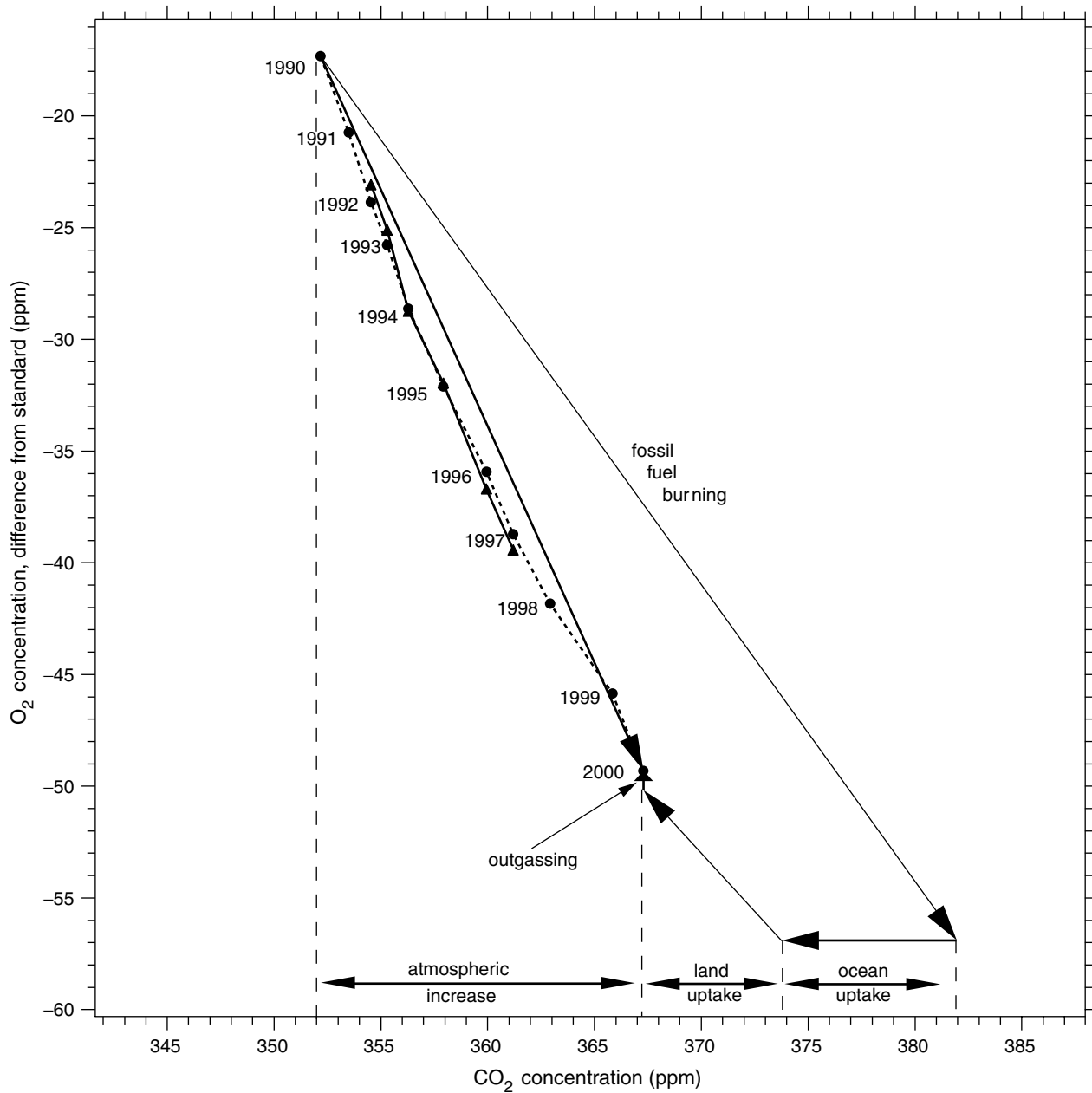
Figure 3.4: Partitioning of fossil fuel CO_2 uptake using O_2 measurements (Keeling and Shertz, 1992; Keeling *et al.*, 1993; Battle *et al.*, 1996, 2000; Bender *et al.*, 1996; Keeling *et al.*, 1996b; Manning, 2001). The graph shows the relationship between changes in CO_2 (horizontal axis) and O_2 (vertical axis). Observations of annual mean concentrations of O_2, centred on January 1, are shown from the average of the Alert and La Jolla monitoring stations (Keeling *et al.*, 1996b; Manning, 2001; solid circles) and from the average of the Cape Grim and Point Barrow monitoring stations (Battle *et al.*, 2000; solid triangles). The records from the two laboratories, which use different reference standards, have been shifted to optimally match during the mutually overlapping period. The CO_2 observations represent global averages compiled from the stations of the NOAA network (Conway *et al.*, 1994) with the methods of Tans *et al.* (1989). The arrow labelled "fossil fuel burning" denotes the effect of the combustion of fossil fuels (Marland *et al.*, 2000; British Petroleum, 2000) based on the relatively well known O_2:CO_2 stoichiometric relation of the different fuel types (Keeling, 1988). Uptake by land and ocean is constrained by the known O_2:CO_2 stoichiometric ratio of these processes, defining the slopes of the respective arrows. A small correction is made for differential outgassing of O_2 and N_2 with the increased temperature of the ocean as estimated by Levitus *et al.* (2000).

Box 3.6: Stable carbon isotopes in atmospheric CO_2.

$\delta^{13}C$, a measure of the relative abundance of the two stable carbon isotopes, ^{13}C and ^{12}C, in atmospheric CO_2 gives in principle similar possibilities to O_2 for the partitioning of atmospheric CO_2 uptake (Keeling *et al.,* 1979, 1980; Mook *et al.,* 1983; Keeling *et al.,* 1989; Francey *et al.,* 1995; Keeling *et al.,* 1995). The principle of using $\delta^{13}C$ to separate land and ocean components of the carbon budget relies on the fractionation during photosynthesis by C_3 plants, which discriminates against ^{13}C. This fractionation leads to biospheric carbon being depleted in ^{13}C by about 18‰ relative to the atmosphere. In contrast, exchanges with the ocean involve relatively small fractionation effects. Changes in the $^{13}C/^{12}C$ ratio of atmospheric CO_2 thus indicate the extent to which concurrent CO_2 variations can be ascribed to variations in biospheric uptake. The calculation also requires specification of the turnover times of carbon in the ocean and on land, because fossil fuel burning implies a continuous release of isotopically light carbon to the atmosphere. This leads to a lowering of the atmospheric $^{13}C/^{12}C$ isotope ratio, which takes years to centuries to work its way through the carbon cycle (Keeling *et al.,* 1980; Tans *et al.,* 1993; Ciais *et al.,* 1995a,b).

There are some complications. C_3 plants discriminate against ^{13}C more strongly than C_4 plants (Lloyd and Farquhar, 1994), thus the distributions of C_3 and C_4 photosynthesis need to be known. The oceanic disequilibrium can in principle be estimated observationally (Tans *et al.,* 1993; Heimannn and Maier-Reimer, 1996; Bacastow *et al.,* 1996; Gruber *et al.,* 1999), while the terrestrial disequilibrium has to be estimated by means of models (e.g., Ciais *et al.,* 1999). Langenfelds *et al.* (1999) and Battle *et al.* (2000) have shown that recently estimated values for the disequilibrium terms lead to consistency between the partitioning of CO_2 uptake into land and ocean uptake based on O_2 and on $\delta^{13}C$ measurements.

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the decadal mean rate of increase, as is further discussed in Section 3.5.2. The salient facts are as follows:

- During the 1980s, fossil fuel emissions were on average 5.4 ± 0.3 PgC/yr and atmospheric CO_2 content increased on average by 3.3 ± 0.1 PgC/yr. Partitioning of CO_2 uptake was estimated based on archived flask O_2 measurements (Langenfelds *et al.,* 1999) for the 1979 to 1997 period, taking the O_2 trend during 1991 to 1997 (Battle *et al.,* 2000) into account. The resulting estimate of the ocean-atmosphere flux was -1.9 ± 0.6 PgC/yr and of the land-atmosphere flux -0.2 ± 0.7 PgC/yr. This partitioning is adopted here in Table 3.1. It is corroborated by independent O_2 measurements in Antarctic firn (Battle *et al.,* 1996). Restricting the analysis to the Battle *et al.* (1996) data for the 1980 to 1989 period, an ocean-atmosphere flux of -1.8 ± 1.0 PgC/yr and a land-atmosphere flux of -0.4 ± 1.0 PgC/yr were obtained, i.e., results indistinguishable from the values in Table 3.1.

- Despite a greater emission rate of 6.3 ± 0.4 PgC/yr (see Section 3.4.1), the average atmospheric increase during the 1990s was 3.2 ± 0.1 PgC/yr, i.e., about the same as during the 1980s. An exceptionally low rate of increase during the early 1990s was balanced by a high rate during the late 1990s. Based on the longest existing O_2 records from La Jolla (California, USA) and Alert (northern Canada) (Keeling *et al.,* 1996b; Manning, 2001; see Figure 3.4), the ocean-atmosphere flux during the 1990s was -1.7 ± 0.5 PgC/yr and the land-atmosphere flux was -1.4 ± 0.7 PgC/yr.

Ocean uptake in the 1980s as estimated from O_2 and CO_2 measurements thus agrees with the estimates in the SRRF (Schimel *et al.,* 1995) and the SAR (Schimel *et al.,* 1996) (although these were model-based estimates; this section presents only observationally-based estimates (Table 3.3)). Considering the uncertainties, the ocean sink in the 1990s was not significantly different from that in

the 1980s. The land-atmosphere flux was close to zero in the 1980s, as also implied by the SAR budget. The land appears to have taken up more carbon during the 1990s than during the 1980s. The causes cannot yet be reliably quantified, but possible mechanisms include a slow down in deforestation (Section 3.4.2), and climate variability that resulted in temporarily increased land and/or ocean uptake in the early 1990s (Section 3.5.2). These budgets are consistent with information from atmospheric $\delta^{13}C$ measurements (see Box 3.6 and Table 3.4) and with budgets presented in the SRLULUCF (Bolin *et al.* 2000) except that estimated ocean uptake is smaller, and land uptake accordingly larger, than given in the SRLULUCF (see Table 3.3, footnote *i*).

Several alternative approaches to estimating the ocean-atmosphere and land-atmosphere fluxes of CO_2 are summarised in Table 3.4. Alternative methods for estimating the global ocean-atmosphere flux, based on surface-water pCO_2 measurements and ocean $\delta^{13}C$ changes (Quay *et al.*, 1992; Tans *et al.*, 1993, Heimann and Maier-Reimer, 1996; Sonnerup *et al.*, 1999), respectively, have yielded a range of -1.5 to -2.8 PgC/yr (for various recent periods). The total anthropogenic CO_2 added to the ocean since pre-industrial times can also be estimated indirectly using oceanic observations (Gruber *et al.,* 1996). A global value of 107 ± 27 PgC by 1990 can be estimated from the basin-scale values of 40 ± 9 PgC for the Atlantic in the 1980s (Gruber, 1998), 20 ± 3 PgC for the Indian Ocean in 1995 (Sabine *et al.*, 1999), and the preliminary value of 45 PgC for the Pacific Ocean in 1990 to 1996 (Feely *et al.,* 1999a) with a large uncertainty of the order of $\pm$ 15 PgC. Assuming that accumulation of CO_2 in the ocean follows a curve similar to the (better known) accumulation in the atmosphere, the value for the ocean-atmosphere flux for 1980 to 1989 would be between -1.6 and -2.7 PgC/yr. Although each individual method has large uncertainty, all of these ocean-based measurements give results comparable with the fluxes presented in Table 3.1. Consideration of model-based estimates of ocean uptake in Table 3.4 is deferred to Section 3.6.2.2.

Table 3.3: *Comparison of the global CO_2 budgets from Table 3.1 with previous IPCC estimates[a,b,c] (units are PgC/yr).*

	1980s				1990s	1989 to 1998
	This chapter	**SRLULUCF** [d]	**SAR** [e]	**SRRF** [f]	**This chapter**	**SRLULUCF** [d]
Atmospheric increase	3.3 ± 0.1	3.3 ± 0.1	3.3 ± 0.1	3.2 ± 0.1	3.2 ± 0.1	3.3 ± 0.1
Emissions (fossil fuel, cement)	5.4 ± 0.3	5.5 ± 0.3	5.5 ± 0.3	5.5 ± 0.3	6.4 ± 0.4	6.3 ± 0.4
Ocean-atmosphere flux	-1.9 ± 0.6	-2.0 ± 0.5 [i]	-2.0 ± 0.5	-2.0 ± 0.5	-1.7 ± 0.5	-2.3 ± 0.5 [i]
Land-atmosphere flux* *partitioned as follows	-0.2 ± 0.7 [g]	-0.2 ± 0.6	-0.2 ± 0.6	-0.3 ± 0.6	-1.4 ± 0.7	-0.7 ± 0.6
Land-use change	1.7 (0.6 to 2.5) [g]	1.7 ± 0.8	1.6 ± 1.0	1.6 ± 1.0	*insufficient*	1.6 ± 0.8 [j]
Residual terrestrial sink	-1.9 (-3.8 to 0.3)	-1.9 ± 1.3	-1.8 ± 1.6 [h]	-1.9 ± 1.6	*data*	-2.3 ± 1.3

[a] Positive values are fluxes to the atmosphere; negative values represent uptake from the atmosphere.

[b] Previous IPCC carbon budgets calculated ocean uptake and land-use change from models. The residual terrestrial sink was inferred. Here the implied land-atmosphere flux (with its error) is derived from these previous budgets as required for comparison with Table 3.1.

[c] Error ranges are expressed in this book as 67% confidence intervals ($\pm 1\sigma$). Previous IPCC estimates have used 90% confidence intervals ($\pm 1.6\sigma$). These error ranges have been scaled down as required for comparison with Table 3.1. Uncertainty ranges for land-use change emissions have not been altered in this way.

[d] IPCC Special Report on Land Use, Land-use Change and Forestry (SRLULUCF) (IPCC, 2000a; Bolin *et al.*, 2000).

[e] IPCC Second Assessment Report (SAR) (IPCC, 1996a; Schimel *et al.*, 1996).

[f] IPCC Special Report on Radiative Forcing (SRRF) (Schimel *et al.*, 1995).

[g] Ranges based on Houghton (1999, 2000), Houghton and Hackler (1999), and CCMLP model results (McGuire *et al.*, 2001).

[h] The sink of 0.5 ± 0.5 PgC/yr in "northern forest regrowth" cited in the SAR budget is assigned here to be part of the residual terrestrial sink, following Bolin *et al.* (2000).

[i] Based on an ocean carbon cycle model (Jain *et al.*, 1995) used in the IPCC SAR (IPCC, 1996; Harvey *et al.*, 1997), tuned to yield an ocean-atmosphere flux of 2.0 PgC/yr in the 1980s for consistency with the SAR. After re-calibration to match the mean behaviour of OCMIP models and taking account of the effect of observed changes in temperature aon CO_2 and solubility, the same model yields an ocean-atmosphere flux of -1.7 PgC/yr for the 1980s and -1.9 PgC/yr for 1989 to 1998.

[j] Based on annual average estimated emissions for 1989 to 1995 (Houghton, 2000).

The land-atmosphere flux based on atmospheric measurements represents the *balance* of a net land-use flux (currently a positive flux, or carbon source, dominated by tropical deforestation) and a residual component which is, by inference, a negative flux or carbon sink. Using the land-atmosphere flux estimates from Table 3.1, assuming that land-use change contributed +1.7 PgC/yr to the atmosphere during the 1980s (Section 3.4.2), then a residual terrestrial flux of -1.9 PgC/yr (i.e., a residual sink of similar magnitude to the total ocean uptake) is required for mass balance. This is the term popularly (and misleadingly) known as the "missing sink". The central estimate of its magnitude agrees with previous analyses, e.g., in the SAR (if "northern forest regrowth" is combined with "residual terrestrial sink" terms in the SAR budget; Schimel *et al.,* 1996) and the SRLULUCF (Bolin *et al.,* 2000) (Table 3.3). The uncertainty around this number is rather large, however, because it compounds the uncertainty in the atmospheric budget with a major uncertainty about changes in land use. Using an error range corresponding to 90% confidence intervals around the atmospheric estimate of -0.2 PgC/yr (i.e., 1.6σ, giving confidence intervals of ± 1.1 PgC/yr), and taking the range of estimates for CO_2 released due to land-use change during the 1980s from Section 3.4.2, the residual terrestrial sink is estimated to range from -3.8 to $+0.3$ PgC/yr for the 1980s. Model-based analysis of the components of the residual terrestrial sink (Table 3.4) is discussed in Section 3.6.2.2.

3.5.2 Interannual Variability in the Rate of Atmospheric CO_2 Increase

The rate of increase in the globally averaged atmospheric concentration of CO_2 varies greatly from year to year. "Fast" and "slow" years have differed by 3 to 4 PgC/yr within a decade (Figure 3.3). This variability cannot be accounted for by fossil fuel emissions, which do not show short-term variability of this magnitude. The explanation must lie in variability of the land-atmosphere flux or the ocean-atmosphere flux or both. Variability in both systems could be induced by climate variability.

An association between CO_2 variability and El Niño in particular has been reported for over twenty years and has been confirmed by recent statistical analyses (Bacastow, 1976; Keeling and Revelle, 1985; Thompson *et al.,* 1986; Siegenthaler, 1990; Elliott *et al.,* 1991; Braswell *et al.,* 1997; Feely *et al.,* 1997; Dettinger and Ghil, 1998; Rayner *et al.,* 1999b). During most of the observational record, El Niño events have been marked by high rates of increase in atmospheric CO_2 concentration compared with surrounding years, in the order of > 1 PgC/yr higher during most El Niño events (Figure 3.3). Direct measurements of oceanic CO_2 in the equatorial Pacific over the last 20 years have shown that the natural efflux of CO_2 from this region is reduced by between 0.2 to 1.0 PgC/yr during El Niño (Keeling and Revelle, 1985; Smethie *et al.,* 1985; Takahashi *et al.,* 1986; Inoue and Sugimura, 1992; Wong *et al.,* 1993; Feely *et al.,* 1997;

Table 3.4: *Alternative estimates of ocean-atmosphere and land-atmosphere fluxes.*

	Ocean-atmosphere flux	Land-atmosphere flux
Oceanic observations		
1970 to 1990 Ocean ^{13}C inventory	-2.1 ± 0.8 [a] -2.1 ± 0.9 [b]	
1985 to 1995 Ocean ^{13}C inventory	-1.5 ± 0.9 [c]	
1995 Surface-water pCO$_2$	-2.8 ± 1.5 [d]	
1990 Inventory of anthropogenic CO_2	-1.6 to -2.7 [e]	
Atmospheric observations		
1980 to 1989 O$_2$ in Antarctic firn	-1.8 [f]	-0.4 [f]
1990 to 1999 Atmospheric CO_2 and δ^{13}C	-1.8 [g] -2.4 [h]	-1.4 [g] -0.8 [h]
Models		
1980 to 1989 OCMIP	-1.5 to -2.2 [i]	
CCMLP *		-0.3 to -1.5 [j] *
partitioned as follows:		*partitioned as follows:*
Land-use change		0.6 to 1.0
CO$_2$ and N fertilisation		-1.5 to -3.1
Climate variability		-0.2 to $+0.9$

Sources of data:

[a] Quay *et al.* (1992).

[b] Heimann and Maier-Reimer (1996).

[c] Gruber and Keeling (2001).

[d] Takahashi *et al.* (1999) with –0.6 PgC/yr correction for land-ocean river flux.

[e] Gruber (1998), Sabine *et al.* (1999); Feely *et al.* (1999a), assuming that the ocean and atmospheric CO_2 increase follow a similar curve.

[f] This chapter, from data of Battle *et al.* (1996).

[g] Updated calculation of Ciais *et al.* (1995b); Tans *et al.* (1989); Trolier *et al.* (1996) (no error bars given).

[h] Keeling and Piper (2000) (no error bars given).

[i] Orr *et al.* (2000), Orr and Dutay (1999).

[j] McGuire *et al.* (2001).

1999b), mainly due to the reduced upwelling of CO_2-rich waters (Archer *et al.,* 1996). The ocean response to El Niño in the most active region thus tends to increase global CO_2 uptake, counter to the increasing atmospheric concentration. Although it cannot be ruled out that other ocean basins may play a significant role for global interannual variability in ocean-atmosphere flux, the existing oceanic measurements suggest (by default) that the response of the terrestrial biosphere is the cause of the typically high rates of CO_2 increase during El Niño.

Associated variations in the north-south gradient of CO_2 indicate that the El Niño CO_2 anomalies originate in the tropics (Conway *et al.,* 1994; Keeling and Piper, 2000). Typical El Niño events are characterised by changed atmospheric circula-

tion and precipitation patterns (Zeng, 1999) that give rise to high tropical land temperatures (which would be expected to increase Rh and reduce NPP); concurrent droughts which reduce NPP, especially in the most productive regions such as the Amazon rain forest; and increased incidence of fires in tropical regions. Increased cloudiness associated with enhanced south-east Asian monsoons during the late phase of El Niño has also been suggested as a factor reducing global NPP (Yang and Wang, 2000). Typically, although not invariably, the rate of atmospheric CO_2 increase declines around the start of an El Niño, then rapidly rises during the late stages (Elliott *et al.,* 1991; Conway *et al.,* 1994). It has been suggested that this pattern represents early onset of enhanced ocean CO_2 uptake,

followed by reduced terrestrial CO_2 uptake or terrestrial CO_2 release (Feely *et al.,* 1987, 1999b; Rayner *et al.,* 1999b; Yang and Wang, 2000).

Atmospheric $\delta^{13}C$ and, more recently, O_2 measurements have been used to partition the interannual variability of the atmospheric CO_2 increase into oceanic and terrestrial components. Analyses based on $\delta^{13}C$ by Keeling *et al.* (1995) and Francey *et al.* (1995) reached contradictory conclusions, but the discrepancies are now thought to be due at least in part to $\delta^{13}C$ measurement calibration problems during the 1980s, which have largely been resolved during the 1990s (Francey *et al.,* 1999a). For the 1990s, a range of analyses using different atmospheric observations and/or data analysis techniques estimate that the amplitude of annual peak to peak variation associated with the ocean is about 2 to 3 PgC/yr and the amplitude associated with the terrestrial biosphere is about 4 to 5 PgC/yr (Rayner *et al.,* 1999a; Joos *et al.,* 1999a; Battle *et al.,* 2000 (O_2-based analysis); Keeling and Piper, 2000; Manning, 2001). A similar partitioning was estimated by Bousquet *et al.* (2000) based on the spatial pattern of CO_2 measurements using the approach described in the next section (3.5.3). However, the various reconstructed time sequences of terrestrial and ocean uptake differ in many details and do not provide conclusive evidence of the mechanisms involved.

The early 1990s were unusual in that the growth rate in atmospheric CO_2 was low (1.9 PgC/yr in 1992), especially in the Northern Hemisphere (Conway *et al.,* 1994), while an extended El Niño event occurred in the equatorial Pacific. Various mechanisms have been suggested, but none fully explain this unusual behavior of the carbon cycle. The slow down in the CO_2 increase has been linked to the predominantly mid- to high latitude cooling caused by the Pinatubo eruption (Conway *et al.,* 1994; Ciais *et al.,* 1995a,b; Schimel *et al.,* 1996), but there is no proof of any connection between these events. Other partial explanations could come from a temporary slow down of tropical deforestation (Houghton *et al.,* 2000), or natural decadal variability in the ocean-atmosphere or land-atmosphere fluxes (Keeling *et al.,* 1995). In any case, the slowdown proved to be temporary, and the El Niño of 1998 was marked by the highest rate of CO_2 increase on record, 6.0 PgC/yr.

3.5.3 Inverse Modelling of Carbon Sources and Sinks

Inverse modelling attempts to resolve regional patterns of CO_2 uptake and release from observed spatial and temporal patterns in atmospheric CO_2 concentrations, sometimes also taking into consideration O_2 and/or $\delta^{13}C$ measurements. The most robust results are for the latitudinal partitioning of sources and sinks between northern and southern mid- to high latitudes and the tropics. The observed annual mean latitudinal gradient of atmospheric CO_2 concentration during the last 20 years is relatively large (about 3 to 4 ppm) compared with current measurement accuracy. It is however not as large as would be predicted from the geographical distribution of fossil fuel burning – a fact that suggests the existence of a northern sink for CO_2, as already recognised a decade ago (Keeling *et al.,* 1989; Tans *et al.,* 1990; Enting and Mansbridge, 1991).
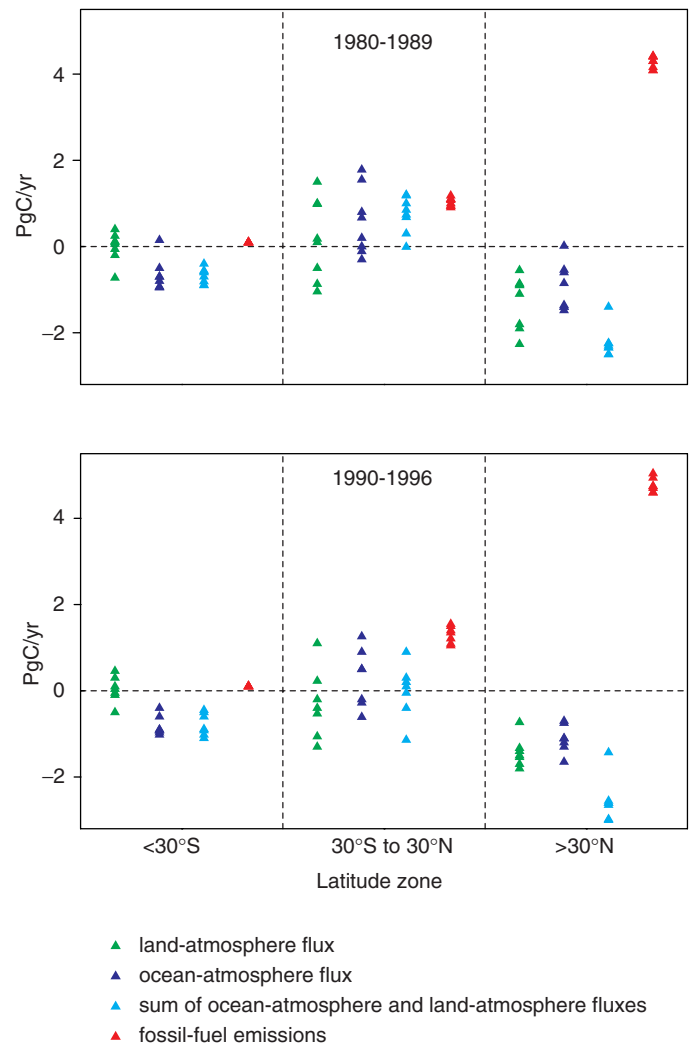

Figure 3.5: Inverse model estimates of fossil fuel CO_2 uptake by latitude bands according to eight models using different techniques and sets of atmospheric observations (results summarised by Heimann, 2001). Positive numbers denote fluxes to the atmosphere; negative numbers denote uptake from the atmosphere. The ocean-atmosphere fluxes represent mainly the natural carbon cycle; the land-atmosphere fluxes may be considered as estimates of the uptake of anthropogenic CO_2 by the land (with some caveats as discussed in the text). The sum of land-atmosphere and ocean-atmosphere fluxes is shown because it is somewhat better constrained by observations than the separate fluxes, especially for the 1980s when the measurement network was less extensive than it is today. The 1990s are represented by the period 1990 to 1996 only, because when this exercise was carried out the modelling groups did not have access to all of the necessary data for more recent years.

The nature of this sink, however, cannot be determined from atmospheric CO_2 concentration measurements alone. It might reflect, at least in part, a natural source-sink pattern of oceanic CO_2 fluxes (Keeling *et al.,* 1989; Broecker and Peng, 1992). This view is supported by the early atmospheric CO_2 data from the 1960s (Bolin and Keeling, 1963) which do not show a clear latitudinal gradient, despite the fact that at that time the fossil
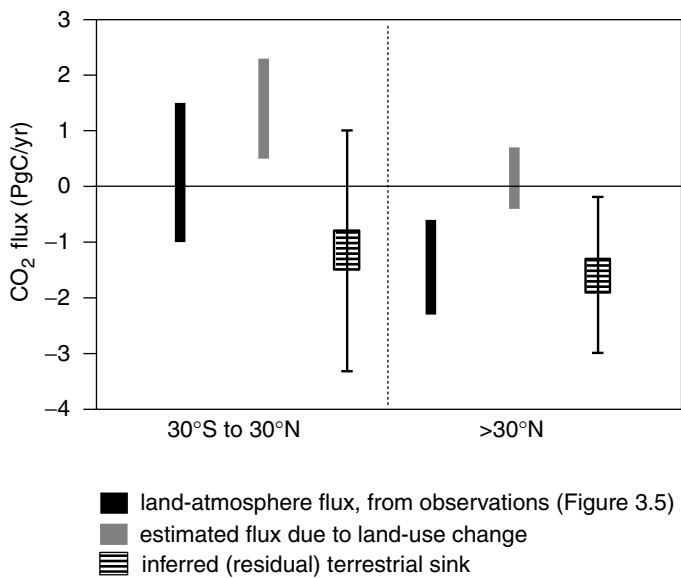
Figure 3.6: Partitioning the 1980s land-atmosphere flux for the tropics and the northern extratropics. The residual terrestrial sink in different latitude bands can be inferred by subtracting the land-use change flux for the 1980s (estimated by modelling studies: Houghton, 1999; Houghton and Hackler, 1999; Houghton *et al.*, 2000; McGuire *et al.*, 2001) from the net land-atmosphere flux as obtained from atmospheric observations by inverse modelling for the same period (Heimann, 2001; results from Figure 3.5). Positive numbers denote fluxes to the atmosphere; negative numbers denote uptake from the atmosphere. This calculation is analogous to the global budget calculation in Table 3.1, but now the model results are broken down geographically and the land-atmosphere fluxes are obtained by inverse modelling. The upper and lower bounds on the residual sink are obtained by pairing opposite extremes of the ranges of values accepted for the two terms in this calculation (for example, by subtracting the bottom of the range of values for land-use change with the top of the range for the land-atmosphere flux). The mid-ranges are obtained by combining similar extremes (for example, subtracting the bottom of the range for land-use change emissions from the bottom of the range land-atmosphere flux).

emissions were already at least half as large as in the 1990s. Quantitative analysis shows that the Northern Hemisphere sink has not changed much in magnitude since the 1960s (Keeling *et al.*, 1989; Fan *et al.*, 1999). On the other hand, the existing air-sea flux measurements do not support the idea of a large oceanic uptake of CO_2 in the Northern Hemisphere (Tans *et al.*, 1990; Takahashi, 1999). An alternative view, therefore, locates a significant fraction of this Northern Hemisphere sink on land. This view is corroborated, at least for the 1990s, by analyses of the concurrent latitudinal gradients of $\delta^{13}C$ (Ciais *et al.*, 1995a,b) and O_2 (Keeling *et al.*, 1996b).

Results of analyses for the 1980s and 1990 to 1996, carried out by eight modelling groups using different atmospheric transport models, observational data, constraints and mathematical procedures, are summarised in Figure 3.5. Only the most robust findings, i.e., estimates of the mean carbon balance for three latitude bands averaged over the two time periods, are

shown. The latitude bands are: "southern extratropics" (>30°S), "tropics" (30°S to 30°N) and "northern extratropics" (>30°N). The carbon balance estimates are broken down into land and ocean compartments within each latitude band (Heimann, 2001).

Although the ranges of the estimates in Figure 3.5 limit the precision of any inference from these analyses, some clear features emerge. The inferred ocean uptake pattern shows the sum of two components: the natural carbon cycle in which CO_2 is outgassed in the tropics and taken up in the extratropics, and the perturbation uptake of anthropogenic CO_2. Separation of these two components cannot be achieved from atmospheric measurements alone.

The estimates for the land, on the other hand, in principle indicate the locations of terrestrial anthropogenic CO_2 uptake (albeit with caveats listed below). For 1980 to 1989, the inverse-model estimates of the land-atmosphere flux are −2.3 to −0.6 PgC/yr in the northern extratropics and −1.0 to +1.5 PgC/yr in the tropics. These estimates imply that anthropogenic CO_2 was taken up *both* in the northern extratropics and in the tropics (balancing deforestation), as illustrated in Figure 3.6. The estimated land-atmosphere flux in the southern extratropics is estimated as close to zero, which is expected given the small land area involved. Estimates of CO_2 fluxes for the period 1990 to 1996 show a general resemblance to those for the 1980s. For 1990 to 1996, the inverse-model estimates of the land-atmosphere flux are −1.8 to −0.7 PgC/yr in the northern extratropics and −1.3 to +1.1 PgC/yr in the tropics. These results suggest a tendency towards a reduced land-atmosphere flux in the tropics, compared to the 1980s. Such a trend could be produced by reduced deforestation, increased CO_2 uptake or a combination of these.

Inverse modelling studies usually attempt greater spatial resolution of sources and sinks than is presented in this section. However, there are large unresolved differences in longitudinal patterns obtained by inverse modelling, especially in the northern hemisphere and in the tropics (Enting *et al.*, 1995, Law *et al.*, 1996; Fan *et al.*, 1998; Rayner *et al.*, 1999a; Bousquet *et al.*, 1999; Kaminski *et al.*, 1999). These differences may be traced to different approaches and several difficulties in inverse modelling of atmospheric CO_2 (Heimann and Kaminski, 1999):

• The longitudinal variations in CO_2 concentration reflecting net surface sources and sinks are on annual average typically <1 ppm. Resolution of such a small signal (against a background of seasonal variations up to 15 ppm in the Northern Hemisphere) requires high quality atmospheric measurements, measurement protocols and calibration procedures within and between monitoring networks (Keeling *et al.*, 1989; Conway *et al.*, 1994).

• Inverse modelling results depend on the properties of the atmospheric transport models used. The north-south transport of the models can be checked by comparing simulations of the relatively well-known inert anthropogenic tracer SF_6 with measured atmospheric concentrations of this tracer, as recently investigated in the TRANSCOM intercomparison project (Denning *et al.*, 1999). Unfortunately there is no currently

measured tracer that can be used to evaluate the models' representation of longitudinal transport. Furthermore, the strong seasonality of the terrestrial CO_2 flux in the Northern Hemisphere together with covarying seasonal variations in atmospheric transport may induce significant mean annual gradients in concentration which do not reflect net annual sources and sinks, but which nevertheless have to be modelled correctly if inverse model calculations are to be reliable (Bolin and Keeling, 1963; Heimann *et al.,* 1986; Keeling *et al.,* 1989; Denning *et al.,* 1995; Law *et al.,* 1996). Even the sign of this so-called "rectifier effect" is uncertain. Some scientists believe that it may be responsible for a part of the apparent Northern Hemisphere uptake of CO_2 implied by inverse modelling results (Taylor, 1989; Taylor and Orr, 2000).

• The spatial partitioning of CO_2 uptake could also be distorted by a few tenths of 1 PgC/yr because the atmospheric concentration gradients also reflect the natural fluxes induced by weathering, transport of carbon by rivers and subsequent outgassing from the ocean (see Figure 3.1) (Sarmiento and Sundquist, 1992; Aumont *et al.*, 2001b). Furthermore, the effects of atmospheric transport of carbon released as CO and CH_4 (especially from incomplete fossil fuel burning, tropical biomass burning, and CH_4 from tropical wetlands) with subsequent oxidation to CO_2 is generally neglected. Their inclusion in the inversion leads to corrections of the latitudinal partitioning of up to 0.1 PgC/yr (Enting and Mansbridge, 1991).

• The distribution of atmospheric CO_2 measurement stations (Figure 3.7) is uneven, and severely underrepresents the continents. This underrepresentation is due in part to the problem of finding continental locations where measurements will not be overwhelmed by local sources and sinks.

• Because of the finite number of monitoring stations, the mathematical inversion problem is highly underdetermined. In principle a multitude of different surface source/sink configurations are compatible with the atmospheric data, within their measurement accuracy. Therefore, in order to extract a meaningful solution, additional information on the sources and sinks has to be introduced into the calculation. Examples of this additional information include maps of air-sea fluxes from observations or ocean models, patterns of terrestrial CO_2 exchanges inferred by terrestrial models, and remote sensing data. Thus, many methodological choices about the use of auxiliary data can influence the outcome of the analysis.

Interannual variability of climate is likely to strongly influence the spatial distribution of CO_2 sources and sinks, so that analyses based on a few years of data are insufficient to establish a long-term trend.

    In conclusion, the present atmospheric measurement network, current information on air-sea fluxes and current understanding of vertical atmospheric transport are not sufficient to allow full use of the potential of inverse modelling techniques to infer geographically detailed source-sink distributions of anthropogenic CO_2.
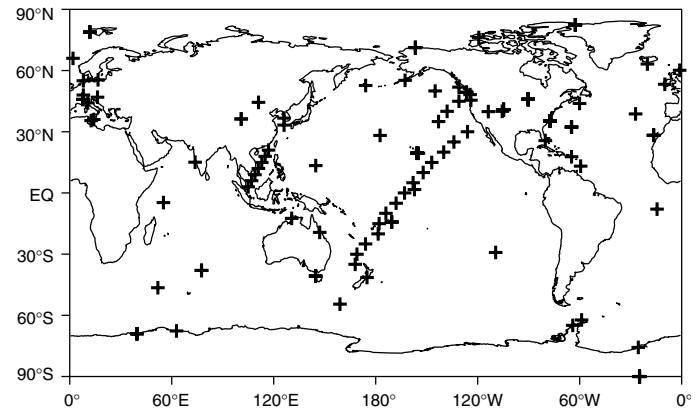

Figure 3.7: The atmospheric CO_2 measuring station network as represented by GLOBAL VIEW–CO_2 (Comparative Atmosphere Data Integration Project – Carbon Dioxide, NOAA/CMDL, http://www.cmdl.noaa.gov/ccg/co2).

3.5.4 Terrestrial Biomass Inventories

Inventory studies measure changes in carbon stocks over large areas, and can thus provide spatially aggregated estimates of large-scale fluxes of CO_2 over multi-annual time-scales (Box 3.1). Mid- and high latitude forests are covered by extensive national inventories based on repeated measurements of many thousands of plots. Inventories in the tropics are by comparison generally inadequate, particularly in view of the high rates of land-use change and extremely heterogeneous carbon density in many tropical ecosystems. There are still therefore large uncertainties in attempting to balance the terrestrial carbon budget on a global scale using inventory data.

    The FAO Temperate and Boreal Forest Resource Assessment (TBFRA-2000) is a recent synthesis of inventories of forests and other wooded lands in Annex I (developed) countries for the early 1990s (UN-ECE/FAO, 2000). Many countries reported substantial increases in forest areas in recent years, as well as increasing carbon density in existing forests. According to TBFRA-2000, the land-atmosphere flux was −0.9 PgC/yr for all Annex I countries combined (the net annual increment of trees accounted for −1.5 PgC/yr, while losses due to fellings were 0.6 PgC/yr). Of this flux, −0.8 PgC/yr was due to uptake in "northern" forests (Europe, CIS, Japan and North America). An earlier review of individual regional and national studies by Dixon *et al*. (1994), highlighted in the IPCC WGII Second Assessment Report (IPCC, 1996b; Brown *et al*., 1996), gave a range of −0.6 to −0.9 PgC/yr for the land atmosphere flux in northern forests. While TBFRA-2000 estimated biomass of woody vegetation only, the analyses reviewed in Dixon *et al*. (1994) included other vegetation, soils, litter and wood products. Under the United Nations Framework Convention for Climate Change (UNFCCC) signatory countries are required to report greenhouse gas emissions, including those from land-use change and forestry. Compilation of these data implies a land-atmosphere flux of −0.6 PgC/yr for all Annex I countries, and −0.6 PgC/yr for Annex I countries in the northern latitudes only (UNFCCC, 2000). While the TBFRA synthesised

country statistics and adjusted data to fit FAO definitions and methodologies for calculating carbon stocks, the UNFCCC report summarises emissions data reported by each country according to IPCC guidelines; interpretation of guidelines is variable, and not all countries had reported data on land use. The implications of definitions and methodologies in calculating carbon fluxes, particularly in relation to implementation of the Kyoto Protocol, is discussed in detail in the SRLULUCF (IPCC, 2000a).

A recent compilation of data from 478 permanent plots in mature tropical moist forests throughout the tropics over at least two decades found these were taking up carbon due to increasing rates of tree growth. Extrapolation from these plots led to an estimated land-atmosphere flux of (0.6 ± 0.3 PgC/yr in Latin America; growth trends in African and Asian forests were not significantly different from zero (Phillips *et al.,* 1998). This net uptake is offset by emissions due to deforestation. Dixon *et al.* (1994) estimated tropical forests overall to be a net source of carbon with a land-atmosphere flux 1.7 ± 0.4, based mostly on FAO (1993b) inventory data and simple models of the effect of land-use change (Houghton, 1995). It will not be possible to assess trends and fluxes for the 1990s in the tropics from inventory data until a full data set is available from the FAO Global Forest Resources Assessment 2000. Among those countries that have reported land-use emissions data to the UNFCCC, there are significant discrepancies between the primary data used in emissions inventories and the data available in international surveys; for example, rates of deforestation differ from rates reported by FAO (1993b) by as much as a factor of six (Houghton and Ramakrishna, 1999).

The results of globally aggregated forest inventories show a greater uptake of carbon in forest growth than model-based calculations of the marginal effects of land-use change (e.g., Houghton, 2000). Thus, inventory studies provide independent evidence for the existence of a residual terrestrial sink; and they show that a substantial part of this sink, at least, is located in northern extratropical and tropical forests. Additional evidence from individual inventory studies in mature forests that have not undergone land-use changes shows that carbon stocks in such forests are increasing (e.g., Lugo and Brown, 1993; Phillips *et al.,* 1998; Schulze *et al.,* 1999). The difference between the northern extra-tropical land-atmosphere flux of around −0.8 PgC/yr calculated by inventories (TBFRA-2000) and that of −0.1 PgC/yr from land-use statistics (Houghton, 2000), both for the early 1990s, implies a residual terrestrial sink on the order of −0.7 PgC/yr in northern mid- and high latitudes. Combining this with the estimated sink of −0.6 PgC/yr in mature tropical moist forests (Phillips *et al.,* 1998) makes it plausible that at least a significant fraction of the current global terrestrial sink (Table 3.1) could be explained by an increase of carbon stocks in extant forests. The inventory-based estimate of land-atmosphere flux in northern forests (−0.8 PgC/yr) is at the positive end of the range calculated by inverse modelling studies for the >30°N latitude band from 1990 to 1996 (−1.8 to −0.7 PgC/yr, Section 3.5.3), either because of biases in inverse modelling that might tend to increase apparent uptake in the north (Section 3.5.3), or because possible sinks in other ecosys-

tems (e.g., temperate grassland soils) have not been considered in the inventories. In the tropics, the difference between the uptake of carbon estimated by inventory studies in mature forests of Latin America (−0.6 PgC/yr) (Phillips *et al.,* 1998) and the estimated emissions due to deforestation in the tropics of 1.7 PgC/yr (Houghton, 2000) yields an estimated land-atmosphere flux of 1.1 PgC/yr, which is at the positive end of the range calculated by inverse modelling studies for 30°S to 30°N (−1.3 to +1.1 PgC/yr, Section 3.5.3). Again, it should be noted that possible additional sinks (e.g., in savannas) are neglected by the land-use and inventory-based calculations.

3.6 Carbon Cycle Model Evaluation

3.6.1 *Terrestrial and Ocean Biogeochemistry Models*

The interactions of complex processes as discussed in Section 3.2 can be analysed with models that incorporate current knowledge at the process level, including syntheses of experimental results. Process-based models make it possible to explore the potential consequences of climate variability for the global carbon cycle, and to project possible future changes in carbon cycling associated with changes in atmospheric and ocean circulation. Models can be run with prescribed inputs such as observations of surface climate and CO_2 or the output of climate models. They can also be coupled to atmospheric general circulation models (Cox *et al.,* 2000; Friedlingstein *et al.,* 2000), to allow simulation of a wider range of interactions between climate and the carbon cycle.

Process-based terrestrial models used in carbon cycle studies are (a) terrestrial biogeochemical models (TBMs), which simulate fluxes of carbon, water and nitrogen coupled within terrestrial ecosystems, and (b) dynamic global vegetation models (DGVMs), which further couple these processes interactively with changes in ecosystem structure and composition (competition among different plant functional types; Prentice *et al.,* 2000). The treatment of carbon-nutrient interaction varies widely; for example, some models treat nitrogen supply explicitly as a constraint on NPP, while others do not. There are currently about 30 TBMs and <10 DGVMs. Cramer and Field (1999) and Cramer *et al.* (2001) reported results from intercomparisons of TBMs and DGVMs respectively. A current international project, Ecosystem Model/Data Intercomparison (EMDI), aims to test models of both types against a large set of terrestrial measurements, in order to better constrain the modelled responses of terrestrial carbon cycling to changes in CO_2 and climate.

Process-based ocean models used in carbon cycle studies include surface exchange of CO_2 with the atmosphere, carbon chemistry, transport by physical processes in the ocean, and transport by marine biology. The parametrization of marine biology can be classified as (a) nutrient-based models where the export of carbon below the surface ocean (approximately the top 50 m) is a function of surface nutrient concentration, (b) nutrient-restoring models in which biological carbon fluxes are set to the rates required for maintaining observed nutrient concentration gradients against dissipation by ocean mixing, and (c) models that explicitly represent the food chain involving nutrients, phytoplankton, zooplankton and detritus (NPZD models). In

current models, the uptake of anthropogenic CO_2 is controlled mainly by physical transport and surface carbon chemistry, whereas the natural carbon cycle is controlled by physical, chemical and biological processes. The Ocean Carbon Cycle Model Intercomparison Project (OCMIP) compared the performance of four ocean models with respect to natural and anthropogenic tracers (Sarmiento *et al.*, 2000; Orr *et al.*, 2001), and is currently undergoing a similar comparison with 13 models and an extended data set (Orr and Dutay, 1999).

3.6.2 Evaluation of Terrestrial Models

Evaluation of terrestrial carbon cycle models requires different types of data to test processes operating on a range of time-scales from hours to centuries (see Section 3.2.2), including short-term environmental responses of CO_2 and water fluxes between vegetation canopies and the atmosphere (e.g., Cienciala *et al.,* 1998), responses of ecosystem carbon balance to interannual climate variability (e.g. Kindermann *et al.*, 1996; Heimann *et al.*, 1997; Gérard *et al.*, 1999; Knorr, 2000; Prentice *et al.*, 2000), and longer-term consequences of historical land-use change (McGuire *et al.*, 2001). Differences and uncertainties in model behaviour have been evaluated through model intercomparison (Cramer *et al.*, 1999, 2001) and sensitivity analyses (Knorr, 2000; Knorr and Heimann, 2001a).

3.6.2.1 Natural carbon cycling on land

Terrestrial model evaluation has traditionally been carried out as comparisons with *in situ* field observations of ecosystem variables (e.g., Raich *et al.*, 1991; Foley, 1994; Haxeltine and Prentice, 1996). The largest data sets of relevant field measurements are for NPP and soil carbon content. Other "target" variables include soil moisture, nitrogen mineralisation rate, and the amounts of carbon and nitrogen in different compartments of the ecosystem. Such comparisons have generally shown reasonable agreement between observed and modelled geographic patterns of these variables, but they do not test the time-dependent response of models to environmental variability.

Time-dependent data sets for *in situ* comparisons are now becoming available, thanks to eddy-covariance measurements of CO_2 fluxes (Section 3.2.2.1; Box 3.1). Daily and seasonal cycles of CO_2 and water fluxes provide a test of the coupling between the carbon and hydrological cycles as simulated by terrestrial models (Cienciala *et al.,* 1998). Flux measurements are now being carried out on a multi-annual basis at an increasing number of stations, although global coverage remains uneven, with the greatest concentration in Europe and North America and few measurements from the tropics (see Box 3.1). Field campaigns have started to retrieve flux data from more remote regions (e.g., Schulze *et al.*, 1999). The Large-scale Biosphere Atmosphere Experiment in Amazonia, LBA, will yield more comprehensive data on the carbon, water and energy exchanges of tropical terrestrial ecosystems and will allow a more rigorous evaluation of the performance of models in the tropics than has been possible up until now (e.g., Tian *et al.*, 1998). As current models show conflicting

responses of global NPP to climate (Cramer *et al.*, 1999), systematic comparisons with seasonal and interannual flux measurements are a priority to reduce uncertainties in terrestrial carbon modelling.

Terrestrial models have also been evaluated at a global scale by comparing simulated ecosystem water balance with river runoff (e.g., Neilson and Marks, 1994; Foley *et al.*, 1996; Kucharik *et al.*, 2000), and simulated seasonal leaf area with satellite observations of "greenness", often based on the normalised difference vegetation index (NDVI) (Field *et al.,* 1995b; de Fries *et al.,* 1995). NDVI data can be translated into estimates of the plant-absorbed fraction of incoming photosynthetically active radiation (FPAR) (Asrar *et al*, 1992), which is related to leaf area index (LAI). The first terrestrial model intercomparison showed differences among model simulations of LAI and its seasonality (Bondeau *et al.*, 1999). More recently, it has been shown that constraining a terrestrial model with remotely sensed spatial patterns of FPAR can lead to a reduction of uncertainty in NPP simulations by about one third (Knorr and Heimann, 2001b). Agreement with patterns of remotely sensed FPAR has thus become a standard benchmark for terrestrial models (Haxeltine and Prentice, 1996; Kucharik *et al.*, 2000) and attention has been focused on improving the simulation of LAI and its seasonal variations.

A more direct test of the simulated net exchange of CO_2 between the terrestrial biosphere and the atmosphere is provided by comparison with atmospheric CO_2 measurements at remote monitoring sites. The comparison requires the use of an atmospheric transport model to simulate CO_2 as a passive tracer (Kaminski *et al.,* 1996). The seasonal cycle of atmospheric CO_2 shows a strong latitudinal pattern in amplitude and phase, and is dominated by the terrestrial biosphere (Heimann *et al.*, 1998). The ability to simulate this seasonal cycle thus constitutes a benchmark for terrestrial models' response to climate (Denning *et al.*, 1996; Hunt *et al.*, 1996; Heimann *et al.*, 1998; Nemry *et al.*, 1999). Generally, the observed seasonal cycles of CO_2 in northern and tropical latitudes can be well simulated, with terrestrial models using NDVI data as input (Knorr and Heimann, 1995), or by fully prognostic models, including DGVMs (Prentice *et al.*, 2000).

Major features of interannual variability of the CO_2 increase are also simulated by terrestrial models (Kindermann *et al.*, 1996; Heimann *et al.*, 1997; Gérard *et al.*, 1999; Ito and Oikawa, 2000; Knorr, 2000; Prentice *et al.*, 2000). This finding supports the hypothesis (Section 3.5.2) that terrestrial effects are important in determining the interannual variability of CO_2 uptake. During typical El Niño events, terrestrial model results consistently show strongly reduced CO_2 uptake or CO_2 release by the land. This result has been obtained with a range of models, even when the models differ substantially in the relative sensitivitivities of NPP and heterotrophic respiration to temperature (Heimann *et al.*, 1997; Knorr, 2000). The low CO_2 growth rate during the early 1990s has been simulated by some terrestrial models (Prentice *et al.*, 2000; Knorr, 2000).

At the longest time-scales of interest, spanning the industrial period, models of the natural terrestrial carbon cycle show a pronounced response to rising atmospheric CO_2 levels
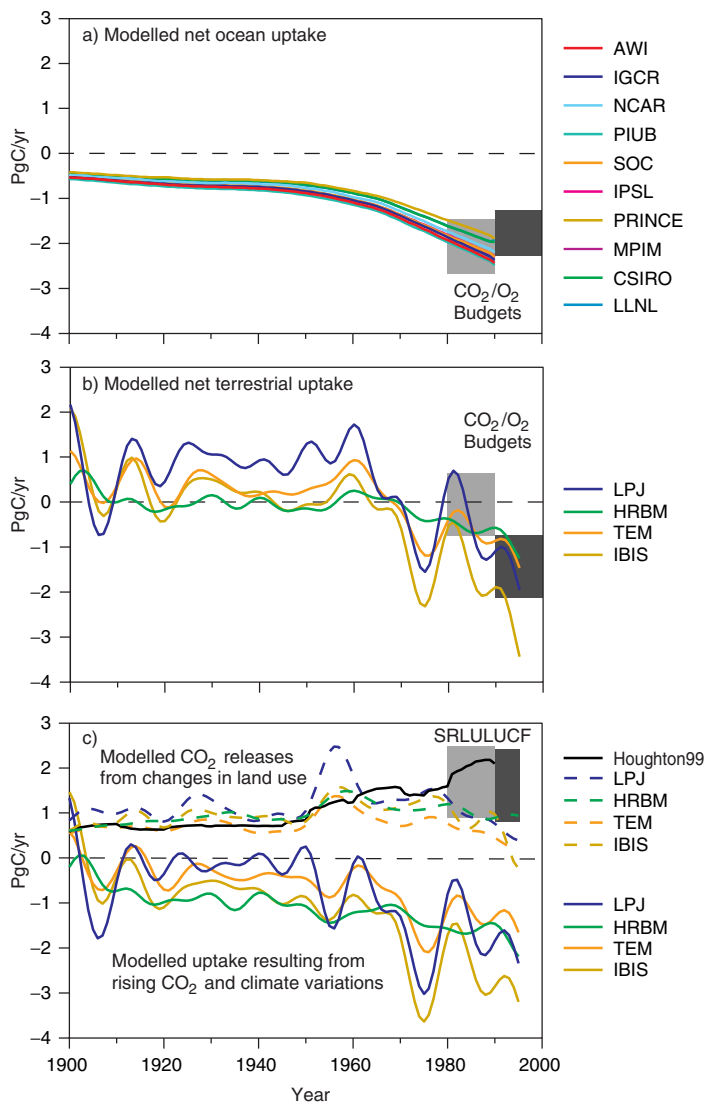
Figure 3.8: Modelled fluxes of anthropogenic CO_2 over the past century. (a) Ocean model results from OCMIP (Orr and Dutay, 1999; Orr *et al.,* 2000); (b), (c) terrestrial model results from CCMLP (McGuire *et al.,* 2001). Positive numbers denote fluxes to the atmosphere; negative numbers denote uptake from the atmosphere. The ocean model results appear smooth because they contain no interannual variability, being forced only by historical changes in atmospheric CO_2. The results are truncated at 1990 because subsequent years were simulated using a CO_2 concentration scenario rather than actual measurements, leading to a likely overestimate of uptake for the 1990s. The terrestrial model results include effects of historical CO_2 concentrations, climate variations, and land-use changes based on Ramankutty and Foley (2000). The results were smoothed using a 10-year running mean to remove short-term variability. For comparison, grey boxes denote observational estimates of CO_2 uptake by the ocean in panel (a) and by the land in panel (b) (from Table 3.1). Land-use change flux estimates from Houghton *et al.* (1999) are shown by the black line in panel (c). The grey boxes in panel (c) indicate the range of decadal average values for the land-use change flux accepted by the SRLULUCF (Bolin *et al.,* 2000) for the 1980s and for 1990 to 1995.

as a result of CO_2 fertilisation, generally larger than the NPP response to the climate change over this period (Kicklighter *et al.*, 1999). According to CCMLP results, the CO_2 increase maintains a lead of NPP over Rh and an increase of the amplitude of the seasonal CO_2 cycle (McGuire *et al.*, 2001), consistent with long-term observations (Keeling *et al.*, 1996a), which indicate an increase in amplitude of about 20% since accurate atmospheric measurements began. However, the magnitude of this effect was greatly over- or under estimated by some models, reflecting unresolved differences in the parametrization of the CO_2 fertilisation response.

3.6.2.2 Uptake and release of anthropogenic CO_2 by the land

The most comprehensive model-based estimates of the terrestrial components of the anthropogenic CO_2 budget are those that have been produced by the CCMLP. McGuire *et al.* (2001) used two TBMs and two DGVMs driven by changes in atmospheric CO_2, then changes in CO_2 with historical changes in climate (from observations), and finally changes in CO_2 and climate with land-use change from Ramankutty and Foley (2000) (Figure 3.8; Table 3.4). In these simulations, CO_2 fertilisation accounted for a land-atmosphere flux of −0.9 to −3.1 PgC/yr, land-use change a positive flux of 0.6 to 1.0 PgC/yr, and climate variability a small additional effect of uncertain sign, −0.2 to 0.9 PgC/yr during the 1980s. The total land-atmosphere flux simulated for the 1980s amounted to −0.3 to −1.5 PgC/yr, which is consistent with or slightly more negative than the observationally-based estimate of −0.2 ± 0.7 PgC/yr (Table 3.1). Net uptake by all models reported in McGuire *et al.* (2001) is shown to be occurring mainly in tropical, temperate and boreal forests − consistent with forest inventory data (Section 3.5.4) − while some regions (notably semi-arid tropical and sub-tropical regions) show net carbon loss. The model estimates of the CO_2 source due to land-use change are substantially smaller than the estimate of Houghton (1999) (Section 3.4.2). This divergence primarily reflects disagreements between the Houghton (1999) and Ramankutty and Foley (2000) data sets as to the timing of tropical deforestation in different regions (see Section 3.4.2).

There is no general agreement on how to model the linkage between reactive nitrogen deposition and vegetation productivity, and recent model estimates of the additional effect of anthropogenic nitrogen fertilisation on the global carbon cycle vary widely. The anthropogenic nitrogen input itself (Holland *et al.*, 1999), the fate of anthropogenic nitrogen in the ecosystem (Nadelhoffer *et al.,* 1999; Jenkinson *et al.,* 1999), and changes in ecosystem nitrogen fixation (Vitousek and Field, 1999) represent major sources of uncertainty. Estimates of the anthropogenic nitrogen effect range from −0.2 PgC/yr (Nadelhoffer *et al.*, 1999) to −1.1 or −1.4 PgC/yr (Holland *et al.*, 1997). The model with the smallest CO_2 fertilisation effect (−0.9 PgC/yr) in the McGuire *et al.* (2001) study has been shown to respond strongly to anthropogenic nitrogen input, yielding a combined (CO_2 and nitrogen) fertilisation effect of −1.5 PgC/yr. A modelling study by Lloyd (1999) suggests that CO_2 and nitrogen fertilisation effects may by synergistic. Evaluation of model results on carbon-nitrogen coupling against experimental results is a current research focus.

3.6.3 Evaluation of Ocean Models

Natural and anthropogenic tracers have been extensively measured, most recently as part of the Joint Global Ocean Flux Study (JGOFS) and World Ocean Circulation Experiment (WOCE). Because of these measurement campaigns, such tracers provide important opportunities to evaluate representations of ocean physics and biogeochemistry in models.

3.6.3.1 Natural carbon cycling in the ocean

Most global ocean models of the carbon cycle are successful in reproducing the main vertical and horizontal features of ocean carbon content (Maier-Reimer, 1993; Aumont, 1998; Murnane *et al.,* 1999). The observed features reasonably reproduced by all ocean models are the mean vertical gradient in DIC, with enriched deep ocean concentrations (Goyet and Davies, 1997), and the spatial patterns of surface pCO_2 with outgassing in the tropics and uptake at higher latitudes (Takahashi *et al.,* 1999). Furthermore, models which incorporate marine biology (including DOC and plankton dynamics) roughly reproduce the seasonal cycle of surface ocean pCO_2, atmospheric O_2 after it has been corrected for seasonal land variability, and surface chlorophyll (Six and Maier-Reimer, 1996; Stephens *et al.,* 1998; Aumont *et al.,* 2001a). Ocean carbon models can also roughly reproduce the phase and amplitude of interannual variability of ocean pCO_2 in the equatorial Pacific (Winguth *et al.,* 1994; Le Quéré *et al.,* 2000) in agreement with available observations (Feely *et al.,* 1997; 1999b; Boutin *et al.,* 1999).

Although many first-order features can be reproduced by global models, there are still important aspects of the ocean carbon cycle that are not well simulated, because either marine biology or ocean physics are imperfectly reproduced. Ocean carbon models have difficulties in reproducing the spatial structure of the deep ocean ^{14}C (Orr *et al.,* 2001), which suggests problems in simulating the physical exchange of carbon between surface and the deep ocean. Models display their largest disagreements where fewest observations exist, in particular in the important region of the Southern Ocean where the mixing of tracers is subject to large uncertainties (Caldeira and Duffy, 2000; Sarmiento *et al.,* 2000; Orr *et al.,* 2001). In spite of these differences, all ocean carbon models estimate zero interhemispheric transport of carbon (Sarmiento *et al.,* 2000) whereas a transport as large as 1 PgC/yr has been inferred from atmospheric CO_2 measurements (Keeling *et al.,* 1989). Consideration of the global transport of carbon by rivers reduces the discrepancy but does not remove it (Sarmiento and Sundquist, 1992; Aumont *et al.,* 2001b). Atmospheric CO_2 and O_2 measurements suggest that interhemispheric transport may be incorrectly simulated by ocean models (Stephens *et al.,* 1998), and could hint at difficulties in modelling heat transport (Murnane *et al.,* 1999). Recent data from the Southern Ocean, however, seem closer to model results (Stephens, 1999) and the question about interhemispheric transport thus remains open. These problems could partly be resolved by a better representation of the physical transport of carbon in the ocean, especially isopycnal diffusion, sub-grid eddy mixing, and sea-ice formation (Stephens *et al.,* 1999).

Three common problems related to marine biology in global ocean models are discussed here. First, most models poorly represent the formation and dissolution of $CaCO_3$, which controls alkalinity. This process is often parameterized as a function of direct or indirect observations (salinity, temperature, nutrients). Although correct for the present day ocean, this parametrisation may not hold for past or future conditions with different ocean circulation and surface water fluxes. The alkalinity cycle is difficult to represent because the rate of $CaCO_3$ formation derived from observations is consistently larger than the one required by models for reproducing observed deep ocean alkalinity (Maier-Reimer, 1993; Yamanaka and Tajika, 1996). Second, marine productivity tends to be underestimated by models in sub-tropical regions and overestimated in the equatorial oceans and at high latitudes in the North Pacific and Southern Oceans. The overestimation may be caused by limitation in plankton growth by iron (Coale *et al.,* 1996; Boyd *et al.,* 2000; Archer and Johnson, 2000), while underestimation in the sub-tropics partly stems from neglecting mesoscale variability (McGillicuddy and Robinson, 1997; Oschlies and Garçon, 1998). The remaining discrepancies might be attributed in part to more complex processes involving nitrogen fixation (Karl *et al.,* 1997). Finally, the tight coupling between carbon and either nitrogen or phosphate, which is generally implicit in ocean carbon models, precludes the simulation of past or future marine biological feedback mechanisms that involve a partial decoupling between carbon and nutrients (see Section 3.2.3).

3.6.3.2 Uptake of anthropogenic CO_2 by the ocean

Ocean uptake is constrained to some degree by observations of anthropogenic tracers. Three transient tracers are commonly used. First, anthropogenic CO_2 itself gives a direct benchmark for model estimates of the quantity and distribution of anthropogenic CO_2 that has penetrated the ocean since the pre-industrial era. Anthropogenic CO_2 can be inventoried by an indirect method whereby carbon concentration is compared to what would be expected from water exposed to pre-industrial air (Gruber *et al.,* 1996). The $^{14}CO_2$ released in the early 1960s by atmospheric nuclear testing (commonly called bomb ^{14}C) provides a second tracer; the content of bomb ^{14}C in the ocean is used to constrain global air-sea CO_2 exchange (Wanninkhof *et al.,* 1992), and ocean model results can be compared with its penetration depth as a benchmark for vertical transport (Broecker *et al.,* 1995). Bomb ^{14}C is computed by subtracting the observed ^{14}C concentration from an estimate of its pre-industrial value (Broecker *et al.,* 1995). Finally, CFCs also constrain the downward transport of tracers in ocean models. No natural background needs to be subtracted from CFCs. None of these three tracers provide a perfect indicator of anthropogenic CO_2 uptake: CO_2 equilibrates with the atmosphere ten times faster than ^{14}C and ten times slower than CFCs; anthropogenic CO_2 and ^{14}C are indirectly estimated. As part of the Ocean Carbon-Cycle Model Intercomparison Project (OCMIP), a comparison of carbon models with respect to all three anthropogenic tracers is in progress (Orr and Dutay, 1999; Orr *et al.,* 2001).

Although regional estimates show discrepancies, modelled estimates of anthropogenic tracers agree reasonably well with observations when integrated globally. The mean value of the penetration depth of bomb ^{14}C for all observational sites during
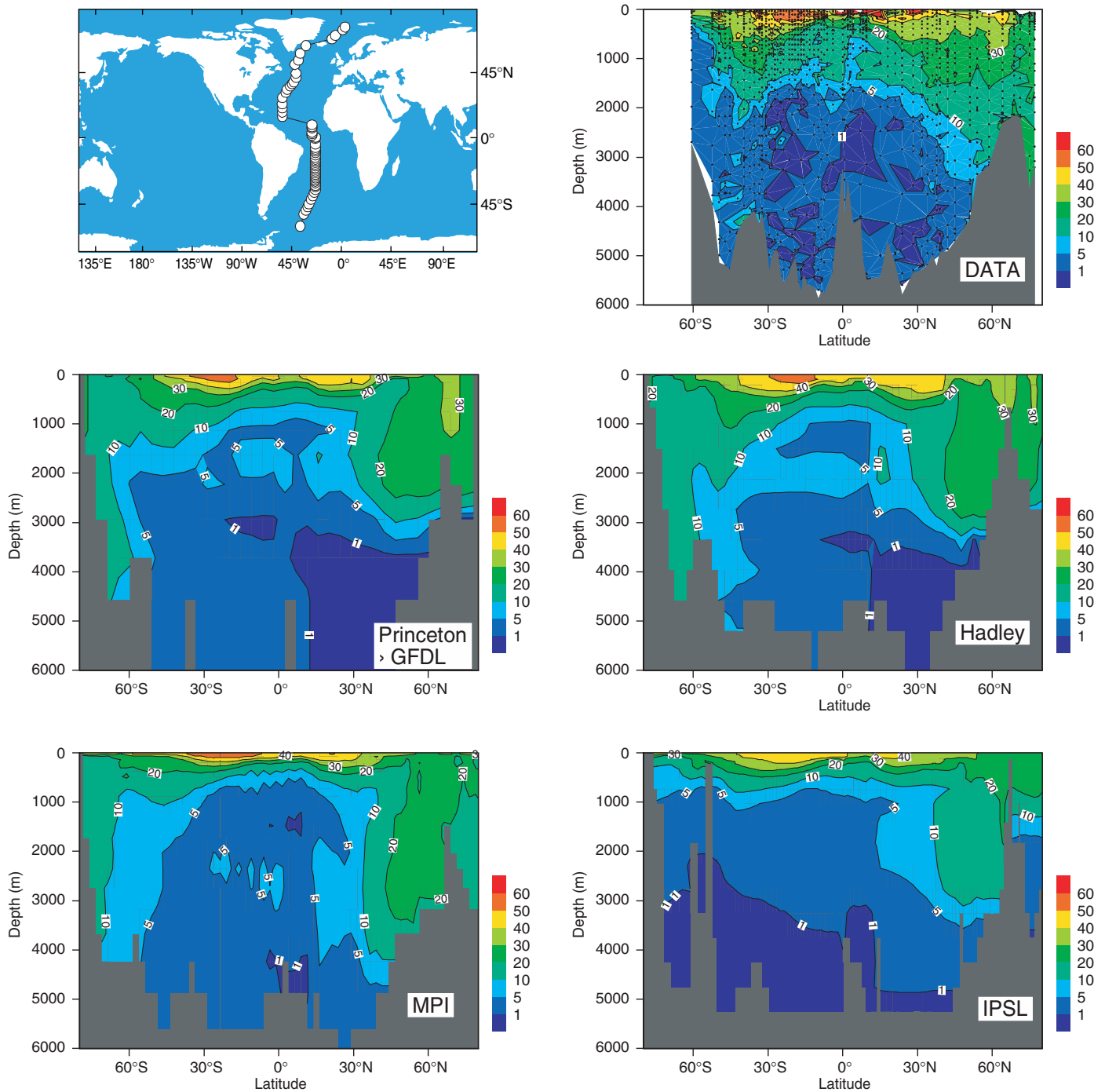
Figure 3.9: Anthropogenic CO_2 in the Atlantic Ocean (μmol/kg): comparison of data and models. The top left panel shows the sampling transect; the top right panel shows estimates of anthropogenic CO_2 content along this transect using observations from several cruises between 1981 and 1989 (Gruber, 1998). Anthropogenic CO_2 is not measured directly but is separated from the large background of oceanic carbon by an indirect method based on observations (Gruber *et al.*, 1996). The remaining panels show simulations of anthropogenic CO_2 content made with four ocean carbon models forced by the same atmospheric CO_2 concentration history (Orr *et al.*, 2000).

the late 1970s is 390 ± 39 m (Broecker *et al.*, 1995). For the same years and stations, modelled estimates range between 283 and 376 m (Orr *et al.*, 2001). Modelled and observed CFC concentrations have been compared locally but not yet globally (England 1995; Robitaille and Weaver, 1995; Orr and Dutay, 1999). Modelled anthropogenic CO_2 inventory since 1800 is

comparable to the estimate of 40 ± 9 PgC for the Atlantic Ocean (Gruber, 1998) and 20 ± 3 PgC for the Indian Ocean (Sabine *et al.*, 1999; Orr *et al.*, 2001). Latitude-depth profiles of anthropogenic CO_2 in the Atlantic, extracted from data and from models, are shown in Figure 3.9. Modelled CO_2 uptake for the global ocean between 1800 and 1990 ranges between 100 and

133 PgC (Figure 3.8), comparable to the preliminary data-based estimate of 107 ± 27 PgC for the global ocean, which includes the Pacific value of 45 ± 15 PgC (Feely *et al.*, 1999a). Although in reasonable agreement with basin and global estimates of anthropogenic CO_2, modelled inventories exhibit large differences at the regional scale: models tend to underestimate the inventory of anthropogenic CO_2 between 50°S and 50°N in the Atlantic and Indian Oceans, and to overestimate it at high latitudes (Sabine *et al.*, 1999; Orr *et al.*, 2001). In the Southern Ocean the uptake of anthropogenic CO_2 varies by a factor of two among models (Orr *et al.*, 2001). The difficulty for models in reproducing the spatial structure of anthropogenic tracers may be indicative of problems in ocean physics mentioned earlier, and may be responsible for the increasing range of model estimates when future CO_2 uptake is projected by the same models (Figure 3.10c).

The most recent model estimates of the ocean-atmosphere flux obtained with process-based models are −1.5 to −2.2 for 1980 to 1989 (Table 3.4), in agreement with earlier model estimates for the same period (Enting *et al.*, 1994; Orr *et al.*, 2001). These estimates are fully consistent with the budget based on atmospheric observations alone (Table 3.1), with estimates based on pCO_2 and $\delta^{13}C$ observations (Table 3.4), and with the SAR estimate of -2.0 ± 0.8 PgC/yr. Figure 3.8 shows modelled ocean CO_2 uptake for 1900 to 2000. (These results do not include natural variability and therefore appear smoother than in reality.) The oceanic regions absorbing the largest quantities of anthropogenic CO_2 according to models are those where older waters come in contact with the atmosphere, such as high latitudes and upwelling regions of the equator. In contrast, modelled sub-tropical regions rapidly saturate at atmospheric CO_2 level and do not absorb large quantities of anthropogenic CO_2 (Sarmiento *et al.*, 1992; Orr *et al.*, 2001).
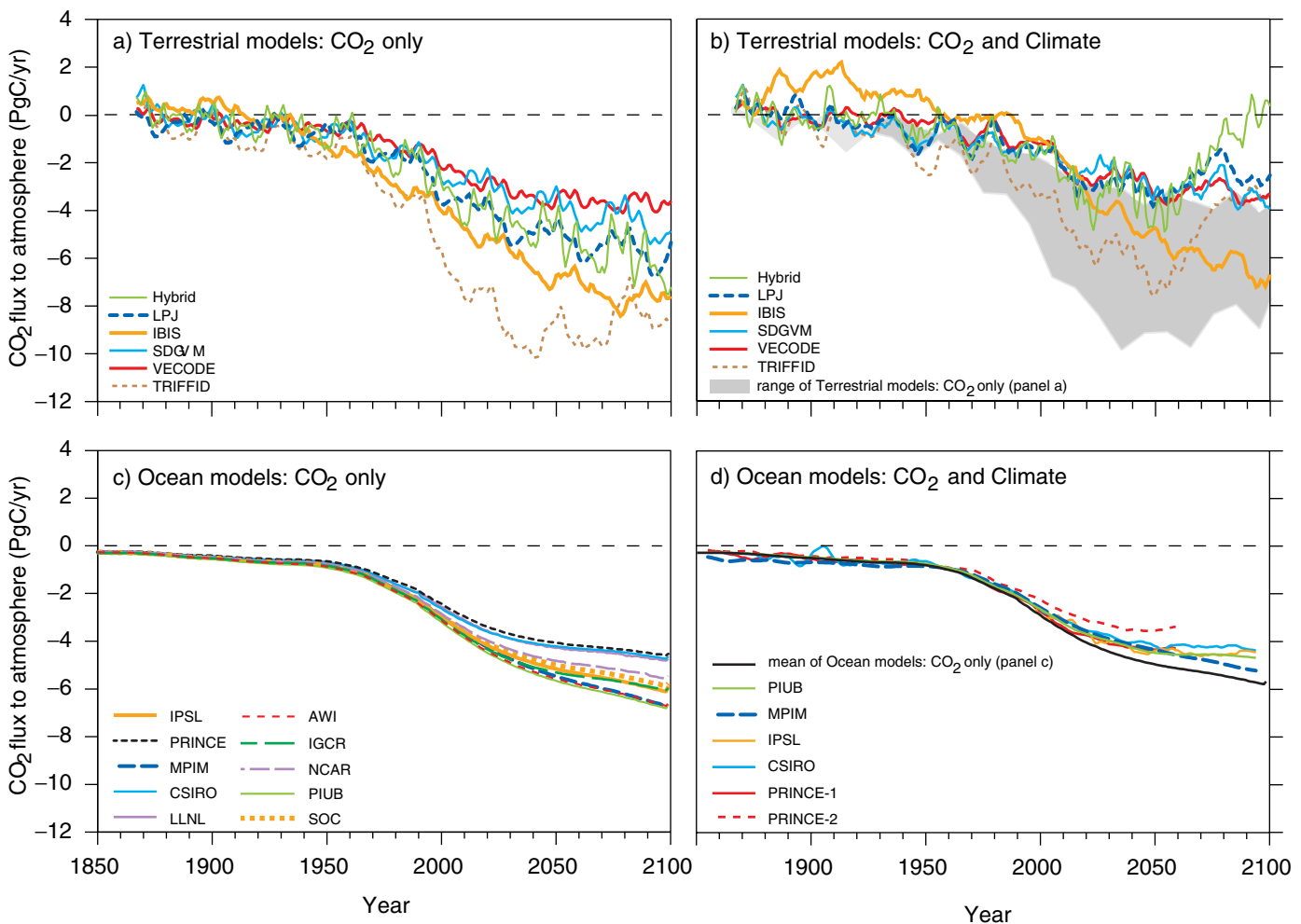

Figure 3.10: Projections of anthropogenic CO_2 uptake by process-based models. Six dynamic global vegetation models were run with IS92a CO_2 concentrations as given in the SAR: (a) CO_2 only, and (b) with these CO_2 concentrations plus simulated climate changes obtained from the Hadley Centre climate model with CO_2 and sulphate aerosol forcing from IS92a (Cramer *et al.*, 2000). Panel (b) also shows the envelope of the results from panel (a) (in grey). (c) Ten process-based ocean carbon models were run with the same CO_2 concentrations, assuming a constant climate (Orr and Dutay, 1999; Orr *et al.*, 2000). A further six models were used to estimate the climate change impact on ocean CO_2 uptake as a proportional change from the CO_2-only case. The resulting changes were imposed on the mean trajectory of the simulations shown in panel (c), shown by the black line in panel (d), yielding the remaining trajectories in panel (d). The range of model results in panel (d) thus represents only the climate change impact on CO_2 uptake; the range does not include the range of representations of ocean physical transport, which is depicted in panel (c).

3.7 Projections of CO_2 Concentration and their Implications

3.7.1 Terrestrial Carbon Model Responses to Scenarios of Change in CO_2 and Climate

Possible feedbacks from terrestrial carbon cycling to atmospheric CO_2 were assessed using multiple models by Cramer *et al.* (2001). Six DGVMs (Figure 3.10a) (Foley *et al.,* 1996; Brovkin *et al.,* 1997; Friend *et al.,* 1997; Woodward *et al.,* 1998; Huntingford *et al.,* 2000; Sitch, 2000) were driven first by CO_2 concentrations derived from the IS92a emissions scenario as in the SAR, and then with CO_2 changes plus climate changes derived from the HadCM2 coupled ocean-atmosphere general circulation model simulation including sulphate aerosol effects as described by Mitchell *et al.* (1995). Except for one empirical model (VECODE; Brovkin *et al.,* 1997), the models included explicit representation of all the following processes: the CO_2 fertilisation effect on NPP (modelled explicitly in terms of photosynthesis, respiration, and feedbacks associated with carbon allocation); responses of NPP to climate specific to each plant functional type (PFT); competition among PFTs for light and water; dynamic shifts in vegetation structure due to climate and CO_2 effects; competitive limits to above-ground biomass; natural disturbance regimes and their interaction with PFT composition; soil temperature and moisture effects on heterotrophic respiration. Two models include an interactive N cycle. Land use and anthropogenic N deposition were not considered.

Driven by increases in CO_2 beyond the present day, the modelled sink due to CO_2 fertilisation continued to increase. By the middle of the 21st century the simulated land-atmosphere flux due to CO_2 was in the range −8.7 to −3.6 PgC/yr. Beyond mid-century the rate of increase became less, due to the declining photosynthetic response to CO_2. When the climate change scenario was included as well as the CO_2 increase, modelled uptake was reduced compared with the CO_2-only analysis. At mid-century, climate change reduced the uptake by 21 to 43%. A marked decline in terrestrial uptake after the mid-century was seen in two models, and one model had zero terrestrial uptake by 2100. By 2100 the range of model estimates of the land-atmosphere flux had widened to −6.7 to +0.4 PgC/yr. Increasing heterotrophic respiration in response to warming (Cao and Woodward, 1998a,b; Cramer *et al.,* 2001) was a common factor (but not the only one) leading to reduced land uptake. The differences among the modelled climate responses were largely due to unresolved discrepancies in the response of global NPP to temperature. The balance of positive versus negative regional effects of climate change on NPP was estimated differently by these models, to the extent that the sign of the global response of NPP to climate change alone was not consistent. In addition, one model simulated a partial replacement of the Amazon rainforest by C_4 grassland. This response was not shown, or occurred on a much smaller scale, in the other models. The details of this modelling exercise are presumably dependent on sensitivity of the particular climate model, and regional aspects of the simulated climate change (Cramer *et al.,* 2001).

3.7.2 Ocean Carbon Model Responses to Scenarios of Change in CO_2 and Climate

Analogous simulations have been performed with several ocean carbon models (Figure 3.10c,d). To compute the impact of increasing CO_2 alone (no climate change), OCMIP models were forced to follow the atmospheric CO_2 concentration derived from the IS92a scenario as in the DGVM experiment (Figure 3.10a,b) (Orr and Dutay, 1999). All models agreed in projecting that the annual ocean-atmosphere flux of CO_2 continues to become larger, reaching −6.7 to −4.5 PgC/yr by 2100 (Figure 3.10c). Since surface conditions (temperature, wind speed, alkalinity) were prescribed, the range in model estimates stems only from different representations of physical transport processes.

Several atmosphere-ocean models were used to project the effect of climate change (Maier-Reimer *et al.,* 1996; Sarmiento *et al.,* 1998; Matear and Hirst, 1999; Joos *et al.,* 1999b; Bopp *et al.,* 2001). These models include most processes previously discussed, including all processes associated with carbonate chemistry and gas exchange, physical and biological transport of CO_2, and changes in temperature, salinity, wind speed, and ice cover. They account for simple changes in biological productivity, but not for changes in external nutrient supply, species composition, pH, or Redfield ratios, all of which could be involved in more complex biological feedbacks. Coupled models estimate the impact of climate change as a departure, reported in per cent, from a "control" experiment modelling the effect of increasing atmospheric CO_2 alone.

In climate change simulations, warming of surface waters and increased stratification of the upper ocean produced an overall positive feedback that reduced the accumulated ocean uptake of CO_2 by 6 to 25% between 1990 and the middle of the 21st century, as compared with the CO_2-only case. In the first part of the simulation, the climate-mediated feedback is mainly due to the temperature effect on CO_2 solubility (Sarmiento and Le Quéré, 1996; Matear and Hirst, 1999). Towards the mid-century, the impact of circulation changes becomes significant in most models, with the net effect of further reducing ocean CO_2 uptake. To investigate the effect of climate change on the IS92a scenario, the average of the OCMIP CO_2-only projections (mean of results in Figure 3.10c) was used as a baseline and the reduction in atmosphere-ocean CO_2 flux caused by climate change (in per cent since the beginning of the simulation) was applied to this curve (Figure 3.10d). The range in model results (Figure 3.10d) must be attributed to uncertainties related to climate change feedback, and not to uncertainties in the modelling of physical transport as shown in Figure 3.10c.

The range of model estimates of the climate change impact is dependent on the choice of scenario for atmospheric CO_2 and on assumptions concerning marine biology (Joos *et al.,* 1999b). At high CO_2 concentrations, marine biology can have a greater impact on atmospheric CO_2 than at low concentrations because the buffering capacity of the ocean is reduced (see Box 3.3) (Sarmiento and Le Quéré, 1996). Although the impact of changes in marine biology is highly uncertain and many key processes discussed in Section 3.2.3.1 are not included in current models, sensitivity studies can provide approximate upper and lower

bounds for the potential impact of marine biology on future ocean CO_2 uptake. A sensitivity study of two extreme scenarios for nutrient supply to marine biology gave a range of 8 to 25% for the reduction of CO_2 uptake by mid-century (Sarmiento *et al.*, 1998). This range is comparable to other uncertainties, including those stemming from physical transport (Figure 3.10c).

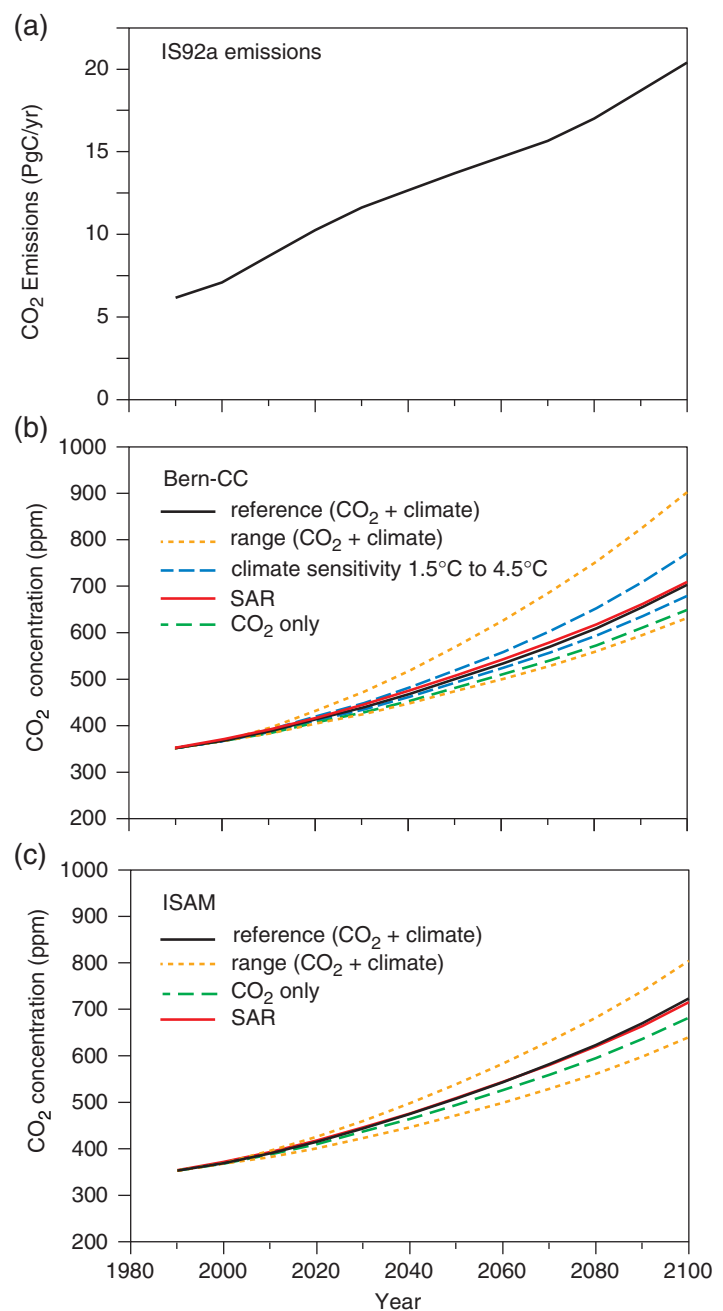### 3.7.3 Coupled Model Responses and Implications for Future CO_2 Concentrations

Carbon cycle models have indicated the potential for climate change to influence the rate of CO_2 uptake by both land (Section 3.7.1) and oceans (Section 3.7.2) and thereby influence the time course of atmospheric CO_2 concentration for any given emissions scenario. Coupled models are required to quantify these effects.

Two general circulation model simulations have included interactive land and ocean carbon cycle components (Cox *et al.*, 2000; Friedlingstein *et al.*, 2001). The Cox *et al.* (2000) model was driven by CO_2 emissions from the IS92a scenario (Legget *et al.*, 1992) and the Friedlingstein *et al.* (2001) model was driven by CO_2 emissions from the SRES A2 scenario (IPCC, 2000b). Both simulations indicate a positive feedback, i.e., both CO_2 concentrations and climate change at the end of the 21st century are increased due to the coupling. The simulated magnitudes of the effect differ (+70 ppm, Friedlingstein *et al.*, 2001; +270 ppm, Cox *et al.*, 2000). In the Cox *et al.* (2000) simulation, which included a DGVM, the increased atmospheric CO_2 is caused mainly by loss of soil carbon and in part by tropical forest die back. The magnitude of the climate-carbon cycle feedback still has large uncertainties associated with the response of the terrestrial biosphere to climate change, especially the response of heterotrophic respiration and tropical forest NPP to temperature (Cox *et al.*, 2000; see Sections 3.2.2.3 and 3.7.1). In the following section, simplified models are used to assess these uncertainties.

3.7.3.1 Methods for assessing the response of atmospheric CO_2
to different emissions pathways and model sensitivities
This section follows the approach of previous IPCC reports in using simplified, fast models (sometimes known as reduced-form models) to assess the relationship between CO_2 emissions and concentrations, under various assumptions about their future time course. Results are shown from two models, whose salient features are summarised in Box 3.7. The models lend themselves to somewhat different approaches to estimating uncertainties. In the ISAM model, "high-CO_2" and "low-CO_2" alternatives are calculated for every emissions scenario, based on tuning the model to match the range of responses included in the model

Figure 3.11: Projected CO_2 concentrations resulting from the IS92a emissions scenario. For a strict comparison with previous work, IS92a-based projections were made with two fast carbon cycle models, Bern-CC and ISAM (see Box 3.7), based on CO_2 changes only, and on CO_2 changes plus land and ocean climate feedbacks. Panel (a) shows the CO_2 emisons prescribed by IS92a; the panels (b) and (c) show projected CO_2 concentrations for the Bern-CC and ISAM models, respectively. Results obtained for the SAR, using earlier versions of the same models, are also shown. The model ranges for ISAM were obtained by tuning the model to approximate the range of responses to CO_2 and climate shown by the models in Figure 3.10, combined with a range of climate sensitivities from 1.5 to 4.5°C rise for a doubling of CO_2. This approach yields a lower bound on uncertainties in the carbon cycle and climate. The model ranges for Bern-CC were obtained by combining different bounding assumptions about the behaviour of the CO_2 fertilisation effect, the response of heterotrophic respiration to temperature and the turnover time of the ocean, thus approaching an upper bound on uncertainties in the carbon cycle. The effect of varying climate sensitivity from 1.5 to 4.5°C is shown separately for Bern-CC. Both models adopted a "reference case" with mid-range behaviour of the carbon cycle and climate sensitivity of 2.5°C.

Box 3.7: Fast, simplified models used in this assessment.

The ***Bern-CC*** model comprises:

• A box-diffusion type ocean carbon model, (HILDA version K(z); Siegenthaler and Joos, 1992; Joos *et al.,* 1996), already used in the SAR. In addition to the SAR version, the effect of sea surface warming on carbonate chemistry is included (Joos *et al.,* 1999b).

• An impulse-response climate model (Hooss *et al.,* 1999), which converts radiative forcing into spatial patterns of changes in temperature, precipitation and cloud cover on a global grid. The patterns of the climate anomalies are derived from the first principal component of the climate response shown by the full three-dimensional atmosphere-ocean GCM, ECHAM-3/LSG (Voss and Mikolajewicz, 1999). Their magnitude is scaled according to the prescribed climate sensitivity.

• The terrestrial carbon model LPJ, as described in Sitch *et al.* (2000) and Cramer *et al.* (2001). LPJ is a process-based DGVM that falls in the mid-range of CO_2 and climate responses as shown in Cramer *et al.* (2001). It is used here at $3.75° \times 2.5°$ resolution, as in Cramer *et al.* (2001).

• A radiative forcing module. The radiative forcing of CO_2, the concentration increase of non-CO_2 greenhouse gases and their radiative forcing, direct forcing due to sulphate, black carbon and organic aerosols, and indirect forcing due to sulphate aerosols are projected using a variant of SAR models (Harvey *et al.,* 1997; Fuglestvedt and Berntsen*,* 1999) updated with information summarised in Chapters 4, 5 and 6. The concentrations of non-CO_2 greenhouse gases, aerosol loadings, and radiative forcings are consistent with those given in Appendix II.

Sensitivities of projected CO_2 concentrations to model assumptions were assessed as follows. Rh was assumed either to be independent of global warming (Giardina and Ryan, 2000; Jarvis and Linder 2000), or to increase with temperature according to Lloyd and Taylor (1994). CO_2 fertilisation was either capped after year 2000 by keeping CO_2 at the year 2000 value in the photosynthesis module, or increased asymptotically following Haxeltine and Prentice (1996). (Although apparently unrealistic, capping the CO_2 fertilisation in the model is designed to mimic the possibility that other, transient factors such as land management changes might be largely responsible for current terrestrial carbon uptake.) Transport parameters of the ocean model (including gas exchange) were scaled by a factor of 1.5 and 0.5. Average ocean uptake for the 1980s is 2.0 PgC/yr in the reference case, 1.46 PgC/yr for the "slow ocean" and 2.54 PgC/yr for the "fast ocean", roughly in accord with the range of observational estimates (Table 3.1, Section 3.2.3.2). A "low-CO_2" parametrization was obtained by combining the fast ocean and no response of Rh to temperature. A "high-CO_2" parametrization was obtained by combining the slow ocean and capping CO_2 fertilisation. Climate sensitivity was set at 2.5 °C for a doubling of CO_2. Effects of varying climate sensitivity from 1.5°C to 4.5°C are also shown for one case.

The ***ISAM*** model was described by Jain *et al.* (1994) and used in the SAR for CO_2-only analyses, with a different set of model parameters from those used here (Jain, 2000). The full configuration of ISAM comprises:

• A globally aggregated upwelling-diffusion ocean model including the effects of temperature on CO_2 solubility and carbonate chemistry (Jain *et al.,* 1995).

• An energy balance climate model of the type used in the IPCC 1990 assessment (Hoffert *et al.,* 1980; Bretherton *et al.,* 1990). In this model, heat is transported as a tracer in the ocean and shares the same transport parameters as DIC.

• A six-box globally aggregated terrestrial carbon model including empirical parametrizations of CO_2 fertilisation and temperature effects on productivity and respiration (Harvey*,* 1989; Kheshgi *et al.,* 1996).

• The radiative forcing of CO_2 projected using a SAR model (Harvey *et al.,* 1997) modified with information summarised in Chapter 6. Radiative forcing from agents other than CO_2 are identical to that used in the Bern-CC model.

In addition to varying the climate sensitivity (1.5 to 4.5°C), parameters of the terrestrial and ocean components (strength of CO_2 fertilisation, temperature response of NPP and heterotrophic respiration; ocean heat and DIC transport) were adjusted to mimic the ranges of CO_2 and climate responses as shown by existing process-based models (Figure 3.10). A reference case was defined with climate sensitivity 2.5°C, ocean uptake corresponding to the mean of the ocean model results in Figure 3.10, and terrestrial uptake corresponding to the mean of the responses of the mid-range models LPJ, IBIS and SDGVM (Figure 3.10). A "low CO_2" parametrisation was chosen with climate sensitivity 1.5°C, and maximal CO_2 uptake by oceans and land; and a "high-CO_2" parametrization with climate sensitivity 4.5°C, and minimal CO_2 uptake by oceans and land.

intercomparisons shown in Figure 3.10. Uncertainties cited from the ISAM model can be regarded as providing a lower bound on uncertainty since they do not admit possible behaviours outside the range considered in recent modelling studies. In the Bern-CC model, "high-CO_2" and "low-CO_2" alternatives are calculated by making bounding assumptions about carbon cycle processes (for example, in the high-CO_2 parametrization CO_2 fertilisation is capped at year 2000; in the low-CO_2 parametrization Rh does not increase with warming). This approach yields generally larger ranges of projected CO_2 concentrations than the ISAM approach. The ranges cited from the Bern-CC model can be regarded as approaching an upper bound on uncertainty, since the true system response is likely to be less extreme than the bounding assumptions, and because the combination of "best" and "worst" case assumptions for every process is intrinsically unlikely.

3.7.3.2 Concentration projections based on IS92a, for comparison with previous studies

Illustrative model runs (Figure 3.11) based on the IS92a scenario (Leggett *et al.,* 1992) are shown first so as to allow comparison with earlier model results presented in the SAR and the SRRF (Schimel *et al.,* 1995). In the SRRF comparison of eighteen global carbon cycle models (Enting *et al.,* 1994; Schimel *et al.,* 1995) the CO_2 fertilisation response of the land was calibrated to match the central estimate of the global carbon budget for the 1980s, assuming a land-use source of 1.6 PgC/yr in the 1980s and attributing the residual terrestrial sink to CO_2 fertilisation. This intercomparison yielded CO_2 concentrations in 2100 of 668 to 734 ppm; results presented in Schimel *et al.* (1996) (from the Bern model) gave 688 ppm. After recalibrating to match a presumed land-use source of 1.1 PgC/yr, implying a weaker CO_2 response, the 2100 CO_2 concentration was given as 712 ppm in the SAR (Schimel *et al.,* 1996). An IPCC Technical Paper (Wigley *et al.,* 1997) evaluated the sensitivity of IS92a results to this calibration procedure. Wigley *et al.,* (1997) found that a range of assumed values from 0.4 to 1.8 PgC/yr for the land-use source during the 1980s gave rise to a range of 2100 CO_2 concentrations from 667 to 766 ppm.

In contrast with the SAR, the results presented here are based on approximating the behaviour of spatially resolved process-based models in which CO_2 and climate responses are not constrained by prior assumptions about the global carbon budget. The CO_2-only response of both models' reference cases (Figure 3.11) leads to a 2100 CO_2 concentration of 682 ppm (ISAM) or 651 ppm (Bern-CC). These values are slightly lower than projected in the SAR – 715 ppm (ISAM; SAR version) and 712 ppm (Bern Model; SAR version) – because current process-based terrestrial models typically yield a stronger CO_2 response than was assumed in the SAR. With climate feedbacks included, the 2100 CO_2 concentration in the reference case becomes, by coincidence, effectively indistinguishable from that given in the SAR: 723 ppm (ISAM) and 706 ppm (Bern-CC). The ranges of 164 ppm or −12% / +11% (about the reference case) (ISAM) and 273 ppm or −10% / +28% (Bern-CC) in the 2100 CO_2 concentration indicate that there is significant uncertainty about the future CO_2 concentrations due to any one pathway of changes in emissions. Separate calculations with the Bern-CC model (Figure 3.11) show that the effect of changing climate sensitivity alone is less important than
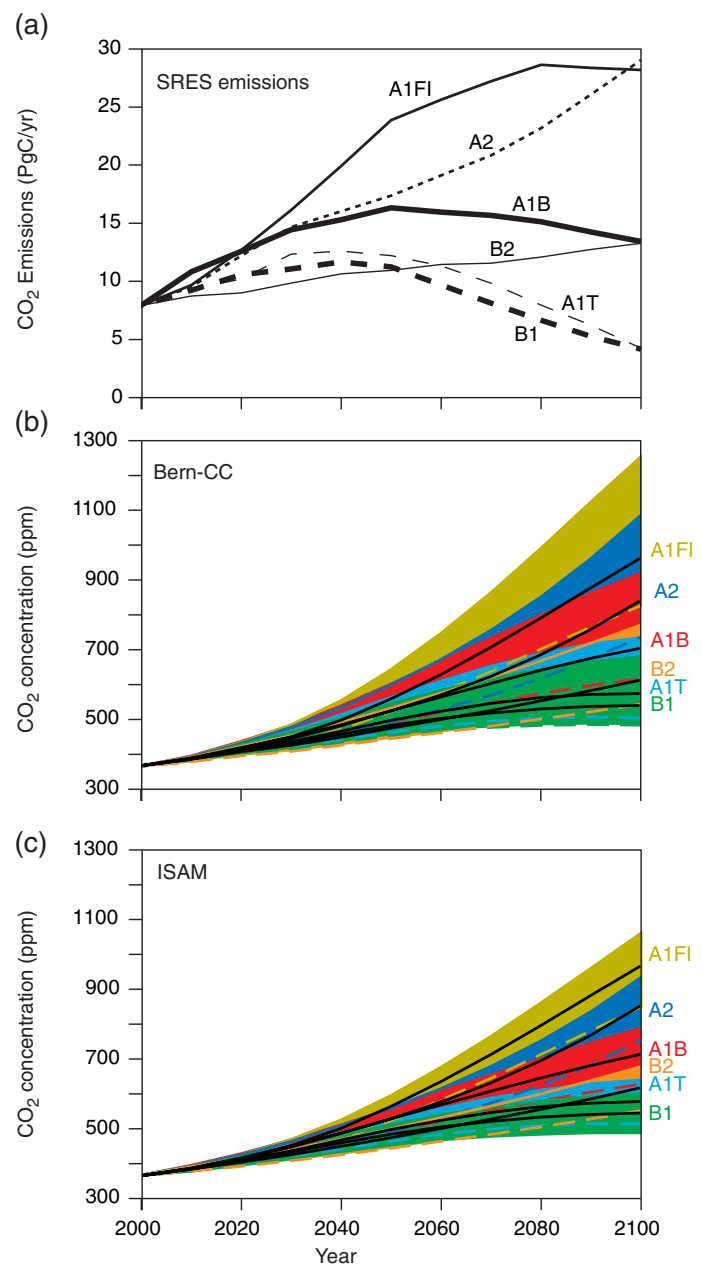
Figure 3.12: Projected CO_2 concentrations resulting from six SRES scenarios. The SRES scenarios represent the outcome of different assumptions about the future course of economic development, demography and technological change (see Appendix II). Panel (a) shows CO_2 emissions for the selected scenarios and panels (b) and (c) show resulting CO_2 concentrations as projected by two fast carbon cycle models, Bern-CC and ISAM (see Box 3.7 and Figure 3.11). The ranges represent effects of different model parametrizations and assumptions as indicated in the text and in the caption to Figure 3.11. For each model, and each scenario the reference case is shown by a black line, the upper bound (high-CO_2 parametrization) is indicated by the top of the coloured area, and the lower bound (low-CO_2 parametrization) by the bottom of the coloured area or (where hidden) by a dashed coloured line.

the effect of varying assumptions in the carbon cycle model's components. The effect of increasing climate sensitivity to 4.5 °C (increasing the climate feedback) is much larger than the effect of reducing climate sensitivity to 1.5 °C. The "low-CO_2" parametrization of Bern-CC yields CO_2 concentrations closer to the reference case than the "high-CO_2" parametrization, in which the terrestrial sink is forced to approach zero during the first few decades of the century due to the capping of the CO_2 fertilisation effect.

The reference simulations with ISAM yielded an implied average land-use source during the 1980s of 0.9 PgC/yr. The range was 0.2 to 2.0 PgC/yr. Corresponding values for Bern-CC were 0.6 PgC/yr and a range of 0.0 to 1.5 PgC/yr. These ranges broadly overlap the range estimates of the 1980s land-use source given in Table 3.1. Present knowledge of the carbon budget is therefore not precise enough to allow much narrowing of the uncertainty associated with future land and ocean uptake as expressed in these projections. However, the lowest implied land-use source values fall below the range given in Table 3.1.

3.7.3.3 SRES scenarios and their implications for future CO_2 concentration

The Special Report on Emissions Scenarios (SRES) (IPCC, 2000b) produced a series of scenarios, of which six are used here, representing outcomes of distinct narratives of economic development and demographic and technological change. In ISAM model runs with these scenarios, past fossil emissions (see Section 3.4.1), CO_2 concentrations (Enting *et al.,* 1994; Keeling and Whorf, 2000) and mean global temperatures (Jones *et al.,* 2000) were specified up to and including 1999; scenario-based analyses started in 2000. In the Bern-CC model runs, observed CO_2 (Etheridge, *et al.,* 1996, Keeling and Whorf, 2000) and past fossil emissions (Marland *et al.,* 1999) were prescribed, and historical temperature changes were modelled, based on radiative forcing from greenhouse gases and aerosols; again, scenario-based analyses started in 2000. Past emissions from changing land use were calculated in order to balance the carbon budget.

The six scenarios lead to substantial differences in projected CO_2 concentration trajectories (Figure 3.12). Significant uncertainties are introduced by the range of model parametrizations considered, so that the trajectories calculated for "adjacent" scenarios overlap, especially during the first half-century. The reference cases of the six scenarios account for a range of 2100 CO_2 concentrations from 541 to 963 ppm in the Bern-CC model and 549 to 970 ppm in the ISAM model. The uncertainties around the 2100 values due to model parametrizations are −12 to +10 % (ISAM) and −14 to +31 % (Bern-CC).

These uncertainties reflect incomplete understanding of climate sensitivity and the carbon cycle. They substantially limit our current ability to make quantitative predictions about the future consequences of a given emissions trajectory. Nevertheless, the results show that higher emissions are always expected to lead to higher projected atmospheric concentrations. They also show that the range of emissions scenarios currently accepted as plausible leads to a range of CO_2 concentrations that exceeds the likely upper bound of uncertainties due to differences among model parameterizations and assumptions.
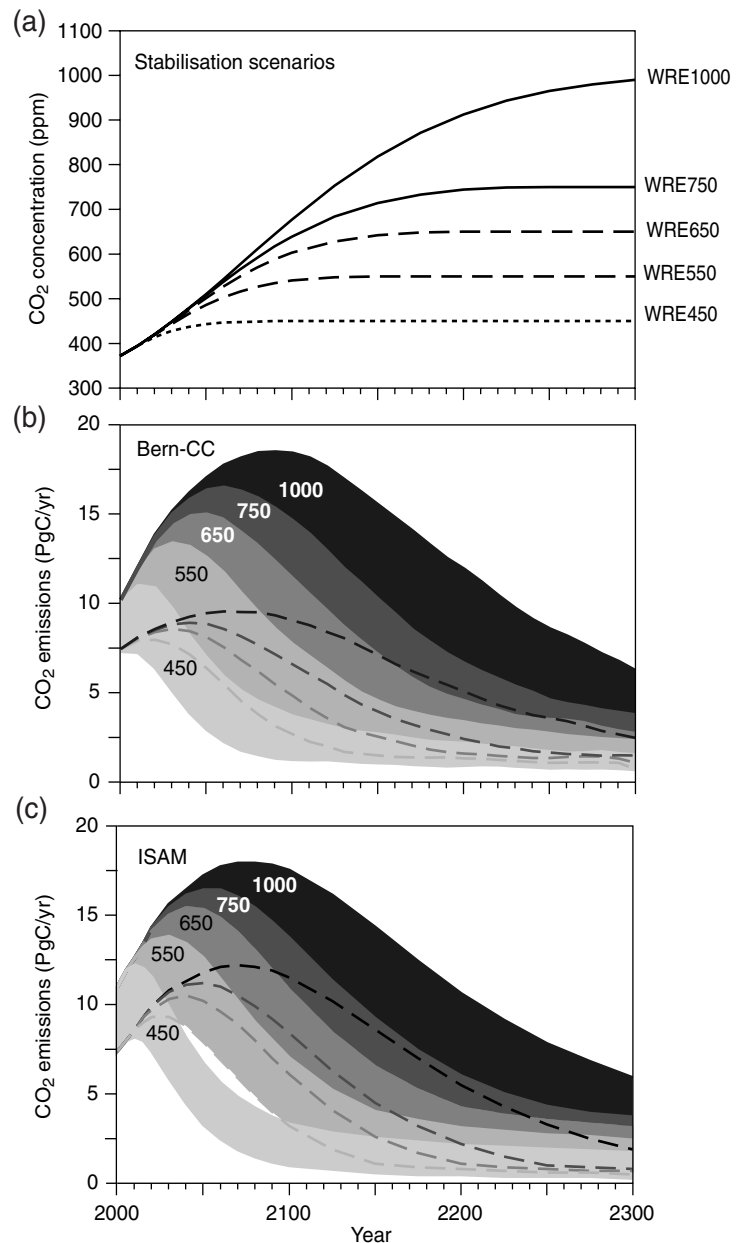
Fig 3.13: Projected CO_2 emissions leading to stabilisation of atmospheric CO_2 concentrations at different final values. Panel (a) shows the assumed trajectories of CO_2 concentration (WRE scenarios; Wigley *et al.,* 1996) and panels (b) and (c) show the implied CO_2 emissions, as projected with two fast carbon cycle models, Bern-CC and ISAM (see Box 3.7 and Figure 3.11). The ranges represent effects of different model parametrizations and assumptions as indicated in the text and in the caption to Figure 3.11. For each model, the upper and lower bounds (corresponding to low- and high-CO_2 parametrizations, respectively) are indicated by the top and bottom of the shaded area. Alternatively, the lower bound (where hidden) is indicated by a dashed line.

3.7.3.4 Stabilisation scenarios and their implications for future CO$_2$ emissions

Stabilisation scenarios illustrate implied rates of CO$_2$ emission that would arrive at various stable CO$_2$ concentration levels. These have been projected using a similar methodology to that applied in the analysis of emissions scenarios. The WRE trajectories follow CO$_2$ concentrations consistent with the IS92a scenario beginning in 1990 and branch off to reach constant CO$_2$ concentrations of 450, 550, 650, 750 and 1,000 ppm (Wigley *et al.,* 1996). The rationale for various alternative time trajectories and stabilisation levels is discussed in Chapter 2 of the IPCC WGIII Third Assessment Report (Morita *et al.,* 2001). Differences in emissions pathways for different time trajectories leading to a certain stabilisation target (e.g., S versus WRE profiles) are discussed in Schimel *et al.,* (1997). Here, we have calculated emissions for one set of emission profiles to illustrate differences in implied emissions that arise from updating models since the SAR.

As in Section 3.7.3.2, the models were initialised up to present. Then anthropogenic emissions for the prescribed CO$_2$ stabilization profiles were calculated; deduced emissions equal the change in modeled ocean and terrestrial carbon inventories plus the prescribed change in atmospheric CO$_2$ content. To estimate the strength of carbon cycle-climate feedbacks, global temperature (ISAM) and changes in the fields of temperature, precipitation and cloud cover (Bern-CC) were projected from CO$_2$ radiative forcing only, neglecting effects of other greenhouse gases and aerosols which are not specified in the WRE profiles. The results for the reference cases are not substantially different from those presented in the SAR (Figure 3.13). However, the range based on alternative model parametrizations is larger than presented in the SAR, mainly due to the range of simulated terrestrial CO$_2$ uptake. CO$_2$ stabilisation at 450, 650 or 1,000ppm would require global anthropogenic CO$_2$ emissions to drop below 1990 levels, within a few decades, about a century, or about two centuries, respectively.

In all cases, once CO$_2$ concentration becomes constant, the implied anthropogenic emission declines steadily. This result was expected. It highlights the fact that to maintain a constant future CO$_2$ concentration, anthropogenic CO$_2$ emissions would ultimately have to be reduced to the level of persistent natural sinks. Persistent terrestrial sinks are not well quantified; peatlands may be a candidate, but the gradual rise in atmospheric CO$_2$ concentration during the present interglacial (Figure 3.2) argues against any such sink. Estimates of current uptake by peatlands are <0.1 PgC/yr (Clymo *et al.,* 1998). Mixing of ocean DIC between surface and deep waters should continue to produce ocean uptake for several centuries after an input of anthropogenic atmospheric CO$_2$ (Siegenthaler and Oeschger, 1978; Maier-Reimer and Hasselmann, 1987; Sarmiento *et al.,* 1992). This mixing is the main reason for continued uptake (and therefore positive calculated emissions) after stabilisation. However, the main, known natural sink expected to persist longer than a few centuries is that due to dissolution of CaCO$_3$ in ocean sediments, which increases ocean alkalinity and thereby allows additional CO$_2$ to dissolve in the ocean. For CO$_2$ concentrations about 1,000 ppm, this sink is estimated to be smaller than about −0.1 PgC/yr (Archer *et al.,* 1998). Thus, for any significant CO$_2$ emissions to

persist over centuries without continuing to increase atmospheric CO$_2$ would require some method of producing an artificial carbon sink.

3.7.4 Conclusions

The differences among the CO$_2$ concentrations projected with the various SRES scenarios considered are larger than the differences caused by inclusion or omission of climate-mediated feedbacks. The range of uptake rates projected by process-based models for any one scenario is, however, considerable, due to uncertainties about (especially) terrestrial ecosystem responses to high CO$_2$ concentrations, which have not yet been resolved experimentally, and uncertainties about the response of global NPP to changes in climate (Cramer *et al.,* 1999). A smaller feedback would be implied if, as some models indicate, global NPP increases with warming throughout the relevant range of climates and no forest die back occurs. Larger positive feedbacks would be implied if regional drying caused partial die back of tropical forests, as some of the DGVMs in Cramer *et al.* (2001), and one coupled climate-carbon model study of Cox *et al.* (2000), suggest; however, another coupled climate-carbon model study (Friedlingstein *et al.,* 2001) suggests a smaller feedback. Uncertainty also arises due to differences in the climate responses of ocean models, especially as regards the extent and effects (biological as well as physical) of increased stratification in a warmer climate (Joos *et al.,* 1999b).

In conclusion, *anthropogenic CO$_2$ emissions are virtually certain to be the dominant factor determining CO$_2$ concentrations throughout the 21st century*. The importance of anthropogenic emissions is underlined by the expectation that the proportion of emissions taken up by both ocean and land will decline at high atmospheric CO$_2$ concentrations (even if absolute uptake by the ocean continues to rise). There is considerable uncertainty in projections of future CO$_2$ concentration, because of uncertainty about the effects of climate change on the processes determining ocean and land uptake of CO$_2$. These uncertainties do not negate the main finding that anthropogenic emissions will be the main control.

Large-scale manipulations of terrestrial ecosystems have been proposed as a means of slowing the increase of atmospheric CO$_2$ during the 21st century in support of the aims of the Kyoto Protocol (Tans and Wallace, 1999; IPCC, 2000a). Based on current understanding of land use in the carbon cycle, the impacts of future land use on terrestrial biosphere-atmosphere exchanges have the potential to modify atmospheric CO$_2$ concentrations on this time-scale. Direct effects of land-use changes are thought to represent about 10 to 30% of total anthropogenic CO$_2$ emissions (Table 3.1), so there is scope for either intended or unintended changes in land use to reduce or increase total anthropogenic emissions. But the possibilities for enhancing natural sinks have to be placed in perspective: a rough upper bound for the reduction in CO$_2$ concentration that could be achieved by enhancing terrestrial carbon uptake through land-use change over the coming century is 40 to 70 ppm (Section 3.2.2.2), to be considered against a two to four times larger potential for increasing CO$_2$ concentraion by deforestation, and a >400 ppm range among the SRES scenarios (Figure 3.12).

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